ANKARA YILDIRIM BEYAZIT UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES



ENERGY STORAGE PERFORMANCE ANALYSIS OF FUEL CELLS AND SUPERCAPACITORS WITH MATERIAL CHARACTERISTICS

M.Sc. Thesis by

Umut YAĞCIOĞLU

Department of Energy Systems Engineering

June, 2021

ANKARA

ENERGY STORAGE PERFORMANCE ANALYSIS OF FUEL CELLS AND SUPERCAPACITORS WITH MATERIAL CHARACTERISTICS

A Thesis Submitted to
The Graduate School of Natural and Applied Sciences of
Ankara Yıldırım Beyazıt University

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Energy Systems Engineering, Department of Energy Systems Engineering

by
Umut YAĞCIOĞLU

June, 2021
ANKARA

M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"ENERGY STORAGE PERFORMANCE ANALYSIS OF FUEL CELLS AND SUPERCAPACITORS WITH MATERIAL CHARACTERISTICS"** completed by **UMUT YAĞCIOĞLU** under the supervision of **ASSOC. PROF. DR. METİN AKTAŞ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. Metin AKTAŞ
Supervisor and Jury Member

Assoc. Prof. Dr. Kuroş SALİMİ
Jury Member

Prof.Dr. Selim ACAR
Jury Member

Prof. Dr. Ergün ERASLAN
Director
Graduate School of Natural and Applied Sciences

ETHICAL DECLARATION

I hereby declare that, in this thesis which has been prepared in accordance with the Thesis Writing Manual of Graduate School of Natural and Applied Sciences,

- All data, information and documents are obtained in the framework of academic and ethical rules,
- All information, documents and assessments are presented in accordance with scientific ethics and morals,
- All the materials that have been utilized are fully cited and referenced,
- No change has been made on the utilized materials,
- All the works presented are original

and in any contrary case of above statements, I accept to renounce all my legal rights.

Date: **Signature:**

Name & Surname: Umut YAĞCIOĞLU

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Assoc. Prof. Dr. Metin AKTAŞ who helped me to prepare my thesis project of «*Energy Storage Performance Analysis of Fuel Cells and Supercapacitors with Material Characteristics*». His immense knowledge and precious recommendations constituted the milestones of this study. His guidance assisted me all the time of my research and while writing this thesis. I would also like to thank Ankara Yıldırım Beyazıt University which provided me good opportunities.

Umut YAĞCIOĞLU

ENERGY STORAGE PERFORMANCE ANALYSIS OF FUEL CELLS AND SUPERCAPACITORS WITH MATERIAL CHARACTERISTICS

ABSTRACT

This study provides better knowledge to understand the energy storage performance analysis of fuel cells and supercapacitors with material characteristics. In today's world, certain forms of energy are utilized everywhere such as in *lighting, heating, running of machines and storing of appliances*, etc. Energy demand increases gradually with increasing the human population. Therefore, energy supplying and energy storing are significant processes pertinent to each other. One of the most important parameters for energy storage issue is the examination and development of material properties used energy storage devices. Developments and investments in energy storage process must keep pace with the energy demands. There are many problems which are faced by fuel cells and supercapacitors such as *weak energy density, fabrication expenses, small voltage each cell and large self-discharging*, etc. [1]. To overcome these types of problems, novel materials need to be improved for them. In order to improve their performances and efficiencies, electrochemical properties must be scrutinized in terms of electrode materials and designed by following some technological processes.

Keywords: Energy storage, fuel cells, supercapacitors, material characteristics

YAKIT PİLLERİ VE SÜPERKAPASİTÖRLERİN MATERYAL KARAKTERİSTİKLERİYLE BİRLİKTE ENERJİ DEPOLAMA PERFORMANSLARININ İNCELENMESİ

ÖZ

Bu çalışma, yakıt pilleri ve süperkapasitörlerin materyal karakteristikleriyle birlikte enerji depolama performans analizini anlamak için daha iyi bilgi sağlar. Bugünün dünyasında, aydınlatma, ısıtma, makinelerin çalıştırılması, depolama uygulamaları gibi her yerde enerjinin belirli formlarından yararlanılır. Enerji ihtiyacı, insan nüfusunun artmasıyla birlikte giderek artmaktadır. Bu nedenle, enerji tedariği ve enerji depolama birbiriyle uyumlu önemli işlemlerdir. Enerji depolama meselesinde en önemli parametrelerden biri, enerji depolama araçlarında kullanılan materyallerin özelliklerinin geliştirilmesi ve incelenmesidir. Enerji depolama işleminde yapılan gelişmeler ve yatırımlar enerji ihtiyacına ayak uydurmak zorundadır. Yakıt pillerinin ve süperkapasitörlerin yüzleştiği düşük enerji yoğunluğu, üretim maliyeti, hücre başına düşük voltaj ve yüksek özboşalım gibi birçok problem vardır. Bu tip problemlerin üstesinden gelmek amacıyla onlar için yeni materyallerin geliştirilmeye ihtiyacı vardır. Onların performanslarının ve verimliliklerini geliştirilmesi maksadıyla elektrot materyalleri açısından elektrokimyasal özellikler irdelenmelidir ve aşağıdaki bazı teknolojik işlemler tasarlanmalıdır.

Anahtar Kelimeler: Enerji depolama, yakıt pilleri, süperkapasitörler, materyal karakteristikleri

CONTENTS

M.Sc THESIS EXAMINATION RESULT FORM……. ii
ETHICAL DECLARATION……iii
ACKNOWLEDGEMENTS iv
ABSTRACT v
ÖZ……..... vi
NOMENCLATURE……..... x
LIST OF TABLES xix
LIST OF FIGURES xxii
CHAPTER 1 – INTRODUCTION……1
CHAPTER 2 - TYPES AND ADVANTAGES AND DISADVANTAGES OF FUEL CELLS AND SUPERCAPACITORS……7
2.1 Types of Fuel Cells…… 7
2.1.1 Alkaline Fuel Cells (AFCs)…… 7
2.1.2 Proton Exchange Membrane Fuel Cells (PEMFCs)…… 11
2.1.3 Direct Methanol Fuel Cells (DMFCs)…… 21
2.1.4 Phosphoric Acid Fuel Cells (PAFCs)……..25
2.1.5 Molten Carbonate Fuel Cells (MCFCs)……... 26
2.1.6 Solid Oxide Fuel Cells (SOFCs)……... 28
2.2 Types of Supercapacitor…….. 30
2.2.1 Electrical Double Layer Capacitors (EDLCs)……. 31
2.2.2 Pseudocapacitors (PCs)…… 32
2.2.3 Hybrid Supercapacitors…… 33
2.3 Advantages and Disadvantages of Fuel cells……. 37
2.4 Advantages and Disadvantages of Supercapacitors…….. . 37
CHAPTER 3 - WORKING PRINCIPLES AND MECHANISMS OF FUEL CELLS AND SUPERCAPACITORS……. 38
3.1Working Principle of Fuel Cells……... 38
3.2Working Principle of Supercapacitors……...39
3.2.1 The Charging Process of The Supercapacitors…….42
3.2.2 The Discharging Process of The Supercapacitors……43
3.3Mechanism of Fuel Cells……...44
3.3.1 Physical-based Hydrogen Storage…… 49
3.3.2 Material-based Hydrogen Storage…… 56

3.4 Mechanism Of Supercapacitors……... 62
3.4.1 Mechanism of EDLCs…….. 65
3.4.2 Mechanism of Pseudocapacitance…… 66
3.4.3 Mechanism of Battery-Type Behavior…… 67
CHAPTER 4 - THE USED MATERIALS IN FUEL CELLS AND SUPERCAPACITORS…… 69
4.1 The Used Materials in Fuel Cells 69
4.1.1 Graphene……69
4.1.2 Perovskites Based Electrodes…… 74
4.1.3 Titanates Based Electrodes……76
4.1.4 Apatite Type Materials…… 77
4.1.5 Porous Ni/YSZ Cermet……..78
4.1.6 Lanthanum Manganite ($LaMnO_3$)…… 79
4.1.7 Cobalt-Based Electrodes……... 80
4.1.8 Yttria Stabilized Zirconia (YSZ)……... 80
4.1.9 Sn-Based Oxides……... 81
4.1.10 Tungsten Oxide (WOx)…….85
4.1.11 Sulfated Zirconia (S-ZrO_2)……90
4.1.12 Silicon Dioxide (SiO_2)…….. 93
4.2 The Used Materials in Supercapacitors……95
4.2.1 Activated Carbon (AC)……95
4.2.2 Carbon Nanotubes (CNTs)…… 96
4.2.3 Conducting Polymers (CPs)…… 97
4.2.4 Aqueous Eletrolyte……99
4.2.5 Ionic Liquids 100
4.2.6 Organic Electrolyte…… 100
4.2.7 Transition Metal Oxides (TMOs)……101
4.2.8 Graphene and CPs (Conducting Polymers) Composites……...103
4.2.9 Graphene and Organic Molecules…….……111
CHAPTER 5 - APPLICATIONS AND ADVANCES IN FUEL CELLS AND SUPERCAPACITORS……... 115
5.1 Applications and advances in Fuel Cells……... 115
5.1.1 Backup Power Systems..... 115
5.1.2 Transportation Applications 115

5.1.3 Stationary Power Applications 119
5.1.4 Space Applications 120
5.1.5 Portable Aplications..... 123
5.1.6 Military Applications..... 125
5.2 Applications and Advances in Supercapacitors 126
5.2.1 Applications of Consumer Electronics 126
5.2.2 Grid Power Buffer Electronics 126
5.2.3 Low-Power Equipment Power Buffer 126
5.2.4 Voltage Stabilizer 127
5.2.5 Microgrids..... 127
5.2.6 Energy Harvesting 128
5.2.7 Street Lights……..... 128
5.2.8 Medical Applications..... 129
5.2.9 Transport Applications 129
5.2.10 Energy Recovery……...130
5.2.11 Hybrid Electric Vehicles (HEVs)……..131
CHAPTER 6 – MARKET ANALYSIS OF FUEL CELLS AND SUPERCAPACITORS AND COMPARISON RESULTS 132
6.1 Energy Storage Comparison of Storage Devices Regarding Various Materials..... 132
6.1.1 Comparison of The Used Materials In Fuel Cells Regarding Various Properties 132
6.1.2 Comparison of The Used Materials In Supercapacitors Regarding Various Properties 138
6.2 Market Analysis of Storage Devices..... 142
6.2.1 Market Analysis of Fuel Cells……142
6.2.2 Market Analysis of Supercapacitors..... 159
6.3 Overview of Energy Storage Background In The World and Turkey 175
6.3.1 Overview of Fuel Cells Background In The World and Turkey 175
6.3.2 Overview of Supercapacitors Background In The World and Turkey.. 184
6.3.3 Overview of Batteries Background In The World and Turkey 191
CHAPTER 7 - DISCUSSION AND CONCLUSION..... 196
REFERENCES..... 209

NOMENCLATURE

Roman Letter Symbols

A	Electrode surface area, (m^2)
Ag	Silver
Ar	Argon
Au	Gold
C_{υ}	Volumetric Stack Capacitance, Farad
C_{device}	Capacitance of the device, Farad
C_G	Gate capacitance (F/g)
$\overline{C}$	Heat mean capacity, J/K
°C	Degree Celsius or Centigrede
$CaTiO_3$	Calcium Titanate
CF_2SO_3H	Perfluorosulfonic acid
CH_3OH	Methanol
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
Co_3O_4	Cobalt(II,III) oxide
dE/dt	Slope of the discharge curve, (V/s)
D	Oxygen diffusion coefficient, cm^2/s
e	Charge on en electron
e_s	Energy density for unit mass
e'_s	Energy density for unit volume
E	Energy density (Wh/kg)
E*	Energy density (Wh/kg)
E	Total energy
E_f	Fermi energy
E_{in}	Input of Energy, J
E_L	Elastic energy of lattice
E_{loss}	Loss Of Energy, J
E_{out}	Energy output, J
E_0	Ground state energy of hydrogen
E_s	Storage energy conten, W

F	Faraday’s constant, coulombs/mol
Fe	Iron
h	hour
H_0	Hammett acidity function
H_2	Hydrogen
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
H_2O	Water
H_2PtCl_6	Chloroplatinic Acid
$H_3PW_{12}O_{40}$	Phosphotungstic acid
HV	Heating Value, J/kg
I	Current, A
Ir	Iridium
IrSe	Iridium Selenide
İ	Integrated area of the CV conducted
i_{app}	Applied current, A
J	Current density, A/m^2
k	Constant multiplier
k	Surface exchange coefficient, cm/s
k	Thermal conductivity ($Wm^{-1}K^{-1}$)
k_x	Crystal momentum of x direction
k_y	Crystal momentum of y direction
KCl	Potassium chloride
K_2CO_3	Potassium carbonate
KOH	Potassium hydroxide
La	Lanthanum
$LaMnO_3$	Lanthanum manganite
La_2NiO_4	Lanthanum nickelate
$La_2Ni_{0.8}Co_{0.2}O_4$	Cobalt doped Lanthanum nickelate
$LiCoO_2$	Lithium cobalt oxide
Li_2MnO_3	Lithium manganite
m	Mass of the electrode material, kg
m	Mass flow rate, kg/s
Mn	Manganese

Mn_3O_4	Manganese(II,III) oxide
MnO_2	Manganese Oxide
NH_4NO_3	Ammonium Nitrate
n	Quantity of electrons produced per mole, e^-/mole
N_A	Avogadro's number, mol^{-1}
$NaBH_4$	Sodium borohydride
NH_3	Ammonia
Ni	Nickel
$Ni(OH)_2$	Nickel hydroxide
NO	Nitric Oxide
O_2	Oxygen
OH^-	Hydroxide
OH_{ads}	Hydroxide adsorption
P	Permeability, mol/(m.s.Pa)
P	Power density, (W/kg)
Pb	Lead
Pd	Paladium
P_{el}	Electric power output, W
Pr	Praseodim
Pt	Platinum
q	Charge of an electron, J/V
R	Resistance, Ω (ohm)
Rct	Electrontransfer resistance
Rh	Rhodium
RhSe	Rhodium Selenide
RuO_2	Ruthenium Oxide
RuSe	Ruthenium Selenide
S	Scan rate of the CV conducted
S	Selectivity
S	Siemens
S-ZrO_2	Sulfated Zirconia
Sb	Antimony
SiO_2	Silicon dioxide
SnO_2	Tin dioxide

$Sr_{1-3x/2}La_xTiO_{3-d}$ Lanthanum doped Strontium titanate

t Discharge time, s

T Temperature, K

T_0 Temperature of the environment or outside, K

υ Scan rate, V/s

V Operation potential range, Volt

$Y_{0.8}Ca_{0.2}Co_{1-x}Fe_xO_3$ Fe-doped cobaltate oxides

wt Weight

WO_3 Tungsten trioxide

X Range of metals

ZrO_2 Zirconia or Zirconium dioxide

Greek Letter Symbols

δ Distance between the center of ion and the electrolyte interface, m

Δ Difference, change

ΔE Range of CV working, Joule

ΔG Difference of Gibbs free energy for a chemical reaction, j/(kg/mol)

ΔS Change of specific entropy, $J.K^{-1}$

Δt Discharge time, seconds

ΔT Temperature difference, K

ε Dielectric constant

η_{cell} The efficiency of the fuel cell

η_s Storage efficiency

σ_e Electrical or electrolytic conductivity, Siemens/cm

σ_i Ionic Conductivity, Siemens/cm

π Pi number

π Occupied valence band

π* Unoccupied conduction band

$\tau_{s,c}$ Storage cycle duration, seconds

Ω Ohm

Subscripts

ads adsorption

app applied

A Avogadro

c cycle

cell	Fuel cell
e	electrical or electronic
el	electric
i	ionic
s	second
s	Storage
V	Volume

Acronyms

AC	Activated Carbon
AC	Alternating Current
AFC	Alkaline Fuel Cell
AMEA	Latin America, the Middle East and Africa
ARPA-E	Advanced Research Projects-Energy
BDU	Battery Disconnect Unit
BET	Brunauer-Emmett-Teller
BMIm	1 – Butyl – 3methylimidazolium
Br	Bromide
CAGR	Compound Annual Growth Rate
CC	Charge/Discharge Curves
CCG	Chemicaly Converted Graphene
CEM10	Clean Energy Ministerial
CCUS	Carbon Capture and Utilization or Storage
Cermet	Ceramic Metal Composite
CNTs	Carbon Nanotubes
Co.	Corporation
COMPO	Reflected Electron Images
COR	Cost of Revenue
CPs	Conducting Polymers
CV	Cyclic Voltammetry
D	Dimensional
DC	Direct Current
DMFC	Direct Methanol Fuel Cell
DOE	Department of Energy
ECs	Electrochemical Capacitors

EDLCs	Electrical Double Layer Capacitors
EERE	Energy Efficiency and Renewable Energy
ELCINA	Electronic Industries Association of India
EMIM	1 – Ethyl – 3 methylimidazolium
EPAct	Energy Policy Act
EVs	Electric Vehicles
FCEV	Fuel Cell Electric Vehicle
GA	Graphene Aerogel
Ga-Silicate-1	Gallosilicate Zeolite
GCD	Galvanostatic Charge Discharge
GDE	Gas Diffusion Electrodes
GmbH	Gesellschaft mit beschränkter Haftung
GNF	Graphene Nanofiber
GNPs/PPS	Graphene Nanoplatelets/Polyphenylene Sulfide
G-PEDOT	Graphene-PEDOT Composite
GO	Graphene Oxide
G-PNF	Graphene PANI Nanofiber Composite
G-PPyNF	Graphene Polypyrrede Nanofiber Composite
GPS	Global Positioning System
GR	Gross Revenue
GWh	Gigawatt-hour
H_2O	Water
H_2-PEFC	Hydrogen Polymer Electrolyte Fuel Cell
HEVs	Hybrid Electric Vehicles
HGO	Holey Graphene Oxide
HGPAs	Holey Graphene/PPy Hybrid Aerogels
IEA	International Energy Agency
ILs	Ionic Liquids
JNNSM	Jawaharlal Nehru National Solar Mission
LED	Light Emitting Diode
LPG	Liquified Petroleum Gas
LSM	Lanthanium Strontium Manganite
LSCF	Lanthanium Strontium Cobalt Ferrite
M	Molar

MCFC	Molten Carbonate Fuel Cell
MDU	Master Disconnect Unit
METU	Middle East Technical University
MH	Metal Hydride
MNRE	Ministry of New and Renewable Energy
MOFs	Metal Organic Frameworks
MOR	Methanol Oxidation Reaction
MP3 Player	Motion Pictures 3 Player
MPPT	Maximum Power Point Tracking
Mt	Metric Tonne
MW	Megawatt
MWCNTs	Multi-Walled Carbon Nanotubes
NASA	National Aeronautics and Space Administration
NECAR	New Electricity Car
NEMMA	National Electric Mobility Mission Plan
NETL	National Energy Technology Laboratory
NFs	Nanofibers
Ni	Nickel
NOK	Norwegian Krone
NTs	Nanotubes
NWs	Nanowires
ORR	Oxygen Reduction Reaction
PAFC	Phosphoric Acid Fuel Cell
PAM-G	Polyacrylamide Gel
PAN	PolyAcrylonitrile
PANI	Polyaniline
PC	Personal Computer
PC	Propylene Carbonate
PCU	Power Control Unit
PDA	Personal Digital Assistants
PDMS	Polydimethylsiloxane
PE	Private Equity
PEDOT	Polyethylenedioxythiphene
PEFC	Polymer Eletrolyte Fuel Cell

PEMFC	Proton Exchange Membrane Fuel Cell
PEO	Polyethylene Oxide
PNT	Polypyrrede Nanotube
PPA	Power Purchase Agreements
PPy	Polypyrrede
PSS	Polystrene Sulfonic Acid
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PV	Photovoltaic
PVDF	Polyvinydifluoride
RAM	Random Access Memory
Redox	Reduction-Oxidation
R&D	Research and Development
rGO	Reduced Graphene Oxide
RHE	Reversible Hydrogen Electrode
SCs	Supercapacitors
SCU	String Control Unit
SDS	Sustainable Development Scenario
SG	Sulfonated Graphene
S-RAM	Static Random Access Memory
SCU	String Control Unit
SEM	Scanning Electron Microscopy
SHS	Solar Home Systems
SOFC	Solid Oxide Fuel Cell
SS	Stainless Steel
STM	Scanning Tunneling Microscopy
SWCNTs	Single-Walled Carbon Nanotubes
TCU	Telematic Control Unit
TEC	Thermal Expansion Coefficient, 1/K
TEM	Tranmission Electron Microscopy
TFMSA	Trifluoromethanesulfonic Acid
TMOs	Transition Metal Oxides
TS	Towel-Gourde Sponge
TVs	Televisions

UK	United Kingdom
UPS	Uninterruptible Power Supplies
US	United States
VC	Venture Capital
YSZ	Yttria Stabilized Zirconia
ZAFCs	Zinc-Air Fuel Cells

LIST OF TABLES

Table 2.1 Classification in Fuel Cell Types 30
Table 2.2 Advantages and Disadvantages of Fuel Cell 37
Table 2.3 Advantages and Disadvantages of Supercapacitors 37
Table 3.1 Classification of Hydrogen Storage Methods 49
Table 3.2 Characteristics of NECAR4 car 53
Table 3.3 Comparing of LH_2 and CGH_2 based on 6.4 kg of hydrogen storage 54
Table 3.4 Hydrogen densities and hydrogen contents for several hydride systems .. 61
Table 3.5 Characteristics of Supercapacitor'types 68
Table 3.6 Important parameters and differences btwn supercapacitor and battery ... 68
Table 4.1 Properties of Graphene 70
Table 4.2 Thrml conductivities of graphne by making use of Raman spectroscopy 73
Table 4.3 Important properties of various Perovskites-based cathode materials 76
Table 4.4 Comparison for various morphology based anode materials for fuel cell 78
Table 4.5 Comparison of TECs between Nickel and YSZ 79
Table 4.6 Properties of Sr-doped Lanthanum Manganite 79
Table 4.7 TECs by depending on the modification of Zirconia 81
Table 4.8 Properties of SnO_2 (Tin dioxide) 81
Table 4.9 Electrical resistivities of SnO_2 and Sr-doped SnO_2 82
Table 4.10 The Rct of the Pt/Ru with SnO_2/graphite and Pt/SnO_2/graphite elctrdes 82
Table 4.11 Properties of Tungsten dioxide 86
Table 4.12 Properties of Zirconia (ZrO_2) 90
Table 4.13 Properties of SrO_2 94
Table 4.14 Specific Capacitances of Activated Carbon in different electrolytes 96
Table 4.15 The properties of Carbon Nanotubes (CNTs) 97
Table 4.16 Characteristics of various types of electrolytes 99
Table 4.17 Specific capacitances of different Manganese oxide materials 102
Table 4.18 Specific capacitances of different types of Ruthenium Oxide (RuO_2). 102
Table 4.19 Capacitance at two different current values in 3 M KCl 108
Table 4.20 Areal Capacitance at various important values 109
Table 4.21 The specific cpcitance of graphene/PPy hydrogel in various cndtions . 110
Table 4.22 The specific capacitances of G-PEDOT in various solutions 110
Table 4.23 Significant Properties of graphene/PEDOT hydrogel 111
Table 6.1 Electrical conductivities of the used materials in fuel cells 132

Table 6.2 Thermal conductivities of the used materials in fuel cells 133

Table 6.3 Thermal expansion coefficients of the used materials in fuel cells..... 135

Table 6.4 Specific surface area of the used materials in fuel cells..... 137

Table 6.5 Specific capacitances of the used materials in supercapacitors 138

Table 6.6 Thermal conductivities of the used materials in supercapacitors..... 139

Table 6.7 Specific surface area of the used materials in supercapacitors 140

Table 6.8 The electrical conductivities of the used materials in the supercapacitors……..141

Table 6.9 Comparison of gross revenue (GR) and cost of revenue (COR) of several companies in different years ……..……146

Table 6.10 The R&D expenditures for important fuel cell companies in several countries for different years……..……148

Table 6.11 Comparisons between assets and liabilities of several companies in years…….. 149

Table 6.12 Businesses Performances of Companies by means of combinations with other companies……....152

Table 6.13 Disclosed top venture capital (VC) and private equity investments in companies……..….. 153

Table 6.14 Ten venture capital and private equity investors and countries for fuel cells……..… 155

Table 6.15 Capital and equity investment activity of outstanding companies for fuel cells…….. 157

Table 6.16 Outstanding projects of America's important investors…… 158

Table 6.17 The relationship between revenue and years in terms of global supercapacitor market……...…168

Table 6.18 Overall market for supercapacitors in India by 2020……169

Table 6.19 Whole revenue opportunity in India in both pessimistic and optimistic situation……170

Table 6.20 Exported supercapacitor values of outstanding countries in different years in terms of US Dollar Thousand……..……172

Table 6.21 Imported supercapacitor values of world and several countries in different years ..…..... 174

Table 6.22 The number of FCEVs in the world and several countries and their targets in several years…….. 180

Table 6.23 The relationship between Metric tonne (Mt)/year in different years…. 181

Table 6.24 The number of hydrogen refuelling stations of countries……..…. 182

Table 6.25 The supercapacitor industry in the world……...185

Table 6.26 Number of patents of important universities……..186

Table 6.27 Number of supercapacitor patents of countries……..187

Table 6.28 The number of patents of supercapacitor investors……....188

Table 6.29 The quantities of patents of the highest cited applicants……189

Table 6.30 Number of patent publications of outstanding institutions and companies…… 190

Table 6.31 The relationship between the companies and their battery market…… 193

Table 6.32 The amount of energy of the outstanding battery companies……..... 193

LIST OF FIGURES

Figure 1.1 Primary energy consumption and supply worldwide in 2018……2

Figure 1.2 CO_2 concentration over the last 1000 years……2

Figure 1.3 General design of an energy storing mechanism…….……..4

Figure 2.1 Mass transfer corrected Tafel plots for Oxygen reduction reaction on Pt/C, Rh/C, Ir/C, RhSe/C, IrSe/C, and RuSe/C within 0.1 M $HClO_4$……...9

Figure 2.2 Schematic diagram of Nafion structure……... 13

Figure 2.3 The conductivity of Nafion versus mole ratio H_2O/SO_3H…….. .15

Figure 2.4 The three-phase boundary in a GDE…… 17

Figure 2.5 The effect of methanol on the efficiency of Pt/C cathode for oxygen reduction…… ……24

Figure 3.1 Schematic diagram of fuel cells……39

Figure 3.2 General diagram of supercapacitors…… .41

Figure 3.3 The charging process of supercapacitors…….43

Figure 3.4 The discharging process of supercapacitors…… 43

Figure 3.5 The relationship between fuel cell voltage and current density……... 46

Figure 3.6 Polarization curve of a PEM fuel cell…….. 47

Figure 3.7 Correlation amidst power density and current density of a fuel cell.....47

Figure 3.8 General illustration of a fuel cell-based power plant……48

Figure 3.9a The schematic diagram of composite high-pressure hydrgn cylinders.. 50

Figure 3.9b General examples of some of them…… 50

Figure 3.10 Comparison of energy content between the LH_2 and CGH_2 at various pressures…….....52

Figure 3.11 General mechanism of NECAR4……... 53

Figure 3.12 Estimated power inputs for hydrogen cooling……55

Figure 3.13 Comparison of volumetric densities between CGH_2 and LH_2 in terms of $g.l^{-1}$……...……... 55

Figure 3.14 The diagram of hydrogen adsorption and desorption of metal/alloy and formation of hydrogen……..…….. 59

Figure 3.15 Self-trap mechanism of hydrogen occupancy in an interstitial region... 60

Figure 3.16 Schematic diagram of water electrolysis…… 62

Figure 3.17 Hybrid energy storing system (HESS) which depends on solar energy mechanism..…… 63

Figure 3.18 CV curves and constant current discharge curves of electric double layer capacitors under various storing systems……64

Figure 3.19 Schematic diagram of energy storing system for electrical double layer capacitance, surface redox capacitance, intercalation capacitance and battery-type behaviour……65

Figure 4.1 The structure of the graphene……... 70

Figure 4.2 The electronic morphology and dislocations in graphene……..….. 71

Figure 4.3 Valence band and conduction band keeps in contact with in K and K' points (Dirac points) b. The relationship between energy and crystal momentum near the Dirac points c. Fermi Energy levels, electrical and optical properties of different graphene layers……... 72

Figure 4.4 The structure of Perovskites based electrodes…….…76

Figure 4.5 Schematic diagram of morphology structure of electrode ingredients; (a) perovskite, (b) double perovskite, (c) titanates, (d) apatite……77

Figure 4.6 The crystal structure of the YSZ ……..80

Figure 4.7 SEM and TEM appearances of SnO_2 NWs improved on carbon fibers of carbon paper with the help of thermal evaporation technique. (a) SEM illustration of SnO_2 NWs on fibers of carbon paper (50 μm). (b) TEM figure of SnO_2 NWs (20 nm). (c) TEM figures of Pt nanoparticles on SnO_2 NWs (20 nm)……..…...84

Figure 4.8 TEM images which belongs to meso-structured 15 wt.% Pt and WO_3 in (a, c), 20 wt.% Pt and WO_3 in (b); high-resolution TEM view in (d) and EDS form in (e) of 15 wt.% Pt and WO_3 ……88

Figure 4.9 Pt particles have been encoloured with white in COMPO figure. (a) Scanning Electron Microscopy appearance for Sulfated Zirconia. (b) SEM appearance for Pt doped S–ZrO_2. (c) reflected electron view for Pt doped S–ZrO_2 ……92

Figure 4.10 (a) Transmission electron microscope (TEM) image of carbon nanotubes. (b) Scanning electron microscope (SEM) image of a carbon nanotube... 97

Figure 4.11 Chemical structures of some conductive polymers…… 99

Figure 4.12 The correlation amidst energy density and specific capacitance……..101

Figure 4.13 IR drop and CV curves of G-PNF30, as-forming PANI-NF, and CCG plates…… 105

Figure 4.14 Relationship of current (Ag^{-1}) and voltage (V) between G-PPyNF1 and G-PPyNF2 ……107

Figure 4.15 Ragone plot of several energy storage devices ……....113

Figure 4.16 Annualy development of supercapacitor electrode materials……...114

Figure 5.1 Automobile application of fuel cells..…… 116

Figure 5.2 NECAR4……116

Figure 5.3 Bus applications of fuel cells…… 118

Figure 5.4 (a,b) Alkaline fuel cell for apollo space program…….. 120

Figure 5.5 Polymer electrolyte fuel cell for Gemini space program……..…..121

Figure 5.6 Schematic diagram of regenerative fuel cell system in space utilizations..……...123

Figure 5.7 Portable applications of fuel cells……...……124

Figure 5.8 Military applications of fuel cells...…… 125

Figure 5.9 The combination of supercapacitors and solar cell in street light…..... 128

Figure 6.1 The illustration of electrical conductivities of the used materials in fuel cells……... 133

Figure 6.2 The relationship between the used materials in fuel cells and their thermal conductivities ($Wm^{-1}K^{-1}$)…….. 134

Figure 6.3 Thermal expansion coefficient (TEC) of the used materials in fuel cells in terms of 10^{-6} (1/K)…… 136

Figure 6.4 The illustration of specific surface area of the used materials in fuel cells..... 137

Figure 6.5 Specific capacitance of the used materials in supercapacitors in terms of F/g…… 139

Figure 6.6 Thermal conductivities of the used materials in supercapacitors in terms of ($Wm^{-1}K^{-1}$)…… 140

Figure 6.7 The illustration of the specific surface area (m^2/g) of the used materials in the supercapacitors…… 141

Figure 6.8 The illustration of electrical conductivities (S/cm) of the used materials in the supercapacitors…… 142

Figure 6.9 The relationship between number of fuel cell systems and years for 3 applications……... 143

Figure 6.10 The relationship between total power and years for 3 applications…. 144

Figure 6.11 The distributions of fuel cells from country to country in terms of applications and Megawatts)…… 144

Figure 6.12 Gross revenue of the several companies in different years…….. 146

Figure 6.13 Cost of revenue of the several companies in different years…… 147

Figure 6.14 Relationship between shipments and years by depending on Megawatts…… 149

Figure 6.15 Distribution by years of fuel cell mechanisms shipments throughout the world……..… 150

Figure 6.16 Comparisons by years in continents throughout the world…… . 151

Figure 6.17 The relationship between the companies and their investment values in terms of million $US……155

Figure 6.18 The relationship between the countriess and their investment with all VC and PE values in terms of $ million US…… 156

Figure 6.19 The investment amount of three outstanding companies in America.. 159

Figure 6.20 Supercapacitor market by depending on product type……. 161

Figure 6.21 Supercapacitor market by depending on applications…….. 162

Figure 6.22 Supercapacitor market by depending on region……... 163

Figure 6.23 The illustration of the relationship between the revenue and years in global supercapacitor market…… 169

Figure 6.24 The usage of supercapacitors in pitch control of wind turbines……... 171

Figure 6.25 The exported supercapacitor values of the world……..…… 173

Figure 6.26 The exported supercapacitor values of Turkey……..……. 173

Figure 6.27 Illustration of imported supercapacitor values of world in different years…….. 175

Figure 6.28 Illustration of imported supercapacitor values of China in different years…….. 175

Figure 6.29 The illustration of the number of FCEVs in the worldwide……. 180

Figure 6.30 The relationship between the amount of Metric tone (Mt)/year and differen years…… 181

Figure 6.31 The illustration of the number of hydrogen refuelling stations of countries…… 183

Figure 6.32 The graph of the number of patents of 10 companies in supercapacitor industry……. 185

Figure 6.33 Illustration of the Table 6.26…… 186

Figure 6.34 Graph of the Table 6.27…… 187

Figure 6.35 The relationship between investors and their patents……... 188

Figure 6.36 The relationship between the highest cited applicants and number of patents……... 189

Figure 6.37 The relationship between institutions and companies and their number of patent publications…… 190

Figure 6.38 Yearly lithium – ion battery requirement for the several applications……... 192

Figure 6.39 The illustration of the relationship between the companies and their battery market……... 193

Figure 6.40 The relationship between outstanding battery companies and their amount of energy…….. 194

CHAPTER 1

INTRODUCTION

Energy is inevitable issue for our life throughout world. By using various forms of energy, we can drive our cars, turn on the lights at nights or cook food for dinner. Energy can be defined as the capacity of substance to do work. It can also be grouped into two categories which contain accumulated (stored) energy and transitional energy. Chemical energy which can also be found in fossil fuels, internal energy within a substance, potential energy which is related to position of a mass, can be given as examples of stored energy. Transitional energy can be defined as the energy which is transported from a system to its ambiance [2]. As examples for this energy form, heat and work can be given. The forms of energy is displayed in below:

- Energy of electromagnetic radiation
- Chemical energy (Chemical reaction energy)
- Nuclear energy (Binding energy of nuclei)
- Mechanical energy (Potential energy, kinetic energy, work)
- Internal energy
- Thermal energy (heat)
- Electrical energy [2]

Nowadays, the whole world is faced with the energy problem. Fossil fuels energy sources in the world have been rapidly depleted due to the increasing in the population. It is known that these energy sources produce greenhouse gases and lead to air pollution, global warming and climate change. Figure 1.1 exhibits the global energy consumption in 2018 [3]. According to this figure, fuel type which possessess the highest share in terms of energy consumption is oil, coal and natural gas, respectively.

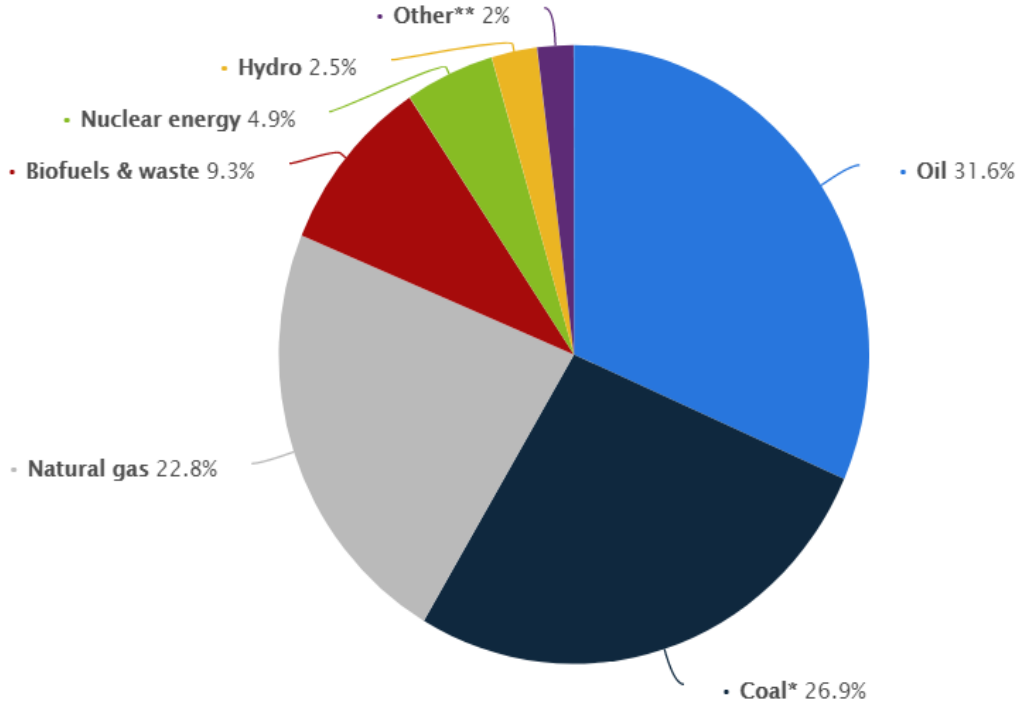

Figure 1.1 Primary energy consumption and supply worldwide in 2018 [3].

Figure 1.2 presents the carbon dioxide concentration over the last 1000 years. The amount of Carbon dioxide has increased since last 50 years. The current level of CO_2 is 390 ppm in the beginnings of 2000's. This level is higher than that of in 1955 (312 ppm) and before pre-industrial era (280 ppm) [4].

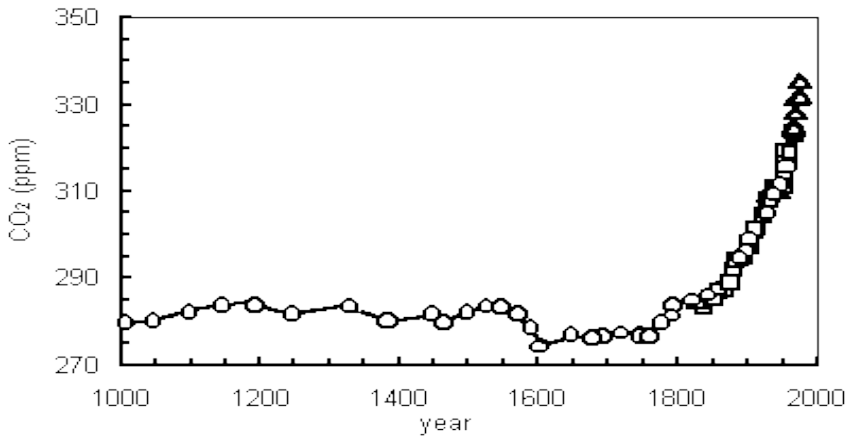

Figure 1.2 CO_2 concentration over the last 1000 years [5]

New alternatives must be found to overcome these problems. There are many energy resources like solar, hydro energy, wind energy, nuclear which less harm to the environment. However, these sources can vary from location of country to country in globe and they cannot entirely be predicted. Therefore, energy storage is an effective method and will reduce the energy problem. It also provides low-cost energy for everyone.

Energy storage systems are going to contribute subjects such as efficiency, reliability, power quality, transmission optimization and refers to capture or storage of energy produced at a certain time for later use. These systems can also contributes also to develop economics of conventional power plants [2]. There are many types of energy storage systems such as chemical (rechargeable battery, flow battery, hydrogen), mechanical (hydroelectricity, pumped hydro, compressed air, flywhell), thermal (sensible heat, latent heat, cryogenic thermal) etc. At the present time, clean energy storage instruments or devices like batteries, fuel cells and supercapacitors have been recognized as the next generation technologies to help in overcoming the global energy crisis.

Fuel cells have been the most preferred energy storage mechanisms owing to their large fuel conversion efficiency as well as working silently. They convert the fuel energy into a direct current of low voltage [2]. Supercapacitors are also most used and preferred energy storing systems by virtue of the their cheapness and environmental friendly. They have also been called as Electrochemical capacitors (ECs) and can be stored energy with the help of capacitance [6]. They can also make energy storing and give energy at extremely great rates. The most outstanding advantages of supercapacitors are that they present larger energy density than conventional dielectric capacitor, high power density and a long cycle, excellent efficiency, low internal resistance.

Energy storing mechanisms have also played a key role on the improvement of the availability and reliability of the energy-producing or energy supply system. The following factors provide determination of performance of energy storage devices or systems:

- Storage capacity or storage energy content
- Energy density for unit mass e_s and for unit volume e'_s
- Rate for storage charging (energy input) E_{in} and discharging (energy output) E_{out}
- Storage efficiency (η_s)
- Storage cycle duration $\tau_{s,c}$
- Storage capital cost, life span, and investment payback period [2]

The storage capacity or energy content can be defined as the highest amount of energy which storable in a mechanism and size during one storage cycle [2]. This factor is based on storage type, storage medium properties, storage reservoir volume, and change of characteristic factor like temperature for thermal energy storage systems when charging and discharging processes occur.

Energy storage systems can possess also a great advantage for both power-producing systems of intermittent sources like solar and wind, and many applications which can be utilized in our daily lives. For example, when power-producing systems are considered, they can make use of energy storage devices or systems in the case of low power production. Therefore, they have become one of the best alternatives in cases where energy generation does not meet the energy needs. Figure 1.3 represents the general design of an energy storing mechanism [2].

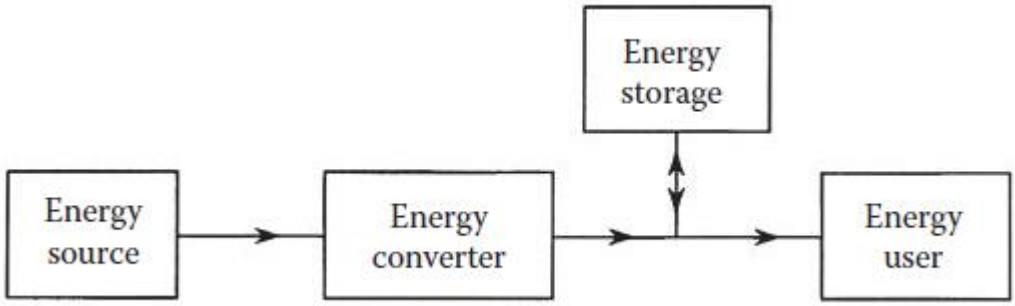

Figure 1.3 General design of an energy storing mechanism [2]

According to this figure, an energy source like solar, wind or natural gas is converted into another form of energy by benefitting from an energy converter. When energy is

needed or excess energy is existed, it can be stored in an energy storage devices like batteries, fuel cells and supercapacitor etc. When such these situations are satisfied, energy users may not encounter any serious problems.

The following equation explains the rate of change in storage energy content (E_s) [2]. As it can be seen in this equation, E_s depends on the rates of the energy input (E_{in}) during the storage charging operation and energy output (E_{out}) during the storage discharging operation. Apart from these factors, energy losses can also take place.

$$dE_s/d\tau=E_{in}-E_{out}-E_{loss} \text{ (W)} \quad \textbf{(1.1)}$$

In this equation, E_s stands for the energy content of the storage and its unit is Joule (J) and τ represents the time and its units is seconds.

The following equation gives the calculation formula of the storage efficiency or energy recovery efficiency [2]. It can be calculated as the ratio of the total energy output during discharging of the storage to the total energy input during the charging of the storage.

$$\eta_s=E_{out}/E_{in} \quad \textbf{(1.2)}$$

In addition to this, total energy output can be calculated as the difference between total energy input and energy losses. The formula of the total energy output is given as following [2].

$$E_{out}=E_{in}-E_{loss} \quad \textbf{(1.3)}$$

In this study, fuel cells and supercapacitors have been investigated. By depending on this, it emphasizes the energy storage performance analysis of fuel cells and supercapacitors with material characteristics. In second chapter, types of fuel cells and supercapacitors with their general characteristics like operating temperatures, electrical efficiency, electrolyte material and their advantages and disadvantages. It was indicated that what kind of benefits and harms are provided to various applications. As well as general properties of fuel cells, several important calculations of types of supercapacitors were also given like power density, energy density and capacitance. Third chapter includes the working principles and

mechanisms of fuel cells and supercapacitors. In this part, the general information was given about how these devices produce electricity. In addition to this, main parts of these devices were shortly explained. In mechanisms of fuel cells, energy production is generally based on hydrogen storage tanks or hydrogen supply because fuel cells provide electricity to the energy consumers when hydrogen was provided for the fuel cell mechanism. When mechanisms of supercapacitors were considerably analyzed, the energy storage depends on the electric or magnetic field and the absorption/desorption of the electrolyte ions. In the fourth chapter, the used materials in the fuel cells and supercapacitors were examined in detail like their general properties, structures. As well as these information, various comparisons were also made between several materials. In the fifty parth, it was mentioned which applications benefit from these devices. As it was expressed above, fossil fuels give rise to form various environmental problems like global warming, climate change, energy criris. In order to solve these problems, many companies or people make use of these devices. In the sixth part, the market analysis of fuel cells and supercapacitors were made. Additionally, several properties of them such as electrical conductivity, thermal conductivity were compared with each other and the situation of fuel cells, supercapacitors and batteries was reviewed in the world and Turkey. In conclusion part, the used materials in fuel cells and supercapacitors were compared. Furthermore, main reasons of usage of fuel cells and supercapacitors in many fields were also explained. Briefly, the basic purpose of this thesis study is to give information about fuel cells, supercapacitors as well as analysing their energy storage performances with materials used in them.

CHAPTER 2

TYPES OF FUEL CELLS AND SUPERCAPACITORS

2.1 Types of Fuel Cells

Fuel cells have generally been classified by depending on the electrolyte that is used within the fuel cell. DMFC (Direct Methanol Fuel Cell) is excepted for this classification because this type of fuel cell uses methanol as a fuel source and methanol is electrochemically oxidised directly in the fuel cell. Fuel cells can also categorized according to their operating temperatures. The operating temperatures of fuel cells are divided into two categories. These fuel cells are known as low-temperature, and high temperature fuel cells. Low-temperature fuel cells involve *Alkaline Fuel cell (AFC), Proton Exchange Membrane Fuel Cell (PEMFC),* Solid Oxide Fuel Cells (SOFC), DMFC (Direct Methanol Fuel Cell) and the Phosphoric Acid Fuel Cell (PAFC). The operating temperature of high temperature fuel cells is at 500 – 1000 ºC and these fuel cells are grouped into two different types. These are Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC) [7].

2.1.1 Alkaline Fuel Cells (AFCs)

AFC exhibits the greatest electrical efficiencies among all other types of fuel cells. However, this type of fuel cells only operates accurately with very pristine gases. This situation forms an important drawback in most applications. AFCs make use of the KOH electrolyte that has concentration of 30-45 wt %. KOH electrolyte presents an important benefit for acidic fuel cells. The oxygen reduction kinetics take place much quicker in alkaline electrolyte within acid that provides efficiently the usage of AFC mechanism. The AFC is utilized in space applications as the first fuel cell. Gemini program made use of PEM fuel cell after Alkaline Fuel cells had discovered many advantages and contributions over this system. Later, the AFC was also utilized on many space missions like Apollo. This fuel cell was also considered to be utilized for the European Hermes Project [7].

A Bacon fuel cell was the first AFC during 1950s and produced 5 kW power. Additionally, it utilized a Ni-anode, a lithiated NiO cathode, and 30 wt% aqueous KOH. It operates at 200 ºC and 5MPa. In the Apollo program, an AFC contained an 85% KOH solution between 200 and 300 ºC was utilized. For space shuttles, there are many purposes to use the fuel cells. These purposes contain providing energy and water, cooling the shuttle compartments. There are three plant modules that are utilized in the space shuttles and each of them produced the highest power of 12 kW [7]. AFCs are generally working at temperatures which are lower than 100 ºC therefore they do not need to enhance oxygen reduction kinetics but higher temperatures provide a promising advantage for the hydrogen oxidation kinetics.

Reactions play an important and a significant role for all of the fuel cells. In AFCs, both oxygen reduction and hydrogen oxidation contain OH^- ions as following reactions [7, 8, 9].

$$\text{Cathode}: \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad \textbf{(2.1)}$$

$$\text{Anode}: H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad \textbf{(2.2)}$$

$$\text{Overall}: H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \textbf{(2.3)}$$

The OH^- species were produced by the cathodic reaction of water [7]. OH^- species move by way of the electrolyte and they reach to the anode. As it can be seen in the reactions, OH^- species combined with hydrogen that oxidised at the anode side of the fuel cell. As a result of these reactions, water is produced as well as electricity and heat.

The most important advantage of AFCs is that the reduction of oxygen into OH^- occurs quicker than the acidic equivalent of oxygen into H_2O because of better and more excellent kinetics.

AFC electrodes are firstly started to use as Ni-based catalysts. They are also activated by making use of platinum. An important point must be expressed that the metal loadings are generally weaker (0,3 mg/cm^2 could be obtained) than for a PAFC

or a PEM fuel cell. There are also promising materials that are utilized and also under research [7]. But the Pt/C gas diffusion electrode are the most prominent electrodes that are utilized in the anode and the cathode.

Pt/Co alloys are preferable electrode materials because Platinum possesses an excellent activity for oxygen reduction because of a larger exchange current density. The Tafel plot is an important plot in order to evaluate the electrochemical kinetics. The Tafel equation expresses that electric current that passes through an electrode, is based on the voltage change which takes place between the electrode and the bulk electrolyte. The Tafel slope of oxygen reduction is same as of Pt catalysts (60mV decade^{-1}) [7]. Additionally, Ag and Co catalysts are also studied in order to substitute several or all of the Platinum in the electrodes. Figure 2.1 shows the Mass-transfer corrected Tafel plots for oxygen reduction reaction on Pt/C, Rh/C, Ir/C, RhSe/C, IrSe/C, and RuSe/C within 0.1 M $HClO_4$.

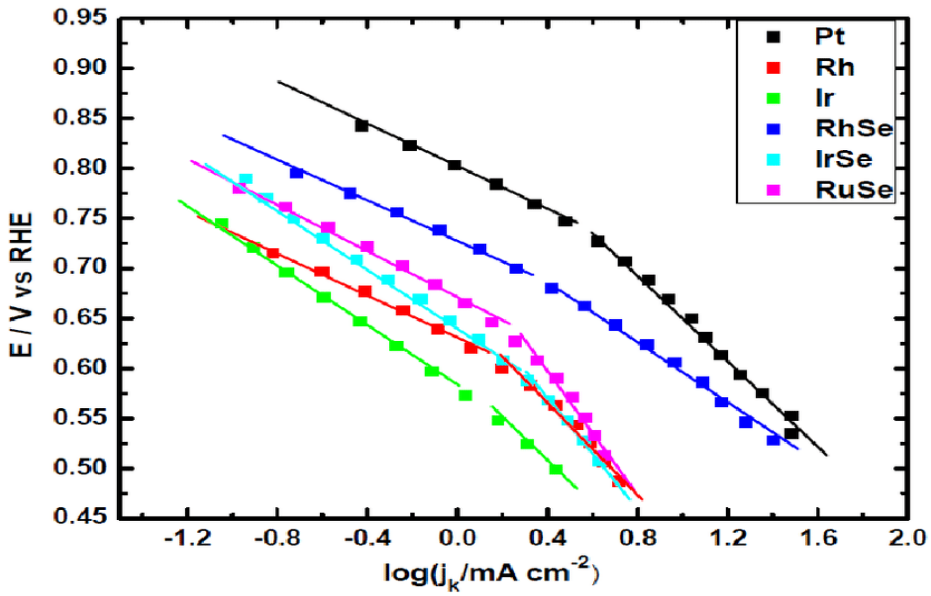

Figure 2.1 Mass-transfer corrected Tafel plots for Oxygen reduction reaction on Pt/C, Rh/C, Ir/C, RhSe/C, IrSe/C, and RuSe/C within 0.1 M $HClO_4$ [10]

A comparison was made between Raney nickel and a Pt/Pd anode in order to determine their stability characteristics. According to this comparison, Raney Ni electrodes exhibit an excellent activity for hydrogen oxidation. However, a decay

take place in performance because of the humidity of the inner pores and alterations in chemical structure under working conditions. With this comparison, a Pt/Pd anode possess higher stability characteristics than the Raney nickel. Moreover, a rapid decay also took place in the Pt/Pd anode but after a while this decay was prevented. Thus, the performance was improved and kept constant.

AFCs make use of KOH as electrolyte in a stabilised matrix. According to the obtained results, circulating KOH electrolyte can provide a much longer working lifetime for AFCs. The circulating KOH electrolyte prevent also gas leakage because of its excellent and good barries property. The most important advantage of this electrolyte is that it can be utilized as a cooling liquid in the cell or stack. There are also important advantages of usage of the circulating KOH electrolyte that provides cleaning of the cell and removal the water that is generated at the anode. The first demonstration that are related to the circulating electrolyte, was provided by Kordesch and partners during the 1970s. Their demonstration is related to the combination H_2/air AFC which can be provided by a lead acid battery within a hybrid device. Among workings, whole fuel cell had been turned off with evacuation of the KOH electrolyte. This situation increases significantly the life time and expectation since the cell voltage becomes extremely great (open-circuit voltage) under unload conditions. Great open-circuit voltages could also provide inducing carbon oxidation operations for obtainment of carbonates which may negatively affect and remove the matrix electrolyte [7].

The most considerable drawback is the obtainment of carbonates. It is usually considered that the CO_2 is naturally existed in the air and can also be produced by the reaction. CO_2 can become a dangerous factor in the fuel cells. CO_2 enters the reaction with the electrolyte according the following reaction.

$$CO_2+2OH^-\rightarrow CO_3^{2-}+H_2O \qquad \textbf{(2.4)}$$

As a result of this reaction, carbonates are produced. This reaction is related to the oxidation of carbon backing within the electrodes during open circuit voltages. Carbonates affect negatively the structure of the pores and they provide also congestion of the pores. Therefore, the gas diffusion is not carried out. As a result of

this situation, the cell performance naturally reduces. Therefore, a circulating electrolyte should abstain from the formation of carbonates.

There are also promising methods in order to remove Carbondioxide from the hydrogen feed and from the air flow and this procedure is expensive and high-cost. An iron-spinge system is used so as to hinder the creation of carbonates or carbondioxide. This system exhibits also similar process with the shift reaction in a reformer. The iron-spinge system is also utilized in a number of ammonia generation plants for the same goal. AFC applications can make use of the iron-spinge system. There are also other important processes such as swing adsorption or normal shift reaction in order to eliminate CO_2. These systems can be utilized in fuel cell systems.

2.1.2 Proton Exhange Membrane Fuel Cells (PEMFCs)

These fuel cells make use of a proton conducting polymer membrane as an electrolyte and work at low temperatures. These temperatures are usually between 85 and 105 ºC [7]. These fuel cells were firstly utilized in space applications such as Gemini program. The main purposes of these fuel cells are to utilize as an auxiliary power source and to produce clean and high-quality drinking water for astronauts. The membrane that is utilized in the PEM fuel cell, contains a polystyrenesulfonate (PSS) polymer. It is stated that this membrane does not have significantly stable structure. This expression provides that NASA selects Alkaline Fuel Cell (AFC) systems for its future space missions.

Nafion membranes are preferable membranes (DuPont) for PEM fuel cell by virtue of their higher acidity, their superb conductivity. These membranes exhibit more stable structure than the polystrene sulfonate membrane. Nafion composes of a polytetrafluoroethylene-based (PTFE) structure that exhibits chemically in an inert structure in reducing and oxidising environments, in opposite to the PSS membranes. The another important membrane is Dow membrane that exhibited current densities approximately four times greater than Nafion at the tantamount voltage.

The reactions that take place in a PEM fuel cell, have shown similarities with in a PAFC because both of them include an acidic electrolyte as it can be seen in the following equation [8, 9].

$$\text{Cathode: } \frac{1}{2}O_2+2H^++2e^-\rightarrow H_2O \quad \textbf{(2.5)}$$

$$\text{Anode: } H_2\rightarrow 2H^++2e^- \quad \textbf{(2.6)}$$

$$\text{Overall: } H_2+\frac{1}{2}O_2\rightarrow H_2O \quad \textbf{(2.7)}$$

The anode reaction is based on the oxidation of hydrogen which is splitted into protons and electrons. Then hydrogen flows from inside of the membrane and moves to the cathode. As it can be seen in the cathode reaction, oxygen is reduced and enters the reaction with protons in order to produce water.

The most important point that should be attached importance for the membrane, is the proton conductivity of the membrane. Many researchers are making an effort in order to improve more excellent membranes. The production of water at the cathode can also be an outstanding factor in order to make use of PEM fuel cell for the future applications.

Nafion is one of the most prominent electrolyte for PEM fuel cells. However, there are also other important perfluorocarbonsulfonic acid ionomers like the membranes from Dow, Aciptex, Gore and Asahi Chemical have been utilized. Membranes generally possess low temperature range where they are stable. Figure 2.2 represents the Nafion structure.

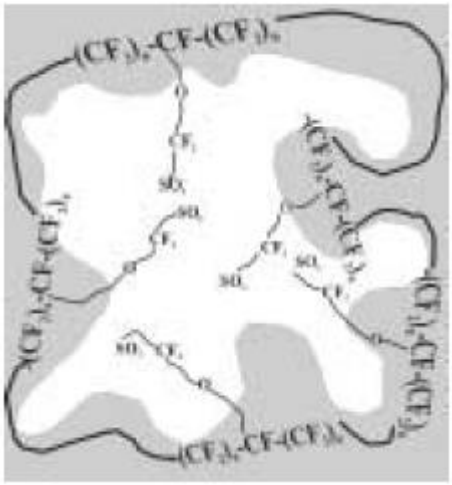

Figure 2.2 Schematic diagram of Nafion structure [7]

Water is an essential substance in order to provide conduction. The main reason for usage of water is that the maximum restrict of temperature is specified with the help of moistening requirements of the membrane.

There are also promising developments about both membrane structure and conductivity. The most effective method for providing these developments is to fabricate composite membranes. This can be provide by using several methods. The first method is to fortify the perfluorocarbonsulfonic membrane with PTFE components. The second method consists of providing absorption a membrane with a solution or with a rigid powder in order to reduce the permeableness of the reactant gases. The other important method is related to carry out the melting the membrane into a suitable resolvent and to obtain a mixture that is combined it with another substance. After these processes are completed and this solvent is provided the evaporation, the fuel cell can make use of the composite membrane.

In order to generate an organic/inorganic composite electrolyte, Poly(ethylene oxide)-like films (PEO) were absorbed or impregnated with lithium silicates. The main advantage of these composite electrolytes is excellent conductivity and their thermally stable structure. They also contribute to get higher performance in lithium batteries. These composite electrolytes have also been researched and studied in order to use them in fuel cell applications.

There are other prominent composites that were obtained by swelling perfluorinated ionic membranes with an ionic liquid. They could exhibited similar conductivity as Nafion 117 (K=0.1 $S.cm^{-1}$) but they can lead to form some important situations. They worked at 180 ºC that leads to increase oxygen reduction kinetics and CO poisoning problems [7].

There are also possibilities in order to produce other membranes. These membranes are obtained by adding SiO_2 or Al_2O_3 ceramic phase with H_2SO_4, H_3PO_4, or CF_2SO_3H (TFMSA). As a result of this method, the maximum conductivity was produced for a SiO_2/(polyvinydifluoride) (PVDF) binder (10%/15%) replenished with a sulphuric acid/H_2O mixture (1/3) [7].

New and high-quality membranes are also fabricated by making use of some important techniques and methods like plasma polymerisation or radiation grafting. The main purpose of usage of plasma polymerised membranes is to obtain thin exchange films. These thin exchange films are preferred to be used in the fuel cell. Because they can decrease ohmic resistance in the mechanism and protect membrane against drying. The main properties of plasma polymerisation is exhibiting highly cross-linked, uniform, and stable thin films.

A plasma polymerised layer of hexafluoropropylene and TFMSA exhibited also excellent cationic permselectivity, stability, and an ion-replacement capacity which is equal to Nafion 117 (0.9 meq g^{-1}) [7]. Permselectivity takes a significant responsibility for the membranes and can be defined as the preferred penetration of specific ionic varieties through ion-exchange membranes [11]. The main property and function of the permselectivity is to determine, evaluate and analyze the quality of the membrane separation. Furthermore, the most important purpose of the permselectivity is to evaluate the capability of a membrane and to separate different components form each other. The selectivity is calculated as following equation that can be defined as the proportion of the permeability of two elements like mixture A and B [12].

$$S_{A,B}^{p}=P_A/P_B \quad \textbf{(2.8)}$$

Other membranes must have some important properties such as oxygen diffusion, solubility and proton transport. Each membrane has their own advantages and disadvantages. For example, thinner membranes exhibit usually a lower resistance however they can possess a larger cross-over gas and this situation leads to decrease their performance.

Water possesses a great effect on the membranes of the fuel cells and should be important that water management must be provided. Because the conductivity must remain high. A dry membrane exhibits a smaller conductivity. Water management has become the most remarkable problems in PEMFC technology. It is known that water is generated from the reactions of cathode in liquid or gaseous form. In spite of this, it is difficult to protect the water content in the membrane. There is an also important factor that affects the water content in the membrane. This factor contains (electro-osmotic) water drag which is also called as air resistance or liquid resistance. Drag is a type of force that moves reverse direction to the relative motion of any matter passing in connection with a surrounding liquid. It can take place amidst two layer or surfaces of a liquid and rigid surface [13]. Figure 2.3 represents the conductivity of Nafion by depending on water content.

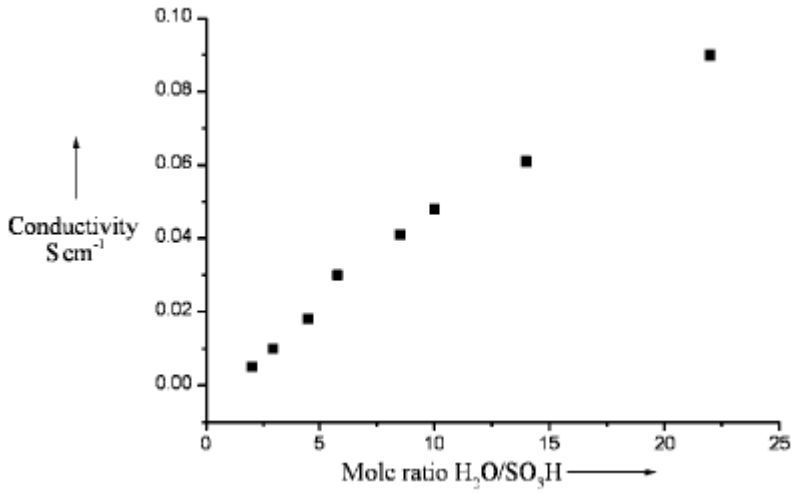

Figure 2.3 The conductivity of Nafion versus mole ratio H_2O/SO_3H [7]

For each proton, a Shell of (approximately 3.5) H_2O molecules is also transferred by making use of the membrane [7]. Additionally, in the inverse direction, the water may also send back from the cathode.

One of the most outstanding way for development of water management is to moisten the gases that take part in the fuel cell. An integrated stack can make use of cooling water that passes through the stach in order to moisten the gases. Polysulfonic membranes that are produced for ultrafiltration processes, exhibited more excellent performance with internal humidification than Nafion 115, as they possess more excellent water permeability.

Phosphoric acid doped polybenzimidaole (PBI) membranes exhibit good and excellent protonic conductivity and the H^+ transfer has not been affected from an elecro-osmotic water drag via the membrane. This situation shows that this membrane becomes an excellent and outstanding member for fuel cells. PBI membranes present also important advantages such as a small gas permeability and methanol cross-over. DMFC can also make use of these membranes that can also be made appropriate for DMFC.

There is also another form of water management that is observed in direct hydration of the membrane by assembling porous fibre wicks. Porous polyster fibres are also important materials in order to protect water content in the membrane. These materials, namely porous polyster fibres, have a twisted structure and they are located between the membrane and a cast thin film of Nafion ionomer. In order to carry out this process, a hot press must be used. This situation provides a direct water supply or source from product water at the cathode to the membrane by making use of a pressure difference.

Another effective way to develop water management was that fuel cell were made use of self-humidifying membranes. These membranes were also obtained by absorbing a Nafion membrane with a low weigh-percentage of SiO_2 and TiO_2. Firstly, the water has been generated at the cathode and then the water is transferred with the help of electro-osmotic drag. After all processes are completed, the water is adsorbed by oxide particles in order to provide hydration of the membrane and to

protect water content of the membrane at all times. Thus, the cell has a good stable structure and exhibits excellent performance under ambient conditions [7].

Electrodes play a significant role in PEM type fuel cells and they must indicate porous structure in order to provide gas diffusion and transfer reactant gases to the active zones. Active zones can be expressed that the noble metal catalysts establis a connection with the ionic and electronic conductor. Gas diffusion electrodes (GDE) are found in the market but the production of them are very complicated process. Structure of GDE affects also the efficiency of the fuel cell and relies on significantly fabrication process. Electrodes contribute to catalyse and quicken a reaction that is made by the catalyst particles. But the function of the electrodes are much more than this catalysing function.

An excellent electrode must possess a three-phase boundary that is found amidst the gas supply, and the catalyst particle and the ionic conductor. Figure 2.4 represents the three phase boundary in gas diffusion electrodes.

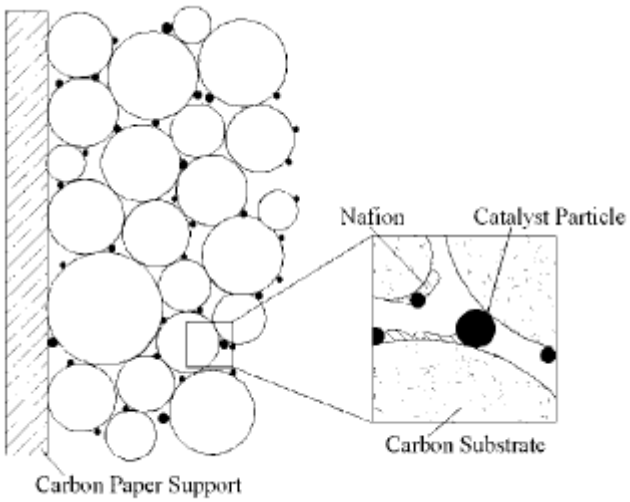

Figure 2.4 The three-phase boundary in a GDE [7]

In Figure 2.4, these particles have to get in contact with an electronic conductor in order to provide supplement of the electrons or removal of electrons from the reaction site. Electronic conductivity has become an important factor and can be

generally carried out by a carbon backing onto the catalyst pieces. The three-phase boundary can be obtained by injecting the catalyst/support powder with some important ionomeric binder before the electrode is assembled and pressed onto the membrane. This situation provides excellent and high-quality contact of most catalyst particles with ionomer chains that get in contact ionically with the membrane.

Gas diffusion electrodes takes place via the backing layer and the carbon support to the catalyst particles. When the fuel cells make use of the moistened gases or a methanol/water mixture, the catalyst layer needs to possess extremely good hydrophobic structure in order to prevent and protect the pores from flooding. This hydrophobic structure can be obtained by presenting PTFE as a in combinstion with Nafion that has a hydrophillic structure. In spite of the high and good solubility of oxygen in PTFE, its diffusivity and permeability (solubility*diffusivity) becomes rather low. One of the most important property of a high PTFE content of the layer is to prevent reachable protons to the catalyst particles.

There are a large amount of non-noble metal catalysts that are also researched. However, platinum-based catalysts are the most preferable and useful materials for oxygen reduction reactions (ORR). Platinum (Pt) particles present excellent performance and are also diffused on carbon or other small particles like colloidal.

Important investigations are also made in order to make use of low-cost materials and more excellent catalysts for the ORR. There are also preparation methods for non-noble metal catalysts. One of the most important method is that they can be prepared by making use of the prolysis of ironacetate adsorbed on perylenetetcarboxylic dianhydride in a $Ar/H_2/NH_3$ gas mixture at 900 ºC. This catalyst that contains the highest iron content of 0.2 wt%, exhibited a similar current density at 0.5 V with 0.2 wt % Pt/C catalyst [7].

In order to increase gas diffusion, the carbon backing layer plays an crucial role and this layer must be analyzed. There are also commercially backing layer that is found at the market. However, all of them does not exhibit the same gas-diffusion properties. Carbon cloth backings exhibit 3-5 fold larger permeation proportions that

carbon paper that are compressed carbon fibres. Carbon cloth is a type of carbon fibers that are coated on a clothlike material. The most important advantage of the usage of carbon cloth in cathode backing layers is to enhance the power density which approaches to 20 % more than with carbon paper [7]. But, the paper backings contribute to acquire some important properties for the electrode like larger stability and rigidity. But, the results that are obtained from distinct groups, are not coherent in this point and the most suitable backing material rely significantly on the cell design.

In order to produce the porous structure of the cathode layer, pore-forming substances can be impregnated to the electrode. When the porosity of the cathode layer reaches to the optimum level, mass-transport resistance decreases. This situation contributes to develop the overall performance of the electrode.

The transportation of water is an important problem through the backing layer. Backings that possess delicate microporous layers, present a higher efficiency. Water passes by the way of the electrode and support layer by abstaining from the complete flooding of the pores.

The main goal of the anode is to carry out the oxidation of hydrogen in the fuel cells but the oxidation of methanol is also carried out in the DMFC. The fuel stream composes of hydrogen and Pt are preferred as catalysts in an ideal system. But the fuel stream includes also traces of some certain and hazardous element sor compounds like CO, S, and NH_3.

CO has been the most dangerous compounds within low temperature fuel cells because it leads to form poisonous morphology of the low temperature fuel cells. In the PEMFC and PAFC, CO poisoning takes place because of the adsorption of the species to the active sites of the catalysts. The most important point of Pt catalysts is that they posess an dangerous property like adsorption of CO. Hence, this situation leads to cover the surface with CO. In order to make use of surface effectively, the CO can be provided conversion and oxidation to the CO_2. This situatoon can be easily carried out in the AFC. In other words, the oxidation of CO to CO_2 takes place easily but this process causes contamination of the electrolyte because of carbonate

formation. When a comparison is made between AFC and PEMFC, the oxidation of CO takes place easier than in the PEMFC, with the help of the higher working temperatures.

In order to abstain from CO contamination in the fuel cell, some important investigation groups developed a number of methods that are used. One of these methods is that a gas clean-up can be constructed amidst the reformer and the fuel cell but the system becomes complexity. This construction gives rise to enhance costs. Some important investigation groups impregnated Oxygen or Hydrogen peroxide to the fuel stream in order to provide the oxidation the CO to CO_2.

Some research groups are also investigating better and high-quality catalysts that provide oxidation of CO at low temperatures and exhibit important advantages. CO-permissive anodes generally composes of a Pt-based compound (like Pt/Ru). There are also triple Pt/Ru/X alloys, where X becomes a kind of other metals. These alloys could be obtained by using a direct-current magnetron spattering method in order to fabricate thin layers on ordinary fuel cell electrode substances. Pt/Ru/X exhibited a developed CO rolerance over both Pt and Pt/Ru catalysts.

Ru has an outstanding effect on the catalytic activity of Pt for the electro-oxidation of methanol. There are also two important techniques that are proposed by Gasteiger et al.. The first statement of these two techniques is expressed that positive effect of Ru is a consequence of its capability to expedite dissociated water adsorption. The second mechanism is expressed that the bifunctional mechanism contributes to adsorb an oxide species onto the Ru surface. This mechanism, namely bifunctional mechanism, provides the generation of OH_{ads}. The main function of this species is to behave like a source in order to complement the oxidation of CO into CO_2. (Ru-O bond which is between Ru and O is slightly weak, helps to enter the OH_{ads} reaction with the CO.) According to the results that are obtained from STM and IR researches and studies of adsorbed CO, nanostructured Pt/Ru electrodes and alloys exhibit very equivalent catalytic efficacy towards CO oxidation. They could be expressed on the basis of a collaborative reaction system. This mechanism states also that CO surface mobility has a great effect on the supportive effect of Pt/Ru and for its maximum tolerance.

Davies and partners made a research about an electronic promotion of Pt/Ru catalysts. They obtained some important information and results. These results include that Ru in the second and third layers will contribute to proceed and support the oxidation of CO.

These two mechanisms that contributes to increase and provide proceedings of oxidation of CO on Pt/Ru catalysts, could be analyzed in order to be used them in different alloys. There is also significant system in order to express the supportive effect of some Pt alloys like some Pt/Sn compounds. This mechanism provides filtering (is also known as leaching) of the secondary metal out of the alloy. Thus, this mechanism brings about enhancement of catalyst's surface area. The supportive effect is attached to the development in surface area. If all the metal leaches out, no more support can completely be accomplished.

2.1.3 Direct Methanol Fuel Cells (DMFCs)

These fuel cells which are based on PEM technology, work at low temperatures. DMFC and PEMFC are similar with each other in terms of working temperature but DMFC can operate at slightly at higher temperatures than PEMFC. Because these higher temperatures are generally related to the electrolyte and used fuel. DMFC does not make use of any intermediate step in order to reform the alcohol into hydrogen. There are also outstanding advantages of methanol and these advantages provide contribution to the DMFC. Methano is produced from natural gas or renewable biomass sources. It exhibits also good, high and large specific energy density. Methanol is also a liquid form at working temperatures. There is also a good infrastructure in order to drill and transform both natural gas and petrol. Methanol is one of the most useful alcohols and fuel in DMFC and may be send directly inside a fuel cell. It could be also transformed electrochemically at the anode [7].

The DMFC is able to make use of a gas or fluid form of fuel and these forms can also be sent into the fuel cell. The liquid DMFC usually utilizes methanol diluted in water (typically 1-2 M) and the small low rate of the methanol is utilized. So, waste products or fuels should be reused and the concentration in the fuel feed should remain constant [7]. In order to provide and this, fuel cells can make use of the

methanol sensors that play also an important role in the fuel cell mechanism. Basic purpose of the methanol sensors is to determine the current from an electro-oxidation of methanol. These sensors contain an electrochemical system.

As the reactions are evaluated, methanol enters directly fuel cell from the anode and the oxidation of methanol takes place at the anode. Protons pass from the anode to the cathode by way of the electrolyte which consists of an acidic membrane. Many researchers have been investigating liquid-acid DMFCs. ORR takes place at the cathode and this reaction does not show a difference from the normal acidic reaction. The following equations show the anode, cathode and overall reactions, respectively [7, 8, 9].

$$\text{Anode: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \textbf{(2.9)}$$

$$\text{Cathode: } \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad \textbf{(2.10)}$$

$$\text{Overall: } CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \quad \textbf{(2.11)}$$

Catalysts play an important role in the fuel cells. The activity of catalysts for methanol oxidations should be developed. Pt-based compounds have exhibited the maximum activity up to now. When methanol oxidation is made a comparison with hydrogen oxidation in terms of catalytic activity, the catalytic activity for methanol oxidation is not more effective than catalytic activity for hydrogen oxidation. So as to improve the activity of the catalyst, other metals can be added to the Pt. These metals include Re, Ru, Os, Rh, Mo, Pb, Bi, and Sn that contribute to a good impact on the catalytic activity in terms of methanol oxidation. One of the most important factors for promotion and support is to produce OH^- species on the secondary metal for all these metals. This production takes place that potential of the secondary metal is smaller than Pt. The OH^- species become important in order to oxidise intermediate adsorbates. There are also other important factors that affect the catalytic activity of the electrode. These factors involve the support, the ionomer content in the active layer, and the fuel feed. It was obtained that the specific activity of supporte Pt/Ru/C becomes much higher than for Pt/Ru black. The maximum

obtained and reachable voltage in the cell as lower and smaller for the supported catalyst. There is also an important disadvantage of the cell that makes use of the unsuported catalyst is smaller cross-over rate. This situation leads to be used a higher methanol. One of the most important and outstanding advantage of usage of a supported metal catalyst is to decrease the metal loadings strongly. A difference is also obtained in performance and this difference can be based and depend on the difference in morphology between the two types of catalyst. So, researchers should delve into the stability of supported and unsupported metal catalysts.

There are also a number of preparation methods of electrodes that include cold spraying and pressing, hot spraying, rolling. The most important point is that these preparation methods affect also the performance of the electrode. According to the observations of these techniques, a rolling technique enhanced the catalytic activity of a Pt/Ru catalyst.

DMFC can also make use of methanol resistant cathode catalysts in order to abstain from methanol cross-over issues. This problem gives rise to affect the cathode. Methanol cross-over becomes one of the most important topics for the DMFCs. The proton movement that passes through the membrane is directly related to water transfer which can carry out within the solvation shells. Because of the equivalent characteristics of methanol (like its dipole moment), it can be transferred to the cathode owing to usage electroosmotic drag. At the cathode, methanol leads to form a complicated potential because of its oxidation and as a consequence of this situation, the cell performance reduces. Figure 2.5 represents the effect of methanol on the efficiency of a Pt/C cathode for ORR.

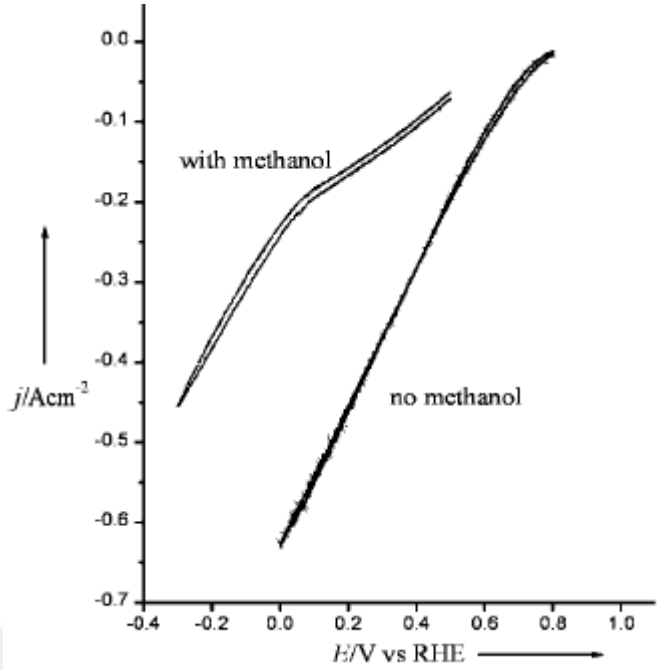

Figure 2.5 The effect of methanol on the efficiency of Pt/C cathode for oxygen reduction [7]

Membranes have become one of the most essential components for fuel cells. They can also be arranged for methanol blockings. Each membrane possesses its own properties. Thinner membrane has smaller resistance however, they can display a greater permeableness for fluid methanol. For DMFCs, an intenser membrane like Nafion 120 have also been preferred.

The cross-over effect is based on the methanol intensiveness in the feed. It is assumed that an optimum concentration of methanol is found about 2 Molar in water (about 6% methanol) [7]. In order to overcome the methanol cross-over problem, methanol-tolerant cathode should be improved. With the help of this concept, the methanol diffusion is not hindered but in place of this concept, cathode with catalysts that are passive and insensitive against methanol oxidation have been used by obstructing the formation of a mixed potential at the cathode. Many research groups have also investigated different methanol-tolerant cathodes. A $Mo_2Ru_5S_5$ catalyst (Chevrel process) exhibits lower efficiency than Pt for pristine Oxygen activity however, in the existence of methanol, the efficacy of Pt catalyst spoiled low that of

the Mo/Ru/S-based catalyst. So as to improve the usability of the mixed transition metal sulfides, a sulphur treatment of carbon support is applied.

The another important methanol tolerant catalyts have taken part in iron-porphyrin materials that have high surface area carbon. A number of experiments were carried out under fuel cell conditions about these catalysts and any deterioration did not take place in the electrode efficiency when fuel cell makes use of methanol as fuel source.

2.1.4 Phosphoric Acid Fuel Cells (PAFCs)

This type of fuel cells is one of the best fuel cells and has an excellent system when it is improved commercially. Stationary power plants can make use of basically phosphoric acid fuel cell and its usage fields are ranging from transported power to on-side generation plants. Power plants that make use of phosphoric acid fuel cells, produce power that is ranging from 0.2 - 20 MW. Phosphoric acid fuel cell displays also some important advantages like their simple construction, their excellent thermal, chemical and electrochemical stability and the small electrolyte vaporization at working temperatures [7].

In the beginnings of the improvement of PAFCs, diluted acid was preferred in order to abstain from corrosion of some of the cell components. The important contribution of larger intensiveness of the acid enhances the conductivity of the electroyte and decreases the decomposition of the carbon-supported electrodes. The following reactions display the anode and the cathode reactions, respectively [7, 8, 9].

$$\text{Anode: } H_2 \rightarrow 2H^+ + 2e^- \quad \textbf{(2.12)}$$

$$\text{Cathode: } \tfrac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad \textbf{(2.13)}$$

$$\text{Overall: } 2H_2 + O_2 \rightarrow 2H_2O \quad \textbf{(2.14)}$$

The electrodes of PAFCs generally make use of Pt-based catalysts and they are also supported with a carbon-base support. In the beginnigs of the 1960s and 1970s, many investigation groups were seeking for novel catalysts so as to enhance the performance of the fuel cells. As a result of these investigations, Tungsten Carbide

has become promising candidate for convenient catalysts because of its long life time, its excellent resistant and stability structure under PAFC condition [7]. In addition to this, this material can not also deteriorate the fuel cell in the existence of CO. In spite of all these advantages, Pt is one of the most preferable material because of its more excellent properties. However, Tungsten carbide possesses a very difficult fabrication process in order to be obtained same and consistent results.

When PAFC made use of a liquid electrolyte, a hydrophobic backing layer must be used. This layer is obtained by submerging into a solution of PTFE (Polytetrafluoroethylene). Electrodes that are obtained from Pt/WO_3, exhibit more excellent efficiency than those of plain Pt/C by about twice the current density for the identical voltage [7]. As a result of this expression, the usage of WO_3 leads to electrochemically active surface area and the performance.

2.1.5 Molten Carbonate Fuel Cells (MCFCs)

The improvement of this type of fuel cells started around the mid-20th century. MCFCs can make use of generally hydrogen, methanol or carbonaceous fuels. When carbonecous fuels are used, they will emit CO_2 throughout their oxidation routes. Therefore, the material selection of a molten carbonate for fuel cells is very important and this selection should be extremely reasonable. Additionally, MCFCs operate at high temperatures (600-700ºC) and can generally make use of fuels that are obtained from natural gas and coal. The high temperatures contributes to enhance the oxygen reduction kinetics significantly and also provide limitation the need for very great loading and/or precious metal catalysts. In other words, MCFCs can make use of non-precious metals as catalysts at the anode and the cathode. This situation can contribute to reduce costs of MCFCs. The efficiency of MCFCs can reach up to 50%-70% when the fuel cell is combined and used with other power generators. The following reactions represent the reactions which come about at the anode and the cathode, respectively [7, 8, 9].

$$\text{Anode: } H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \quad \textbf{(2.15)}$$

$$\text{Cathode: } \tfrac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \quad \textbf{(2.16)}$$

Overall: $H_2 + ½O_2 \rightarrow H_2O$ **(2.17)**

Carbonate ions take place when hydrogen is oxidized and are obtained from the movement by way of the electrolyte (a molten carbonate). Cathodes in MOFC consist of NiO that is obtained by an anodic oxidation of a Ni sinter or from an insitu oxidation of Ni metal when the cell is started to operate. NiO cathode possesses sufficiently an active structure for oxygen reduction at high temperatures, therefore usage of Pt-based metal is not required. There are also important alternatives for MCFC cathodes like $LiFeO_2$, Li_2MnO_3 and $LiCoO_2$, also in combination with NiO materials in order to produce double-layer electrodes. For example, NiO/$LiCoO_2$ double-layer electrode contributed to develop the stability significantly. Oxygen reduction reaction (ORR) was develope at these double-layer cathodes and this situation leads to reduce the resistance.

Ni/Al or Ni/Cr alloys are the most promising materials for MCFC anodes. These materials are started to use since Ni anodes do not possess sufficiently stable structure under the MCFC working conditions as Ni is filtered.

MCFCs make use of molten carbonate as electrolyte that is balanced and stabilised by an Alumina-based matrix. MCFCs made use of firstly Li_2CO_3/K_2CO_3 materials as electrolytes. But, these materials leads to degrade and deteriorate components of the fuel cell. Therefore, other materials were decided to use. A Li_2CO_3/Na_2CO_3 materials has important advantages like more excellent endurance and smaller decay rate than Li_2CO_3/K_2CO_3 rate.

The choice of the materials possesses a great importance in high temperature fuel cells because of degradation, sealing, and thermal expansion properties. The selected materials must also prevented and remove a number of disadvantages. For this, fuel cells can make use of some important high temperature steel alloys like Ni-, Co-, and Fe-based alloys or Cr/Al alloys which exhibit further stable structure than normal stainless steel (SS). An Fe/Cr feritic SS materials could be utilized in constituents of fuel cell because of the low-cost of these materials. However, these materials do not have an excellent corrosion resistance. Another important material is an Fe/Ni/Cr austenitic material that exhibited an excellent resistance for the cathodic reduction

however this is not valid for the anodic reaction. The most effective way is to make use of Ni coating in order to decrease anodic corrosion. The most important factor that affects significantly the corrosion resistance, is the Cr content in the stainless stell compound. When the Cr content is higher level, the corrosion rate will decrease. Another promising compouns is $LiCrO_2$ that leads to reduce the corrosion.

2.1.6 Solid Oxide Fuel Cells (SOFCs)

They benefit from a solid oxide material as electrolyte. Therfore, SOFCs exhibit a better stable structure than MCFCs. The main reason of this is that they do not encounter any leakage problems because of a fluid electrolyte. This fuel cell consists of a two-phase gas-solid mechanism. Therefore, SOFC does not meet any problems that are related to water management, deluge of catalyst layer, or low oxygen reduction kinetics [7]. In order to provide thermal and chemical stability characteristics for working at great temperatures, good and high-quality materials must be selected. The following reactions show the anode and the cathode reactions, respectively [7, 8, 9].

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ **(2.18)**

Cathode: $½O_2 + 2e^- \rightarrow O^{2-}$ **(2.19)**

Overall: $H_2 + ½O_2 \rightarrow H_2O$ **(2.20)**

SOFCs use solid oxide electrolyte that has more stable structure than MCFCs and this electrolyte prevents the leakage. This leakage can be a major problem for molten carbonate electrolyte of MCFCs.

Since the beginnings of SOFC improvement, LSM electrodes have been more preferable and useful for SOFCs as cathodes. Because these electrodes exhibited a large efficacy for oxygen reduction at large temperatures and they possessed also stable structure under SOFC working circumstances. Single-phase LSM cathodes exhibit small oxide dispersion coefficient, therefore a two-phase cathode is more preferable to use. Two-phase cathode leads to a smaller overpotential for the oxygen reduction reaction. YSZ is one of the most preferable and useful electrolyte in the

SOFC. A composite LSM/YSZ cathode exhibited higher and more excellent O^{2-} conductivity and the active area was higher. Many R&D groups sought for Perovskite-type materials as cathodes for SOFCs. Iron doped cobaltates $Y_{0.8}Ca_{0.2}Co_{1-x}Fe_xO_3$/YSZ presented a more excellent thermal stability than undoped Cobaltates and their activity for oxygen reduction was also excellent to LSM cathodes. Another important perovskite material is Lanthanide-based perovskites that exhibited good conductivity and large catalytic activity for oxygen reduction. One of the most outstanding cathode material is $Sm_{0.2}Sr_{0.8}CoO_3$ because of its highest performance [7].

SOFC can utilize Ni cermets as anode material. Ni cermets can provide also contribution to the anodes such as stabilization. NiO anodes can also be solved within the YSZ electrolyte however this provides the stabilization the cubic phase of the electrolyte. Doped cerium oxide based YSZ anodes possessed some important advantages like more excellent ionic and electronic conductivity than a nickel-based anode. Additionally, doped cerium oxide based YSZ anodes display less sensibility and susceptible to carbon production. Some important additive materials can also be used like addition of MnO_2 in order to develop the adhesion between the anode and the YSZ electrolyte. However, addition of MnO_2 reduces the performance of the electrode. In high temperature working fuel cells, most ceramics give high conductivity in order to produce high overall performance. Zirconia-supported electrolytes are more stable and exhibit a good conductivity. Ceria-based electrolytes have become one of the most outstanding candidates because of their high conductivity than Yttria-Stabilised electrolytes and can contribute to the SOFCs with ferratic stainless steel materials. Special metallic or ceramic materials must be use in order to abstain from differences in the thermal expansion coefficients and to strenghten the fuel cell for high working temperatures. Additionally, high-quality cathodes and more conductive electrolytes should be used. Chromium-based alloys are the preferable materials for bipolar plates because of their excellent conductivity, large corrosion resistance at high temperatures, simply formation. Calcium-doped lanthanum plates played an important role and were also used as bipolar plate materials when they were combined with small amounts yttrium binder. Chromium

doped ferritic steels are conductive enough for low temperaure applications. Table 2.1 summarizes the types of fuel cells with their important properties.

Table 2.1 Classification in fuel cell types [14]

Fuel Cell	**Electrolyte**	**Operating Temperature**	**Electrical Efficiency**	**Fuel 'Mixture'**
AFC	KOH solution	Room temperature to 90 ºC	60-70%	H_2 - O_2
PEMFC	Proton exchange membrane	Room temperature to 80ºC	40-60%	H_2 - O_2 or Air
DMFC	Proton exchange membrane	Room temperature to 130ºC	20-30%	CH_2OH - O_2 or Air
PAFC	Phosphoric acid	160-220ºC	55%	Natural Gas, Biogas, H_2 - O_2 or Air
MCFC	Molten mixture of alkali metal carbonates	620-660ºC	65%	Natural Gas, Biogas, Coalgas, H_2 - O_2 or Air
SOFC	Oxide ion conducting ceramic	800-1000ºC	60-65%	Natural Gas, Biogas, Coalgas, H_2 - O_2 or Air

2.2 Types of Supercapacitors

Supercapacitors can be classified into three types. These types are Electrical Double Layer Capacitors, Pseudocapacitors and Hybid Capacitors.

2.2.1 Electrical Double Layer Capacitors (EDLCs)

In this type of supercapacitors, the charge aggregated amidst the electrode and electrolyte interface. Capacitance (C) can be calculated by making use of the following equation.

$$C = \frac{\varepsilon}{4\pi\delta} \int dS \quad \textbf{(2.21)}$$

In this equation, ε represents the dielectric constant of the electrolyte, S means the electrode interface surface area and δ stands for distance between the center of ion and the electrolyte interface [15]. When publications were analyzed in recent times, the specific capacitance can also be found with the help of the following formula.

$$C = k\frac{\int i}{mS} \quad \textbf{(2.22)}$$

In this formula, i and S are the integrated area of the CV (Cyclic Voltammetry) curve and the scan rate of the CV conducted, respectively. m means the mass of the electrode material, and k represents a constant multiplier. In addition to this, the specific capacitance can also be calculated by using galvanostatic discharge profile as following formula.

$$C = k\frac{it}{\Delta V.m} \quad \textbf{(2.23)}$$

As it can be seen in eqn. (2.23), i and t stand for the current and the time elapsed when discharge process occurs, respectively. As well as these elements, m and V are mass of the electrode material and the operation potential range, respectively. In EDLCs, the energy density (E) and power density (P) are calculated by utilizing the CV profile as the following formulas [15].

$$E_{cell}(Wh/kg) = \frac{1}{2}CV^2 \quad \textbf{(2.24)}$$

$$P_{cell}(W/kg)=\frac{Ecell}{\Delta t} \quad \textbf{(2.25)}$$

In the equation of power density, Δt means the discharge time.

2.2.2 Pseudocapacitors (PCs)

These capacitors show differences from EDLCs and are also known as faradaic supercapacitors. They depend on quick reversible faradaic (redox) reactions. In other words, these reactions take place transfer of charge acroos the double layer and as a reault of this process, faradaic current which moves through the supercapacitor cell, is obtained. This process contributes to improve the energy density and the specific capacitance. The most important drawback for pseudocapacitors is that they display lower power density and cycling stability than EDLCs [16].

The charge which is stored in the electrodes of the pseudocaoacitors, is calculated as the following equation [15].

$$q=C*\Delta E*m \quad \textbf{(2.26)}$$

In this equation, m represents the mass of the pseudocapacitors (PC) material, C is the specific capacitance and ΔE stands for the range of CV working.
The following equations explain that the electrochemical capacitances for CV and galvanostatic charge and discharge calculations in pseudocapacitors are measured.

$$C=\frac{\int i(V)dV}{2v\Delta VS} \quad \textbf{(2.27)}$$

$$C=\frac{I\Delta t}{\Delta V} \quad \textbf{(2.28)}$$

In above equations i, V, I and S are current, scan rate (mV/s), applied current density, and active electrode area, respectively.

Energy density (E) and power density (P) have been two important parameters for both supercapacitors and other energy storing devices. The calculation of these parameters is based on the galvanostatic discharge profile as the following formulas could be given [15].

$$E_{cell}\ (Wh/kg) = \frac{1}{2} CV^2 \quad \textbf{(2.29)}$$

$$P(W/kg)=\frac{V^2}{4RS} \quad \textbf{(2.30)}$$

In formula (2.30) of power density (P), R means the total resistance that is measured by utilizing the voltage decline among two points in the discharge profile (ΔiR) and the applied current (i). This parameter are calculated as the following equation [15].

$$R = \frac{\Delta iR}{2i} \quad \textbf{(2.31)}$$

Both power and energy densities have layed outstanding role on performance on pseudocapacitors and other types of supercapacitors.

2.2.3 Hybrid Supercapacitors

The main purpose of usage of hybrid supercapacitors is to solve problem of energy density restrictions of carbon-basis supercapacitors. By depending on study which is carried out by Melanie Ihns and partners, they fabricated 3D high-performance hybrid supercapacitors and microsupercapacitors. These supercapacitors are produced from graphene and MnO_2. According to this study, hybrid electrodes which was used in these supercapacitors, produced ultrahigh volumetric capacitance of over 1100 F/cm^3 [17].

Hybrid supercapacitors have become the most prominent energy storage mechanism. They display greater energy and power density than EDLCs by making use of Faradaic and non-Faradaic operations. In order to create hybrid supercapacitors, researchers and scientists have benefitted from several combination of materials like RuO_2, Co_3O_4, NiO, V_2O_5, $Ni(OH)_2$, and MnO_2. When a comparison is made between

these outstanding materials, many researchers and scientists have attached importance to the MnO_2-based systems or materials which have become more preferable and useful than other materials owing to its (MnO_2) abundant in the earth and unharming substance withal large theoretical specific capacitance of 1380 F/g [17]. But, these substances exhibit the low conductivity (10^{-13} S/cm) and electronic (10^{-5}-10^{-6} S/cm) conductivity of pure MnO_2. This situation gives rise to the limitations of the electrochemical performance of the hybrid supercapacitors. So as to abstain from and solve this drawback, ultrathin MnO_2 films were fabricated and contributed to enhance the performance of the hybrid supercapacitors. Furthermore, they present also several tens of nanometers in terms of thickness. However, both thickness and the area-normalization capacitance which belongs to these electrodes have not become sufficient on the purpose of usage in various systems. In order to overcome this obstacle, MnO_2 can also be combined with largely conducting backing substances which show large surface areas like Nickel nanocones, Mn NTs, Activated Carbon, Carbon cloth, CPs, CNTs and Graphene. As a result of these combinations, excellent specific capacitances (148-410 F/g) were obtained [17]. However, these values have ben achieved under low charge-discharge rates. Moreover, these values are also based on improvement of the discharge rate. In other words, these values are inversely proportional to the discharge rate. If the discharge rate increases, these values will start decreasing. As well as these situations, several of these materials display also low packing density with high pore voume. This statement indicates that a huge amount of electrolyte must be require in order to construct the supercapacitor. Additionally, both the energy density and power density of these mechanisms have also decreased. So as to prevent these problems, excellent and outstanding hybrid electrodes which depend on 3D graphene doped with MnO_2 nanoflowers were obtained and improved. This composite or hybrid material contributes to increase the conductivity, pore structure, specific surface area, gravimetric capacitance and volumetric capacitance. Graphene plays an importan role on achieving of these properties. Furthermore, MnO_2 helps to create extra active regions in the Faradaic reactions and reduce the ion spread lanes which have a great effect on enhancement of the capacitance. According to the obtained results, hybrid supercapacitors which use this composite material (graphene/MnO_2), possess energy

density of up to 42 Wh/l. When a comparison was made with a carbon-based supercapacitors, graphene/MnO_2 based hybrid supercapacitors present higher energy densities than carbon based supercapacitors (7 Wh/l). As well as this comparison, these hybrid supercapacitors (graphene/MnO_2) benefit from aqueous electrolytes and can also easily assembled in air [17]. In other words, they do not need any dry rooms in order to construct today's supercapacitors.

Many researchers and scientists strive to create macroscale hybrid supercapacitors. Additionally, the studies which are related to fabrication of microscale hybrid supercapacitors have also been found. However, the design and the combination of hybrid materials into microscale supercapacitors are less than macroscale hybrid supercapacitors because of complicated microfabrication techniques of microscale hybrid supercapacitors so as to produce 3D microelectrodes with micrometer separations. According to reference [17], they offer a simple and suitable method for the production of 3D hybrid microsupercapacitors which depends on the graphene-MnO_2. These microdevices show also an maximum capacitance per area which is nearly equal to 400 $mFcm^{-2}$ [17]. This capacitance value has become the largest capacitance value for microsupercapacitor.

These hybrid supercapacitors exhibits also an energy density of approaching 22 $Wh.l^{-1}$ which is twice as much as lithium thin film batteries [17]. They contribute to be used in many microelectronic devices like biomedical devices and radio frequency identification cards. Improvement of capacity for each footprint have played a significant role on these applications. As a result of these advantages and properties, hybrid microcapacitors which are based on graphene and MnO_2 have become one of the most promising canditates or materials.

The capacitances of the supercapacitors is measured by depending on CV profiles and galvanostatic charge and discharge curves (CC). Both equations of specific capacitances are given below [17].

$$C_{device} = \frac{\int i dV}{\upsilon * \Delta E} \qquad \text{(By depending on the CV technique)} \qquad \textbf{(2.32)}$$

$$C_{device} = \frac{i_{app}}{dE/dt} \quad \text{(By depending on the CC curves)} \quad \textbf{(2.33)}$$

In the (2.27) equation (CV technique), υ is the scan rate and calculated in accordance with the following formula [18].

$$\upsilon = V/t \quad \textbf{(2.34)}$$

ΔE stands for the operating voltage window. In the (2.33) equation, i_{app} and dE/dt mean the current applied and the slope of the discharge curve (in volts per second, $V.s^{-1}$), respectively. Additionally, the energy density can also be measured by utilizing the following equation [17].

$$E = \frac{1000}{2*3600} C_{\upsilon} \Delta E^2 \quad \textbf{(2.35)}$$

As it can be understood from the equation of energy density, value of volumetric stack capacitance (C_{υ}) must be known. This type of capacitance is based on capacitance of device (C_{device}) and volume (V- cm^3) of the device. C_{υ} is obtained from the following equation. Its unit is F/cm^3 [17].

$$C_{\upsilon} = C_{device}/V \quad \textbf{(2.36)}$$

Device's volume involves the active material's volume, the collector of current and the separator with electrolyte.

Power density for the supercapacitor is calculated by making use of the following equation [17].

$$P = E/t \quad \textbf{(2.37)}$$

In this formula, P means the power density and t stands for the discharge time in hours.

2.3 Advantages and Disadvantages of The Fuel Cells

Table 2.2 represents the advantages and disadvantages of fuel cells.

Table 2.2 Advantages and disadvantages of fuel cells

Advantages	Disadvantages
No moving parts. Therefore, it needs low-maintenance [19].	Problems about infrastructure
Environmentally friendly	High-cost
Reliable and silent	Not commonly used in many applications
Larger efficiency than internal combustion engines.	Very sensitive structure to temperature
Hydrogen is one of the most abundant elements all over the world	Transportation losses of hydrogen [20]
Not depend on fossil fuels. Therefore, they don't produce any greenhouse gas emissions.	Hydrogen Storage Complications [21]

2.4 Advantages and Disadvantages of The Supercapacitors

Table 2.3 represents the advantages and disadvantages of supercapacitors.

Table 2.3 Advantages and disadvantages of supercapacitors

Advantages	Disadvantages
Small internal resistance, Most reliable and suitable devices in terms of performance	Expensive
No greenhouse gas emissions, fast transfer energy or charges	The voltage changes by depending on the energy stored
Quick charging time and long life cycle	Lower energy density than batteries
Excellent cycle efficiency (95%) and working at wide temperatures (- 40 ºC to 60 ºC)	Each of cells displays low voltages in supercapacitors. Therefore, they must be connected in series so as to improve the voltage.
large specific power up to 17 kW/kg and long life cycle	Large self-discharge rate
During overcharged, no explosion like batteries	No usage in AC and large frequency circuits [22]
Storage of larger amount of charge than the conventional capacitors and large capacitance [23]	

CHAPTER 3

WORKING PRINCIPLES AND MECHANISMS OF FUEL CELLS AND SUPERCAPACITORS

3.1 Working Principle of Fuel Cells

Fuel cells contains four major elements. These are the anode which can be defined as the negative side of the fuel cell, the cathode which can be called as the positive side of the fuel cell, the catalyst which splits hydrogen atoms into protons and electrons and helps to accelerate easily the reactions at the both of the electrodes and the electrolyte which provides transportation of electrically charged particles from one electrode to the other one. The electrolyte plays also an important role in order to permit appropriate ions. Generally, they benefit from hydrogen and oxygen in the air as fuel source [24].

Firstly, hydrogen gas comes in the fuel cell from the anode and oxygen gas comes in the fuel cell from the cathode. Hydrogen atoms are split into its negative and positive ions at the anode. Protons are able to move via the electrolyte but electrons do not have this permission because they are forced through a circuit. Therefore, they wander around the external circuit and the fuel cell generate electricity as well as excess heat. Furthermore, oxygen atoms combine with the electrons that come from the external electrical circuit. The oxygen combines also with the hydrogen to generate water as byproduct. Figure 3.1 exhibits the schematic diagram of the fuel cells [24].

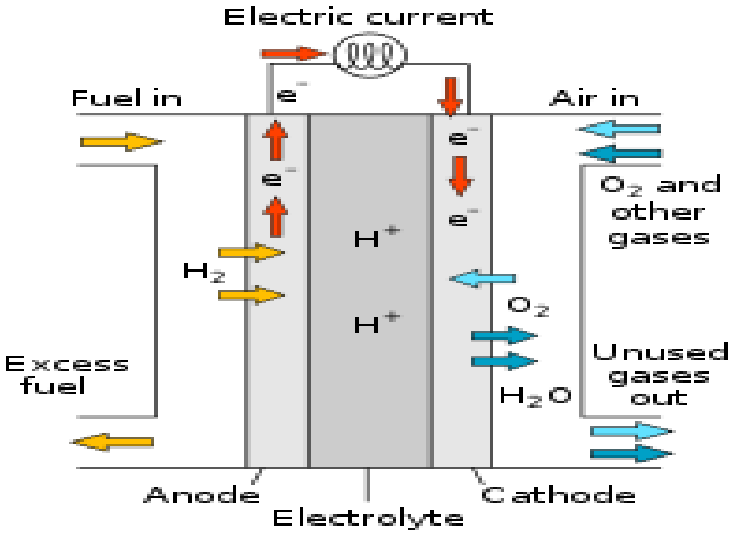

Figure 3.1 Schematic diagram of fuel cells [25]

3.2 Working Principle of Supercapacitors

Capacitors are another way of storing energy and store their energy electrostatically or in other words create a difference in charge. A capacitor basically consists of two parallel metal plates called electrodes. They are physically separated from each other by an additional layer (dielectric) that can be made of specific materials like plastic or simply air. This means that the plates are not directly connected and as a consequence there is no current between them. When a voltage is applicated on the electrodes, the electrons will begin flowing and the capacitor will get the potential difference as well as creating energy and storing it between the two plates. If the original voltage source is removed, the capacitor will keep its charge. This means that if another component that needs power like light bulb or a motor, is connected to the capacitor, the capacitor will discharge again [26].

Supercapacitors can show several similarities with conventional capacitors. But, one of the most important differences between them is that the distance between two plates or electrodes is very short in supercapacitors. Supercapacitors mainly consist of two porous electrodes, a separator, electroyte and two current collectors. The main purpose of the separator is to separate both electrodes from each other [27]. These two current collectors are connected to the two electrodes. Charges can also be made

storage on the surface of the both electrodes. One of the most important properties of the separator is to display ion permeable and electrically insulative structure. The another function of the separator is to hinder short circuit by separating both electrodes from each other and to contribute to transfer of ions by way of the electrolyte. Both the electrodes and separator are immersed into the electrolyte that can be an aqueous or organic solution. Aqueous electrolytes provide better interaction with the pores of the eletrodes than organic electrolytes. This interaction is related to the penetration of ions to the pores of the electrodes. Moreover, organic electrolytes exhibit also larger breakdown voltages than aqueous electrolytes. The breakdown voltages of aqueous electrolytes and organic electrolytes are measured as about 1 V and 4 V, respectively. This expression explains that supercapacitors work at larger voltages when they use organic electrolytes. Therefore, aqueous electrolytes provide more benefits than organic electrolytes like low-cost, more excellent ionic conductivity, reliable usage such as less toxic and nonflammable. When the electrodes present low electrical conductivity, supercapacitors must make use of current collectors. The electrode material that can generally be powder form, is connected to the metallic current collectors with a polymeric binder. The main property of the polymeric binder is to decrease the charge capacity and enhance the internal electrical resistance in the supercapacitor. When the current collector and the electrode powder substance are compared with each other in terms of their mass, the current collector shows larger mass than the electrode powder material [28].

In order to operate supercapacitor, a battery or an external electrical load is connected to the supercapacitor. In other words, negative terminal of the battery is combined with the negative side of the supercapacitor and the positive side of the battery is combined with the positive terminal of the supercapacitor. The plates or electrodes comprise generally of metals and are immersed into electrolytes as it can be seen in the Figure 3.2. In cases where opposite charges can be obtained on each sides of the separator, an electric double layer is obtained and as a result of this process, the electrodes start to charge. Thus, supercapacitors are also charged with the electrodes and present larger capacitance. One of the most important functions of supercapacitors is to supply large power for many applications. Additionally, they can provide also large load currents with small resistance. Supercapacitors have also

high-cost due to their large charging and discharging capacitance. An electric-double layer is obtained during charging process of the electrodes or supercapacitor. As a result of this process, charges have been generated on both sides of the electrodes. Thus, the supercapacitors have been known as EDLCs by being dependent on obtaining of electric double layer. If the area of the electrodes enhances and the distance between the electrodes reduces, the capacitance of the supercapacitor will enhance [29].

If the charging process of the supercapacitor does not carry out, all the charges will randomly move in the supercapacitor or cell. During the charging process, all the positive charges will move toward to the negative side. In addition to this, negative charges are going to move toward to the positive terminal. Figure 3.2 illustrates the general diagram of supercapacitors [28].

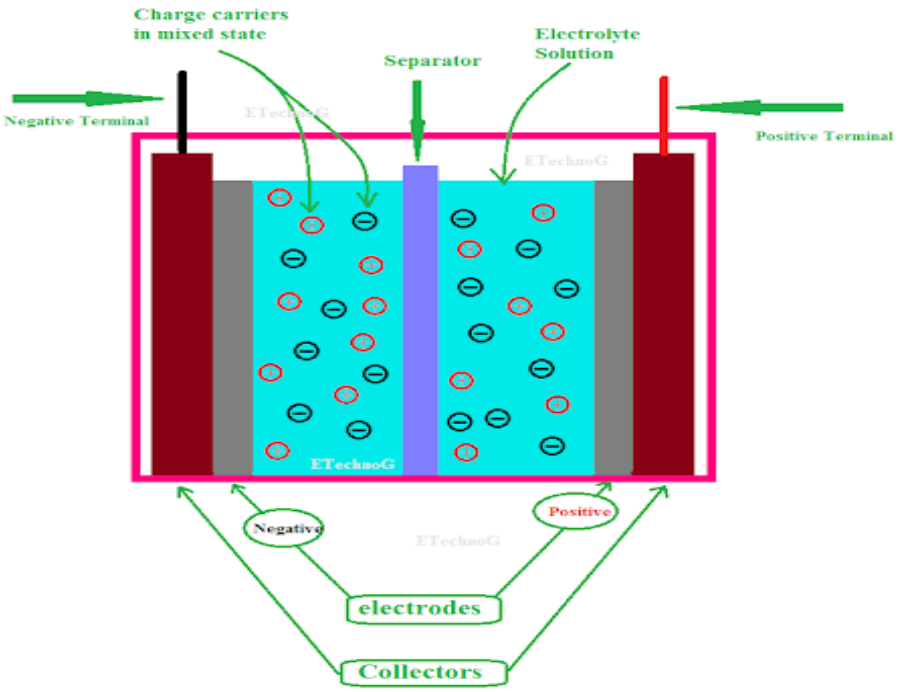

Figure 3.2 General diagram of supercapacitors [28]

3.2.1 The Charging Process of The Supercapacitors

One of the most important properties of the supercapacitor is its self-discharging capacity and unrestricted charging and discharging cycles. Another outstanding property of supercapacitors is their operation with low voltages like 2-3 Volts. So as to increase the voltage, supercapacitor may also be connected in series. When a comparison is made between supercapacitors and batteries, supercapacitors have the ability of more energy storage than batteries. Furthermore, supercapacitors can deliver quicker energy or power than batteries.

During connection of supercapacitors to the circuit or DC voltage source, the electrodes start to store charges. By depending on this process, opposite charges are obtained and observed on both sides of the separator that contribute to be produced a double-layer electrolytic capacitor. In order to make charging process of a supercapacitor, the positive part of the voltage source must be connected to the positive part of the supercapacitor and the negative part of the voltage source must be connected to the negative part of the supercapacitor. For example, when the supercapacitor is made the connection to 15 Volts voltage supply during its charging process, it will be charged until it reaches to 15 Volts. If the voltage exceeds the amount of voltage of an external supply, the supercapacitor can significantly impaired. In order to abstain from this problem, a resistor must be provided connection in series with the voltage supply. Resistor is going to contribute to minimize the current that moves through the supercapacitor. As a result of this process, supercapacitors can not be negatively affected from this situation. Supercapacitors can benefit from the constant current supply and restricted voltage supply so as to not encounter like these problems. If the enhancement of the voltage is gradually and regularly provided, the amount of current that moves through the supercapacitor, will naturally change. If the supercapacitor is fully charged mode, the current will decrease [28].

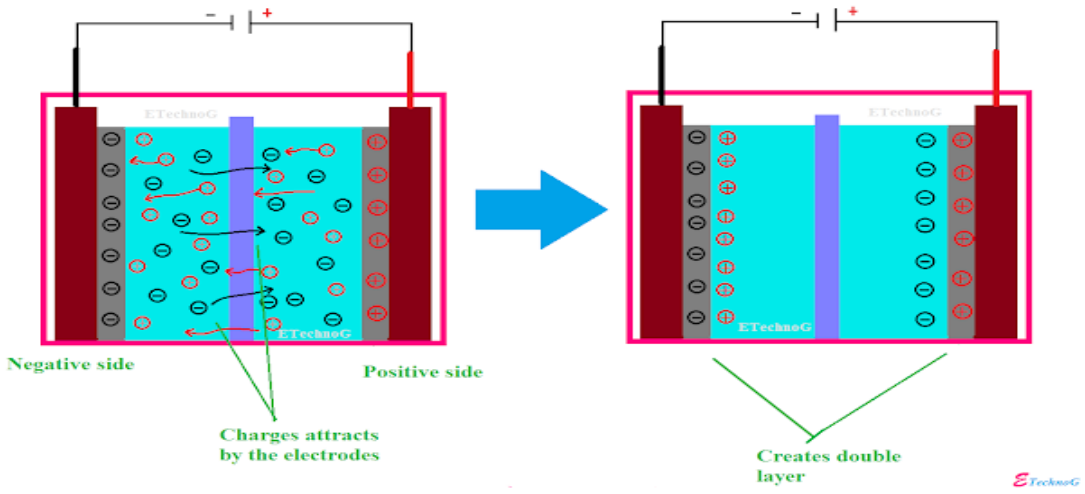

Figure 3.3 The charging process of supercapacitor [28]

3.2.2 The Discharging Process of Supercapacitors

As it can be seen in the Figure 3.4, when the connection is provided between the load and supercapacitor, the electrodes ıf supercapacitors maynot provide the attraction of ions which will begin diffusing toward the electrolyte solutions. As a result of this process, the negative ions and positive ions are found in mixed state.

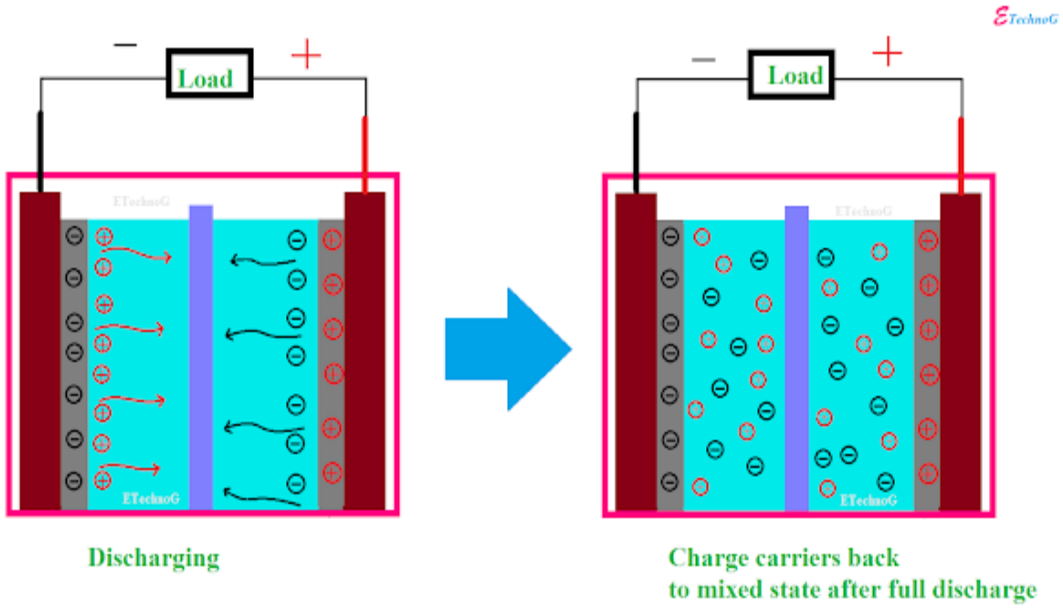

Figure 3.4 The discharging process of supercapacitor [28]

3.3 Mechanisms of Fuel Cells

For fuel cell mechanism, the energy is stored in fuel which is used. One of the most preferred and used fuels is hydrogen (H_2) in fuel cells. As wells as hydrogen, fuel cells can also make use of other type of hydrogen-based fuels like natural gas, naptha. Hydrogen storage have occupied an important place for fuel cells. As long as hydrogen is stored in fuel cells, they produce electricity. In addition to this, hydrogen can be obtained by benefitting from many methods or techniques. The most important properties of hydrogen are its abundance and its energy carrier. Utilization of hydrogen which is important for energy transporter and storage as well as fuel source, depends generally on the exothermic reaction between hydrogen and oxygen. When hydrogen is generated with the help of water's electrolysis, and the efficiency of the electrolyser ranges between 60% and 75%, and the real power consumption for the generation of 1 m^3 (STP: Standard Temperature and Pressure) of hydrogen gas range from 4 to 5 kWh [30].
The following reaction gives the overall reaction which takes place in fuel cells [2].

$$Fuel+Oxidant \rightarrow OxidationProducts+UsefulWork+Heat \quad \textbf{(3.1)}$$

This reaction shows differences by depending on the fuel source which are used in fuel cells. For example, when fuel cells benefit from hydrocarbon like methane (CH_4), the following reaction takes place in fuel cells. This reaction is also known as the reaction of oxidation of the fuel [2].

$$CH_4+2O_2 \rightarrow CO_2+2H_2O+Heat \quad \textbf{(3.2)}$$

Figure 3.5 gives a relation among the cell voltage (V) and the current density (J). The current density is also based on the electrode surface area. This figure expresses also the voltage-current characteristics of a fuel cell. As it can be seen in this figure, 1.23 V is the value of the reversible cell voltage [2]. This reversible cell voltage is calculated by depending on the following reaction [4].

$$H_2+1/2O_2 \rightarrow H_2O \Delta H=-285.8 kJ/mol \quad \textbf{(3.3)}$$

The enthalpy of this reaction is -285.8 kJ/mol. The main reason of this negative enthalpy value is that this reaction is exothermic. In other words, it gives out the heat. Electrical energy can also be calculated by making use of the difference of the Gibbs free energy as the following equation [4].

$$\Delta G = \Delta H - T\Delta S = -285.8 + 48.7 = -237.1 \ kJmol^{-1} \quad \textbf{(3.4)}$$

In this reversible (ideal) process, the efficiency of conversion can be made calculation as the ratio of Gibbs free energy to the enthalpy and this expression is defined as the following equation [4].

$$\frac{\Delta G}{\Delta H} = \frac{-237.1 \ kJ/mol}{-285.8 \ kJ/mol} = 0.83 = 83\% \quad \textbf{(3.5)}$$

The following reversible cell voltage can be made calculation in accordance with the following formula [4].

$$\Delta G = \Delta QV = nN_A eV \quad \textbf{(3.6)}$$

In this formula, n, N_A, e represent the quantity of electrons produced per mole, quantity of molecules in 1 mole (Avogadro' number), and charge on an electron, respectively. In this equation, the product ($-N_A e = F$) of N_A by e is equal to the Faraday constant which possesses the value $9.65 * 10^4$ Coulombs per mole. One hydrogen molecule produces two electrons. So, the Faraday constant is multiplied by 2 in order to calculate the produced voltage. The following equation gives the calculation of produced voltage [4].

$$V = \Delta G/(nN_A e) = (237.1*10^3)/(2*9.65*10^4) = 1.23 Volts \quad \textbf{(3.7)}$$

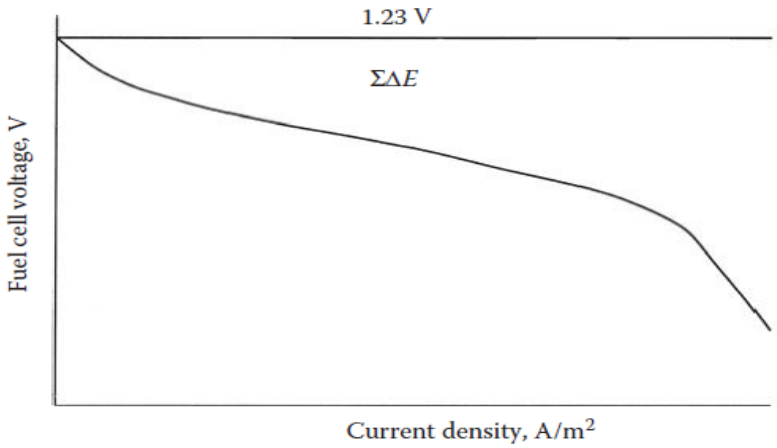

Figure 3.5 The relationship between fuel cell voltage and current density [2]

Figure 3.6 gives a more detailed information of above figure. This figure is also knowns as polarization curve. The main purpose of this curve is to test the fuel cell. The poarization curve. As it can be seen in the following figure, The polarization curve of a fuel cell contains three different regions as following [31]:

- At smaller densities of power, the potential of cell decreases by virtue of the *activation polarization*.
- At middle densities of current, the potential of cell reduces linearly with current density by virtue of *resistance* or *ohmic losses*.
- At larger densities of current, more *concentration polarization* gives rise to decrease the cell potential. This drop can not show the linear relation with the current density.

In accordance with the Figure 3.6, the initial decrease in voltage leads to decrease the activation energy which must be necessary for occurrence of electrochemical reactions. This loss is known as *activation loss*. As well as the activation loss, when the current enhances, resistance will have a great effect on the decreasing in voltage with the enhancing current. This is called as *ohmic or resistance loss*. Additionally, *gas or mass transport loss* has become one of the most outstanding factors. Electrodes must display the porous structure. So, gas moves through the electrodes. However, several important losses like *gas transport losses*, can also take place. The main reason of this situation is related to the formation of water which is restricting factor for *gas transportation* [4].

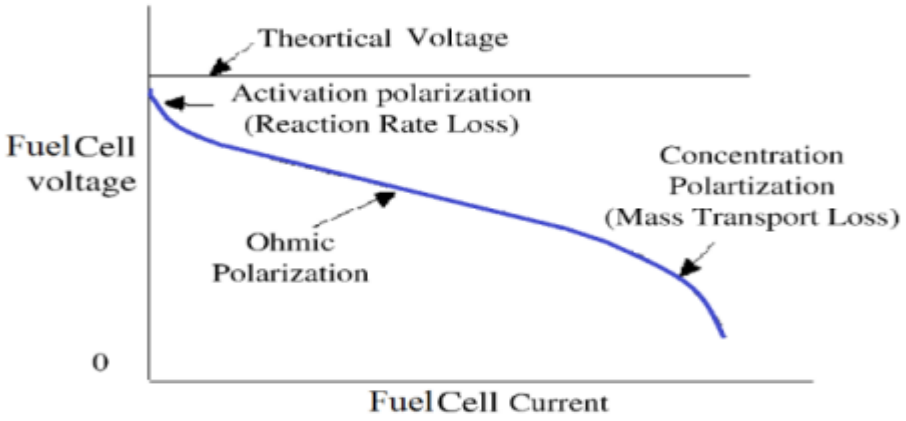

Figure 3.6 Polarization curve of a PEM fuel cell [32]

Following equation displays electric power output of a fuel cell.

$$P_{el}=VJA(W) \quad \textbf{(3.8)}$$

As it can be understood from this equation, voltage (V) has inversely proportional relationship with the current density (J). V, J and A represent the the voltage of fuel cell (V), current density (A/m^2), and electrode surface area (m^2), respectively. Figure 3.7 gives the power density – current density illustration of fuel cell.

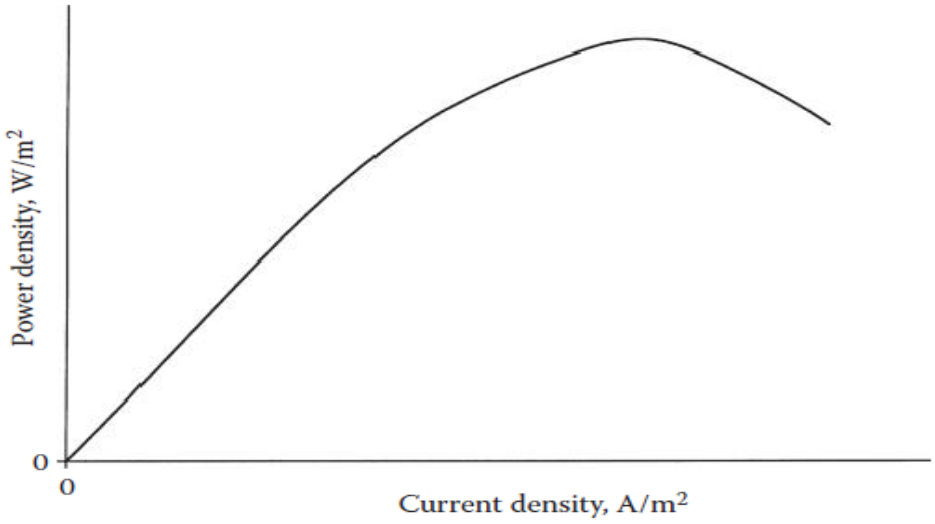

Figure 3.7 Correlation amidst power density and current density of fuel cell [2]

When the efficiency of fuel cell is equal to approximately 50%, the highest power output was obtained. The efficiency of fuel cell is made calculation as follows [2].

$$\eta_{cell}=P_{el}/(HVm) \quad \textbf{(3.9)}$$

In this equation, P_{el}, HV and m mean the power output, heating value (J/kg), and mass flow rate (kg/s), respectively.

Figure 3.8 exhibits the schematic diagram of a fuel cell power plant. According to this figure, the fuel cell based power station contains the following elements:

- Fuel processing unit (Reformer: fuel processor)
- Fuel cell stack
- Current inverter and current conditioner

As it can be seen in this figure, fuel source like coal, natural gas, oil, naptha or hydrogen-based fuels are converted into hydrogen-rich gas. Basically, the reformer or the fuel processor involves a restater, gasifier, and gas cleanup plant. After the conversion process of fuel source into hydrogen-rich gas, this gas moves toward the fuel cell and as a result of these processes, electricity is produced. This electricity is in DC power which can be converted into AC power with the help of an inverter. The main purpose of current conditioner is to control the current characteristics like current, voltage and frequency [2]. Oxygen is obtainmed from air. As well as this, wayer which is produced from fuel cell, can also be used in reformer or fuel processor.

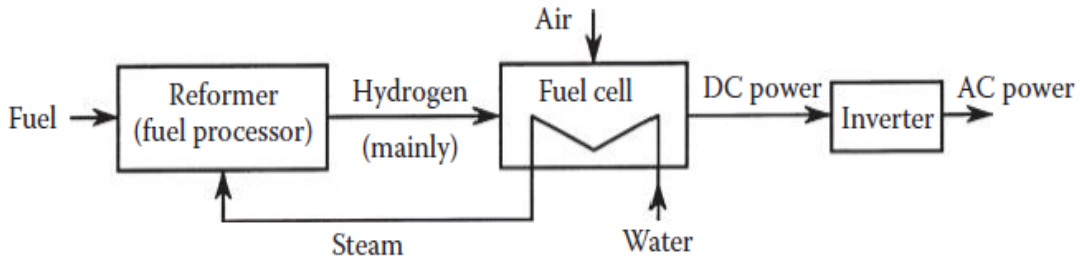

Figure 3.8 General illustration of a fuel cell-based power plant [2]

In recent times, hydrogen have annually produced approximately 50 billion m^3 (STP) or 45 millions tons. Storage of hydrogen is related to directly applications of fuel cells. Low total weight of hydrogen storage system has become one of the most important points for mobile or portable applications. However, this situation does not

create a great problem for stationary system. A fuel cell car consumed hydrogen of 1-3 g/s so as to gather speed [30]. For this situation, as long as approxiamtely 5 kg H_2 which is equal to 600 MJ, is used for fuel cell automobile, this automobile can run same distance as a petrol-depletive car. U.S. DOE classified hydrogen storing methods into two sections. These sections include physical methods and material-based methods. Physical methods can be classified into three categories which contain compressed hydrogen gas, liquid hydrogen, and cold/cryo compressed. The material-based method is generally divided into three categories which are adsorbent, complex hydride, interstitial hydride. Table 3.1 summarizes the classification of hydrogen energy storage system.

Table 3.1 Classification of hydrogen energy storage methods [33]

Hydrogen Energy Storage	
Physical-based	**Material-based**
Compressed Gas	Adsorbent
Liquid H_2	Complex Hydride
Cold/Cryo Compressed	Interstitial Hydride

3.3.1 Physical-Based Hydrogen Storage

Compresed hydrogen gas storage (CGH_2) is one of the most important and outstanding types of hydrogen storage and is provided by kepting hydrogen gas under pressures in order to enhance the storage density. Hydrogen gas can be stored between 350 bar (5000 psi) and 700 bar (10000 psi) in hydrogen tanks. Nissan, Honda and other prominent car producers have improved their cars which make use of hydrogen storage. This type of hydrogen gas storage involves several methods like high-pressure cylinders, large-volume stationary hydrogen storing systems and pipelines.

High-pressure cylinders have become one of the most outstanding types of hydrogen storage. Stell gas cylinders have been prefered and used in terms of hydrogen storing and transferring of the compressed hydrogen at the surrounding temperature which ranges between -50 ºC and +60 ºC. This type of cylinders are available as the low (up to 12 l) and medium (from 20 to 50 l) capacity. The most promising methods for improvement of properties of hydrogen storing is to decrease cylinder mass by

making use of lightweight metals ond/or composite substances, and to improve the operation pressure. Figure 3.9a and b represents the the schematic diagram of composite high-pressure hydrogen cylinders and common examples of several of them.

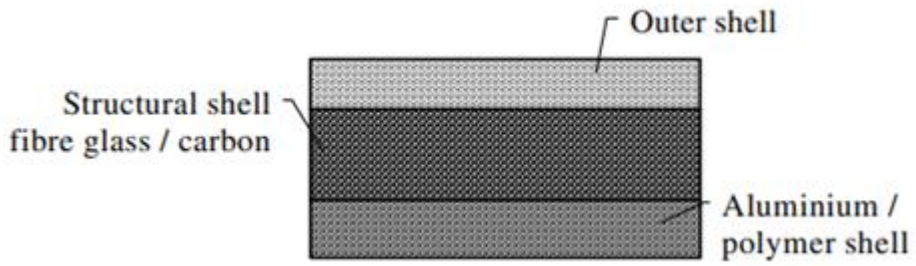

Figure 3.9.a The schematic diagram of composite high-pressure hydrogen cylinders. [30]



Figure 3.9.b. General examples of some of them [30]

High-pressure hydrogen cylinders comprise of thin aluminum or plastic shell, structural shell (fibre glass/carbon) and outer Shell. On design of these cylinders, thin aluminum or plastic shell is coated outside by using many forms of plastic which are strenghthened with the help of fibre glass. Then, the structural shell is sandwiched between outer shell and aluminum/polymer shell as it can be seen in the Figure 3.9a.

These high-pressure hydrogen cylinders have also been used in motor-car applications. These cylinders contribute to store hydrogen under the pressure up to 350 bar. As well as this, many researchers and scientists have made efforts in order to develop the material and the morphology or structure of high-pressure hydrogen cylinders for increasing of the pressure up to 690 bar. This situation can be achieved by benefitting from changing of fiber glass with carbon fibers. One of the most

significant benefits of hydrogen storing within cylinder is that any power consumption does not take place so as to supply hydrogen.

Large-volume stationary hydrogen storing systems and pipelines are also based on the storing of pressed hydrogen and display larger storage capacity than cylinders. The storing capacity of these mechanisms can reach up to a number of millions of cubic meters of hydrogen. Therefore, these systems have become one of the most preferable and excellent candidates for the large scale hydrogen storage. The most known example is underground storing of the large volume of hydrogen. This storage method can also be either naturally formed or artificially obtained. In this type of hydrogen storage, natural gas and hydrogen-based fuels are stored. In the hydrogen storage, several leakage problems can also occur. So as to overcome this problem, the porous rock is saturated by water and brine.

In early times, the coal gas which consists of a large quantity of hydrogen, could be made storage in the several rock formations in Germany and in France [30].

One of the most significant drawbacks of the large-scale hydrogen storage is the requirement for kepting of 50% of the gas in the mechanism, so as to become it durable. This gas is also known as the cushion gas which is not suitable for utilization. The losses which are formed by this gas, lead to increase the cost of the systems and are equal to nearly 25% of the total annual capital costs. Another serious loss is obtained from hydrogen leaks.

As well as large-scale underground hydrogen storing systems, there ale also several excellent methods or techniques for hydrogen storage. Among these systems, industrial compressed hydrogen storage facilities have become one of the most useful alternatives in order to provide efficiently hydrogen storage. These facilities comprise of generally large spherical containers which exhibit the pressure capacity of 12-16 bar and volume of 15000 cubic meters or more. Pipelines network can also be utilized as hydrogen storage system with pressure 35-75 bar. Natural gas industry benefits from this network. In this industry, natural gas may easily be transformed into hydrogen [30].

Many companies and scientists improved the mechanism *of hydrogen liquefaction and Liquid hydrogen storing (LH_2).* Hydrogen can be stored as higher weight capacity than other hydrogen storage methods with the help of cryogenic vessel which involve screen-vacuum heat isolation. LH_2 storage is more preferable than other hydrogen storage methods due to its simple transportation, especially aerospace applications. Several companies have improved highly efficient cryogenic tanks, fuelling infrastructure. Furthermore, safety has become the most serious issues for hydrogen storage and was also developed by storing liquid hydrogen. Figure 3.10 presents the relationship between liquid hydrogen storage (LH_2) and compressed gas hydrogen storage (CGH_2) in terms of energy content and pressures. As it can be seen in the Figure 18, the working pressures of LH_2 system range between 1 and 3.5 bar and the working pressures of CGH_2 system range from 240 bar 700 bar. Nowadays, 240 bar is widely used for CGH_2. 350 bar will be utilized in near future for CGH_2. Many researchers and scientists are going to aim at usage of pressure of 760 bar. It is used as prototype. According to the following figure, the specific energy content of LH_2 1.6 - 4 times larger than CGH_2.

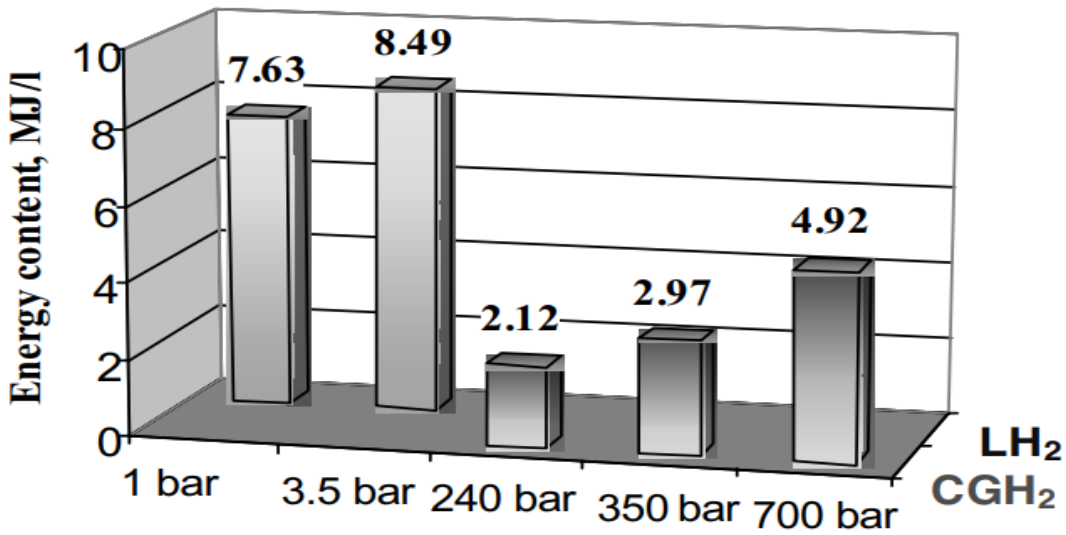

Figure 3.10 Comparison of energy content between the LH_2 and the CGH_2 hydrogen at various pressures [30]

Many prototypes of liquid hydrogen storage have also been obtained for automotive applications and consist of basically both LH_2-fueled automobiles and cryogenic

charging stations [30]. One of the most outstanding examples for these prototypes is the NECAR4 automobile with LH_2 at Munich airport. Table 3.2 gives the important characteristics of the NECAR4 car. Figure 3.11 displays the general mechanism of NECAR4.

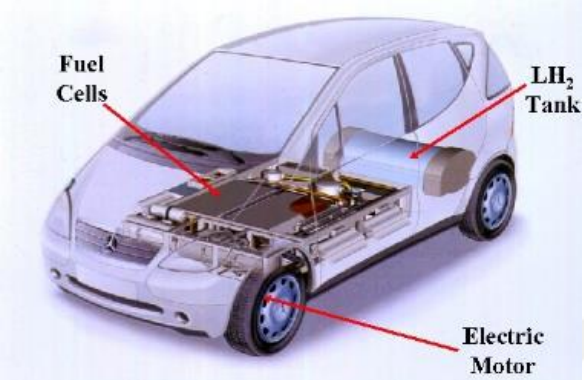

Figure 3.11 General mechanism of NECAR4 [34]

Table 3.2 Characteristics of the NECAR4 car [30]

Range	450 km
Speed	145 km/h
Fuel	LH_2
Evaporation Rate	1% / day
H Volume Density	50 $g.l^{-1}$

Table 3.3 represents comparison between LH_2 and CGH_2 storage when 6.4 kg H_2 was utilized for fuel cell cars. As it can be shown in the following table and carefully analyzed, the most significant obstacle of LH_2 is that it is larger power consumption than CGH_2. As well as this obstacle, another outstanding drawback is evaporation losses which take place during filling LH_2 tanks and times of inactivity (dormancy), by virtue of heat permeation from surrounding. These losses are based on a container design and volume, substance of heat insulation.

Table 3.3 Comparing of LH_2 and CGH_2 based on 6.4 kg of hydrogen storage [30]

Performance		LH_2:vacuum-insulated cryostat , P=1 bar	CGH_2: Commercial composite cylinder, P=200 bar
System Volume in litres		110	495
System Weight in kg		86	250
Energy Consumption	MJ	254	136
	% of H_2 heating value	28	15
	Predicted "ideal" value in MJ	nearly 200	nearly 45

Cryogenic Pressure Containers have also been preferred for hydrogen storage. Many researchers and scientists have made efforts in order to improve the hydrogen storage methods. These systems benefit from combination benefits of both compressed and liquid H_2 storing. Moreover, they make use of pressure vessels for liquid hydrogen storing. In these systems, pressure vessels are located within cryogenic heat insulation shell. The word of "cryogenic" means freezer. The pressure vessels contain aluminium-lined glass – or carbon fibre-wrapped. In these systems, hydrogen can be stored as either liquid phase or compressed phase as well as by cooling it. Coolong process of hydrogen in pressure vessel does not decrease its strength performances.

The cooling process of hydrogen can also be carried out by cooling it down to liquid nitrogen temperatures. Figure 3.12 shows the predicted power inputs (ideal mechanical work) for hydrogen refrigerating [30]. According to this figure, it is indicated that a sharp enhancement of power inputs can be seen at the temperatures which are lower than 50 K.

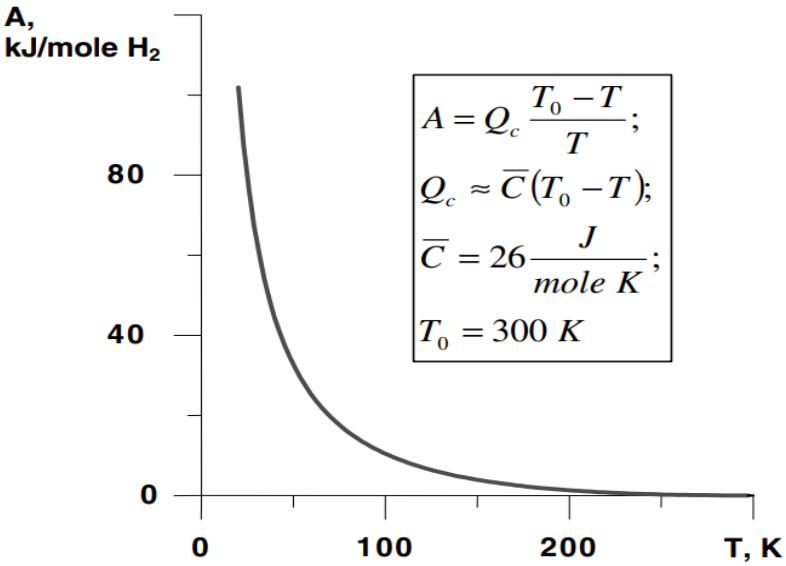

Figure 3.12 Estimated power inputs for hydrogen cooling [30]

Figure 3.13 displays the comparison of volumetric densities between liquid and compressed hydrogen. Vertical and horizontal axis express the volumetric densities and pressures of compressed and liquid H_2, respectively.

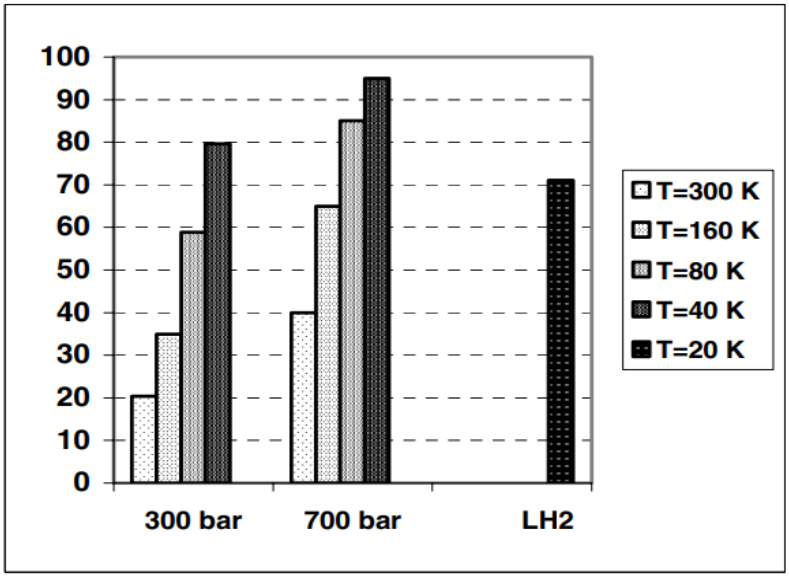

Figure 3.13 Comparison of volumetric densities between compressed and liquid H_2, in terms of $g.l^{-1}$ [30]

3.3.2 Material-Based Hydrogen Storage

Adsorbents have become one of the most preferable and useful hydrogen storage methods like zeolites and metal-organic adsorbents, hydrogen storage in carbon nanomaterials, hydrogen cryo-adsorption on activated carbon etc.

In Zeolites and Metal-organic adsorbents, hydrogen adsorption by several zeolites occurs by making use of reversible hydrogen storing in the temperature range between 20 and 200 ºC and pressures between 25 and 100 bar. When a comparison was made between zeolites and other hydrogen storage systems in terms of storing capacity, the highest storage capacity (less than 10 $cm^3.g^{-1}$) is smaller than other hydrogen storage systems. Several researchers and scientists have developed this and other important properties of zeolites by means of modern methods of their synthesis and modification. For this, novel synthetic hydrogen adsorbents which have similar microporous structure with zeolites, can also be used. One of the most outstanding examples of these adsorbents is Metal Organic Frameworks (MOF). $Zn_4O[O_2C\text{-}C_6H_4\text{-}C0_2]_3$ has become the most preferable MOFs and exhibits large porousness cubic frame structure and specific surface area of between 2500 and 3000 $m^2.g^{-1}$. Apart from these properties, this type of MOFs adsorbs also up to 4.5 wt. % H at 70 K and 20 bar, or up to reaching 1 wt.% H at room temperature and the same pressure [30].

Hydrogen Cryo-Adsorption on Activated Carbon is an excellent hydrogen storage technique and benefits from the operation of a low temperature absorption of hydrogen on a small density (380 g/cm^3) activated carbon. Tempterature ranges generally from 65 to 78 K. Charging process of hydrogen storage takes place at pressures approximately 40 bar. As well as charging process, hydrogen discharging process occurs at the same temperature when pressure is decreased to about 2 bar. 60 – 65% of hydrogen can be reversibly stored by adsorbing it on carbon surface. Adsorbent presents also hydrogen sorption capacity of nearly 7 – 8 wt.% and the density of storage energy of approximately 1.7 kWh/kg or 0.645 $kWh.m^{-3}$ [30].One of the most promising points is that the energy consumption which is required for refrigerating of the adsorbent bed and the compression of hydrogen, is extremely large. When a comparison was made between this type of storage and liquid

hydrogen storing in terms of power consumption, it is lower than LH_2. In addition to this, cryo-adsorption technique utilizes low-cost cooling system, because the working temperature of this technique is close to the boiling point of nitrogen (77 K), which is generally used as refrigerant. This type of hydrogen system can also be utilized by combining it with compressed H_2 storing in the cryogenic pressure containers.

Various studies have also been made abuout hydrogen adsorption on avtivated carbon. According to these studies, the H storing density at 77 K and 55 bar has become 35 $g.l^{-1}$ (10 – 13 wt.%). The main reason of this density value is the condensation of liquid hydrogen in the micropores of activated carbon.

Hydrogen Storage in Carbon Nanomaterials have also been preferred. Carbon exhibits a number of different nanoscale morphologies such as fullerenes and nanotubes, apart from graphite nanofibers. These materials have become the most outstanding candidates for hydrogen storage. As well as fullerenes, other important types of carbon nanomaterials have also been used in order to provide interaction with hydrogen gas by utilizing either Van der Waals attractive forces (physiorption) or a dissociative chemisorption of H_2 molecules. The interaction between fullerenes and hydrogen depends on a chemical process which shows similarity to the formation and decomposition of organic hydrides.

There are also prominent studies on hydrogen storage in carbon nanomaterials. By depending on the used materials, hydrogen storage capacities of these carbon nanomaterials show differences. The most significant factors which affect the hydrogen storage capacity, are sample weight, degree of purity, and pressure (P) – temperature (T) circumstances [30]. There are also several important errors which originate from wrong volume calibrations, bad measurement of density of the sample. For large-pressure tests and studies, one of the most attractive points is that thermal control of the measuring mechanism must be effectively adjusted and controlled. This wrong management can be solved by abstaining from temperature fluctuations and considering the exothermal effects as a result of the introducing of pressurised gas into the reactor, and decreasing temperature.

Complex Hydrides (Alanates) have become one of the most outstanding inorganic materials because of their possible applications. Many researchers and scientists have improved these materials so as to make use of efficiently them. The main reason of usage of these materials in hydrogen storage systems is that they exhibit high hydrogen fraction (7.4 wt. % H for $NaAlH_4$) [27-30]. Chemical formula of complex hydrides is $A_xMe_yH_z$. In this formula, the A elements represent basically elements which is found in the first and second groups of the periodic table, and the Me part stands for Aluminum (Al) or boron (B). Al and B present excellent hydrogen storage properties for moible and portable applications when they are made a combination with a low-atomic-weight cation like Li, Be, Na or Mg. The following reaction gives two stage reversible reaction of $NaAlH_4$ and according to this reaction, a theoretical reversible hydrogen storing capacity of 5.6 wt.% is obtained [30].

$$NaAlH_4 \leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \leftrightarrow\ NaH + Al + 3/2\ H_2 \qquad \textbf{(3.10)}$$

Additionally, hydrogen is also obtained at nearly 100 ºC. This system have not been commercially used very much due to low kinetics of the reversible hydrogen adsorption-desorption and the degradation of the reversible hydrogen sorption characteristics during long cycle. This drawback has been pertinent to their large chemical activity and can also give rise to the explosion. Therefore, safety has played a remarkable role on their usage in applications.

Interstitial Hydrides have also been selected for hydrogen storage. Intermetallic compounds have presented good hydrogen-absorbing substances. After absorbing process of hydrogen completes, these compounds produce triple hydrides or intermetallic composite hydrides. Many researchers and scientists have tried to make use of interstitial hydrides in hydrogen storing system such as heat pumps, high-performance secondary batteries, hydrogen storage containers. Ternary hydrides offer also excellent properties like fast absorption and desorption of high quantities of hydrogen, and associated changes in physical properties.

In the years of 1990s, Ti based-solid materilas have become one of the most preferable alternatives for hydrogen absorption and desorption under normal

circumstances. Interstitial hydrides are also called as metallic hydrides and include hydrogen bonds with transition metals [35].

Figure 3.14 exhibits the diagram of hydrogen adsorption and desorption of metal/alloy [35]. As it can be seen in the following figure, hydrogen molecules (H_2) in the gas phase are absorbed on the surface and separated into two hydrogen atoms. After this separation process, hydrogen molecules move toward metallic lattice and occupy an interstitial site of the metal sublattice. As a result of these processes or steps, interstitial hydrides are also produced. This figure explains aso the formation of interstitial hydride. Figure 3.15 shows a self-trap mechanism of hydrogen occupation in an interstitial site. As it can be seen in the following figure, the formation of interstitial hydride is explained by two potentials which are ground-state energy of hydrogen (hydride formation energy) and elastic energy of lattice. According to Figure 3.15, the hydride formation energy provides stabilization of the mechanism with an enhancement of displacement of M-H bonding. As well as ground-state energy of hydrogen, the elastic energy of lattice provides destabilization of the system. Additionally, displacement can also be optimum and presents a local minimal amount of the total energy of the mechanism. This situation contributes to appear hydrogen atom and diffuse into the lattice to its occupancy site by itself. Because of this characteristic, it is known as a self-trapping mechanism [35].

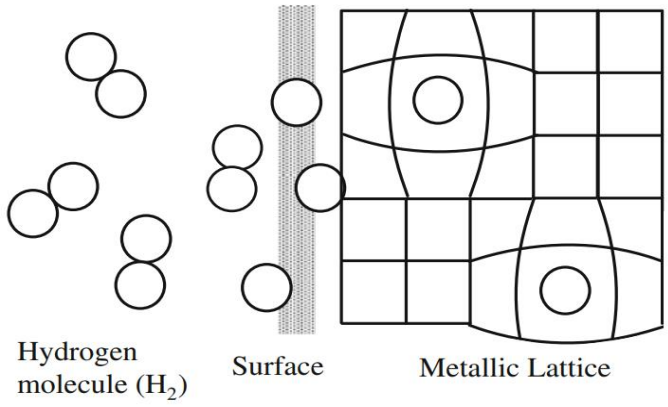

Figure 3.14 The diagram of hydrogen adsorption and desorption of metal/alloy and formation of hydrogen [35].

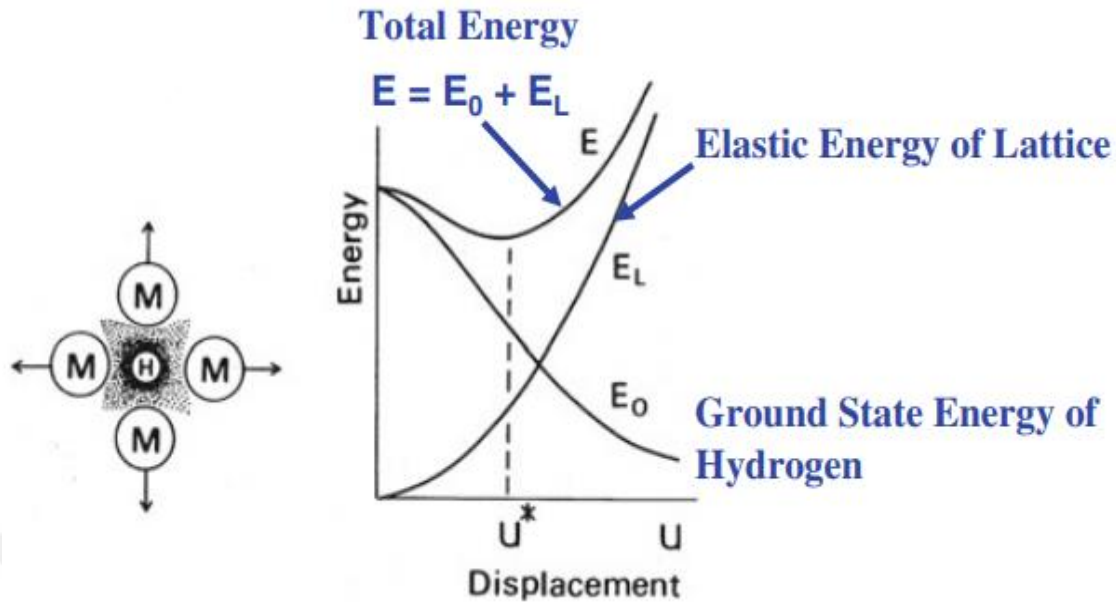

Figure 3.15 Self-trap mechanism of hydrogen occupancy in an interstitial region [35].

There are also outstanding characteristics of interstitial hydrides. An interstitial hydride is obtained by way of the reaction which takes place between intermetallic compounds or solid solution of metals and gaseous hydrogen. Alloy-hydrogen system exhibits better properties than a pure metal-hydrogen system and following properties are given for the alloy-hydrogen system [35].

- Broader range of hydride stability
- More excellent sorption kinetics
- A greater variety of hydrides could be generated.

Due to these characteristics or properties, interstitial hydrides have become more preferable and useful hydrides than other types of hydrides.

Table 3.4 represents the hydrogen content and hydrogen density of interstitial hydrides. In the beginnings of 1970s, an energy crisis was occuring. So as to overcome this obstacle, hydrogen was used as storage element. As a result of this situation, intermetallic compounds – hydride systems were improved. Israel and Japan have researched and improved hydride-forming intermetalling compounds.

Table 3.4 Hydrogen densities and hydrogen contents for several hydride systems [35]

([a]Includes weight of the cylinder, [b]Hydrogen cylinders for Toyota MIRAI (2014))

System	Hydrogen density (mol. H_2 /dm^3)	Hydrogen content (wt %)
Hydrogen gas (273 K, 1 atrn)	0.045	100
Liquid hydrogen (20 K)	35	100
Water (293 K)	56	11.2
MgH_2	55	7.6
Mg_2NiH_4	47	3.6
$LaNi_5H_6$	52	1.4
$TiFeH_2$	47	1.9
$(Ti–V–Cr)H_2$	102	4.0
High pressure cylinder (1.5 MPa)	6.6	1.2a
High pressure cylinder (70 MPa)	20	$5.7^{a,b}$

Water electrolysis has become the most outstanding way for hydrogen generation. Electrolysis can be defined as a process which contributes to decompose chemical components of a compond in a liquid with the help of an electrical current (DC: Direct Current). This electrical current provides also the energy which is required for occurence of chemical reactions. This method can also be used as an energy storage method via the generation of hydrogen. The decomposition rocess is carried out by oxidizing (substance gives an electron) or reducing (a substance takes an electron). The process of electrolysis is applied in an electrolytic tank which includes two electrodes and electrolyte. These two electrodes are soaked into the electrolyte. The chemical reaction which occurs during the electrolysis process of water, was given in below [4, 2].

$$\text{Anode(Positive Potential)}: 2H_2O \rightarrow O_2(\text{Oxygen Gas}) + 4H^+ + 4e^- \quad \textbf{(3.11)}$$

$$\text{Cathode(Ngtv. Potential)}: 4H^+ + 4e^- \rightarrow 2H_2 \quad \textbf{(3.12)}$$

$$H_2O + \text{Energy} \rightarrow H_2 + \tfrac{1}{2}O_2 \quad \textbf{(3.13)}$$

According to these reactions, hydrogen is agglomerated at the cathode and the agglometration of oxygen occurs at the anode. As it can be shown in these reactions,

water is obtained by combining one oxygen atom and two hydrogen atoms. Enthalpy of this overall reaction is equal to approximately 3 – 5 kWh/m^3 [2]. Figure 3.16 gives the schematic diagram of the water electrolysis. By depending on this figure, direction of the current is from the cathode to the anode.

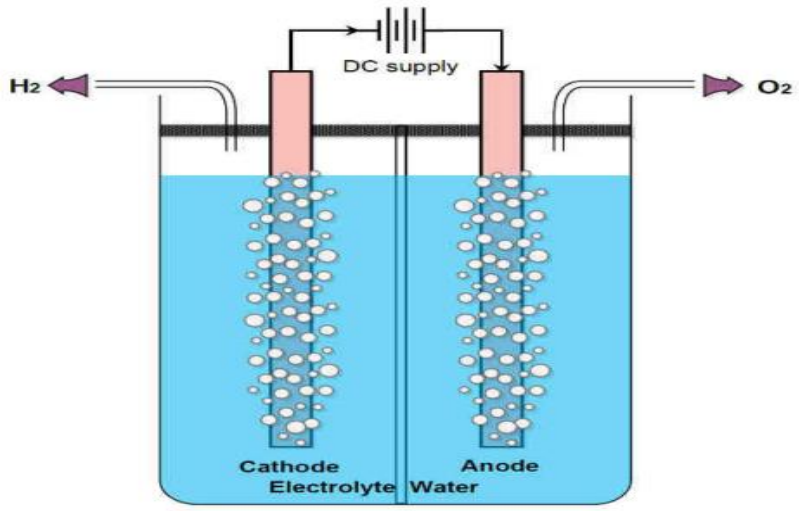

Figure 3.16 Schematic diagram of water electrolysis [36]

The electrolysis efficiency is calculated by calculating the ratio of the theoretical energy to actual energy. Additionally, one of the most excellent methods for enhancement of the electrolysis efficiency is to reduce energy losses. So, the electrolysis efficiency can reach to 90% [2]. The water electrolysis can also be utilized in fuel cells in order to produce hydrogen. It includes also many types of electrolyzer like alkaline, membrane and high temperature steam eletrolyzers.

3.4 Mechanisms of Supercapacitors

Supercapacitors have also great potential to use in the hybrid vehicles. Additionally, significant factors influence the electrochemical performance of supercapacitors (SCs). These factors consist of the physicochemical characteristics of electrode substances, the choice of electrolyte, and the voltage variety of electrodes [37]. So as to enhance the electrochemical efficiency of supercapacitors, one of the most preferable methods is to develop high quality electrode materials. The main purpose and function of these materials is to contribute to increase the electron transfer and

ion diffusion. Transition Metal Oxides (TMOs) have become one of the most outstanding and popular members and candidates of electrochemically active materials for the future applications and generations of supercapacitors because of their good and high electrochemical performance.

Figure 3.17 gives the structure of supercapacitor power plant and depends on PV system. As it was shown in the following figure, there are two buck-boost converters which provides regulation of the energy of battery and supercapacitor. These converters are also birectional connections. PV modules benefit from the another converter in order to fulfill maximum power point tracking (MPPT) according to this figure [38]. Main purpose of buck converter is to adjust the conversion of voltage and current. This converter contributes to enhance the current and decrease the voltage. In other words, DC output voltage has become smaller than DC input voltage [39]. After the conversion process completes, necessary inversions must be made. So, energy consumers can meet their energy demands.

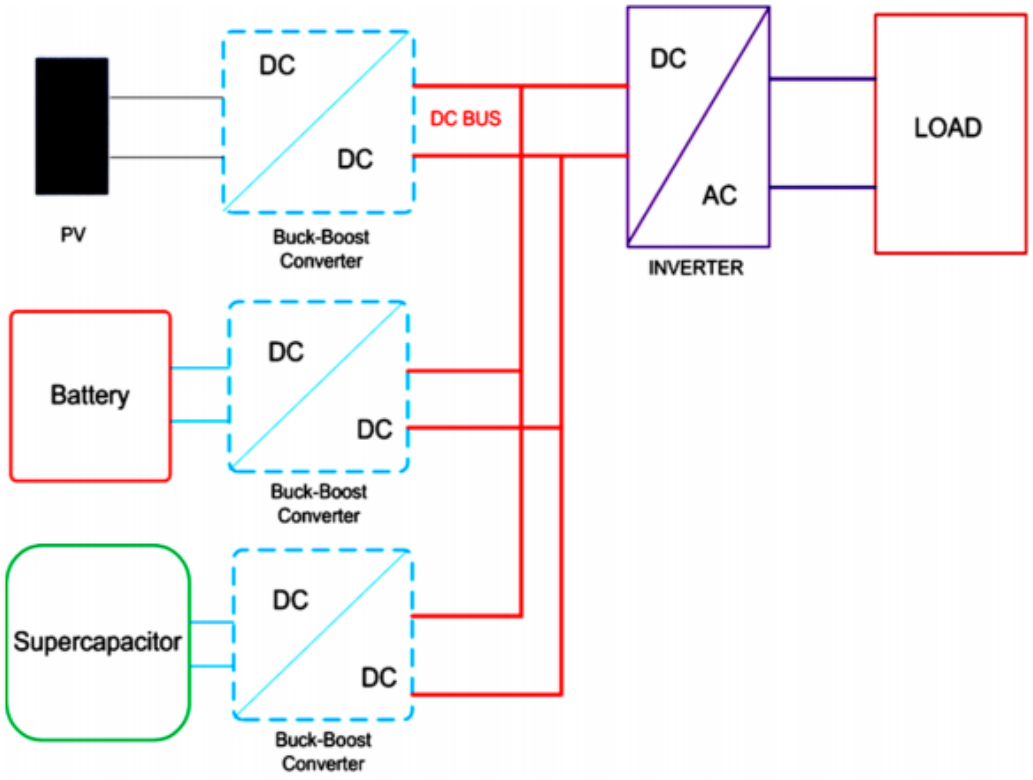

Figure 3.17 Hybrid energy storing system (HESS) which depends on solar energy mechanism [38]

Figure 3.18 gives the CV curves and constant current discharge curves of supercapacitors under various storing systems. Cyclic voltammetry curves and constant current discharge curves provide understanding of energy storage performance mechanism of supercapacitors. The Figure 26a and 26c show the the cyclic voltammetry curve and the constant current discharge curve of the supercapacitor electrode, under the storing system of electric double layer capacitance and pseudocapacitance, respectively; *b and d* respectively exhibit the cyclic voltammetry curve and constant current discharge curve of the supercapacitor electrode under the Faraday capacitor storing system [27].

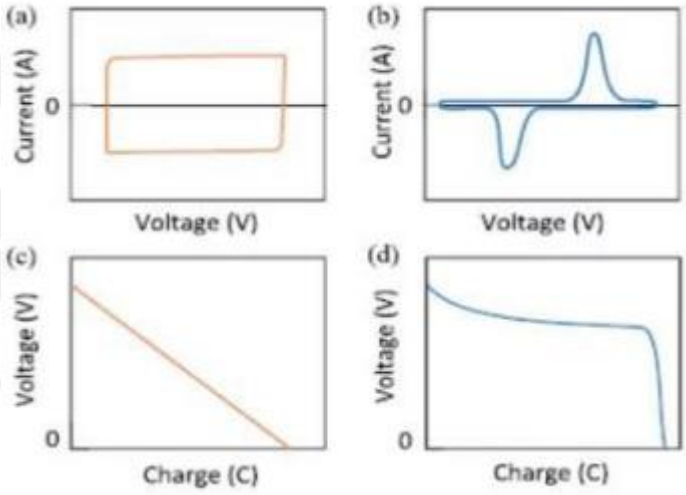

Figure 3.18 CV curves and constant current discharge curves of electric double layer capacitors under various storing systems [27]

The energy storage mechanism of supercapacitors can be classified into three categories and Figure 3.19 presents the schematic diagram of this classification. These categories contain (a) electrical double layered capacitance (EDLC), (b) pseudocapacitance, and (c) battery-type behavior [37].

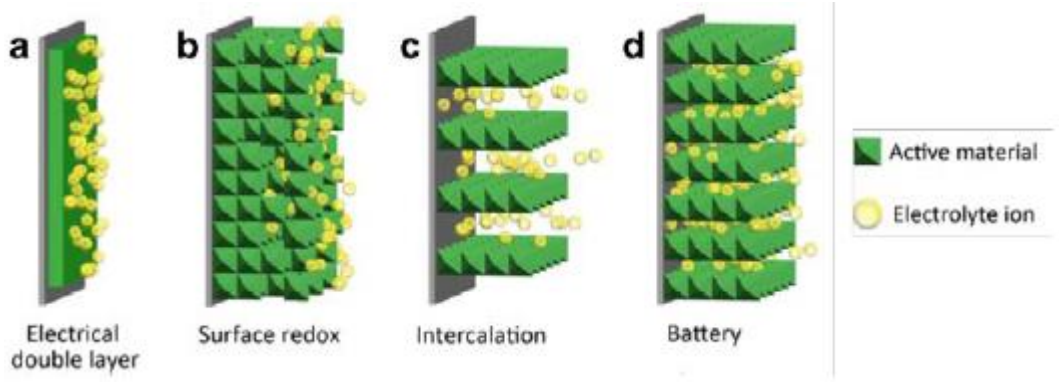

Figure 3.19 Schematic diagram of energy storing system for (a) electrical double layer capacitance, (b) surface redox capacitance, (c) intercalation capacitance, and (d) battery-type behavior [37].

3.4.1. Mechanism of EDLC

As the Figure 3.19 is carefully analyzed, the energy storing system of EDLC is related to the absorption and desorption of electrolyte ions on the interface that takes part in between the electrode and electrolyte during the charge and discharge operation without the charge transport reaction [37].

Electrochemical double layer capacitors (EDLCs) are also called as ultracapacitors and exhibit greater energy density than classical capacitors and greater power density than batteries. In EDLC, the main method of energy storage is physically based on storing electric charges between two conductive plates in the presence of an electric field.

Supercapacitor is one of the most preferable energy storage devices because they can store a high quantitiy of energy and can quickly deliver it. The behavior and working of EDLC depend on electrochemical activity and the kinetic property of the electrode substances so as to occur adsorption and desorption of electrolyte ions. Because of this situation, the surface area, porosity structure and pore distribution of the electrode substances should be improved in order to increase capacitance [37]. According to investigations and report of Largeot and partners, they found that there is a connection and interaction between the electrolyte ion size and the pore size of the electrode substance in an EDLC. By depending on this report, it is noticed that

EDLC can obtain the maximum double-layer capacitance when the electrolyte ion size and the pore size of the electrode material is close to each other.

Materials that are used in EDLC, are generally based on carbon materials like graphene, CNTs, active carbon and so on. These materials exhibit also similar properties with EDLC such as high surface area, porous structures, and excellent conductivity). But, the specific capacitances of carbon materials (<200 F/g) are smaller than that of faradaic active substances [37].

3.4.2 Mechanism of Pseudocapacitance (PC)

Pseudocapacitance provides contribution charge storage capacitance with the help of faradaic redox reactions. As it can be seen in the Figure 3.19b and c, pseudocapacitance can be classified into two types. These are *surface redox pseudocapacitance* and *intercalation pseudocapacitance* [37].

Surface redox pseudocapacitance takes place on surface or close to the surface of electrode substance when electrolyte cations and anions are adsorbed and desorbed with charge storing operation. Besides this, electrode materials with surface redox pseudocapacitance exhibit also some important characteristics. They possess generally linear and triangle shape of galvanic charge and discharge (GCD) curves and nearly rectangular CV curves. The most outstanding and prominent candidates are *conducting polymers* and *some transition metal oxides (RuO_2), Mn* and *Fe-based oxides*. In conducting polymers, the material structures are exposed to some important changes due to the volume expansion when charge/discharge process takes place. This situation leads to low cyclic stability that restricts their practical SC applications. RuO_2 is one of the most outstanding and important transition metal oxides (TMOs) for supercapacitors. The highest theoretical capacitance of RuO_2 may be obtained 1450 F/g when a potential of 1 V is applied [37]. This value is larger than that of carbon-basis substances (>100F/g) [40]. But RuO_2 is not preferred for large-scale Supercapacitor application because of the high-cost of Ru. In order to overcome this restriction, high-quality and cheap transition based electroactive substances should be used.

Intercalation pseudocapacitance contains an operation that electrolyte cations such as Na^+, K^+, Li^+, H^+, etc. intercalate and deintercalate (this terms are also known as “add and subtract” in diary life) into/from the channels or layers of electrode materials with the help of a faradaic charge-transfer involving no phase change. Intercalation managed pseudocapacitance electrode substances that contain rigid lamellated lattice construction which involves V_2O_5, WO_3, MoO_3, Nb_2O_5, and TiO_2 [37].

3.4.3 Mechanism of Battery-Type Behavior

The choice of electrode substances has been the most significant topic in both supercapacitors and fuel cells. Electrode materials can be exposed to a phase change when charge/discharge process is carried out. This situation provides that these electrode materials can be misused as pseudocapacitance substances for a long duration. In recent years, many researchers have perceived that above electrode materials that have different properties from conventional pseudocapacitance materials. By depending on the novel introduction, electrode substances displays a phase changing during charge and discharge operation must be named and grouped as “battery-type” substances. Figure 18d gives information that the charge storing of battery-type substances is arranged with the help of cation dispersion. In addition to this, this charge storage contains also ion intercalation and deintercalation reaction, phase changing, and/or alloying reactions [37]. There are also important parameters to explain the electrochemical properties of battery-type substances. These important parameters are CV and GCD curves with distinct redox CV peaks and GCD platform regions, respectively. Battery-type substances exhibit usually excellent specific capacity however they have also low rate performance. The main reason of their low rate erformance is based on the slow kinetics. These unquick kinetics correlated with slow phase changing when the charge and discharge operation was carried out. Battery-type substances that will be used in the electrode, play an important role on energy storage devices. Therefore, some outstanding properties should be attached importance. Large surface area can contribute to obtain abundant active regions for redox reactions. It decreases also the the diffusion distance of electrolyte ions. The porous nanostructures provide sufficient fields to arrange and control volume expansion during charge and discharge operation, that develop the cycle stability of

battery-type substances. Battery-type materials can generally be made a combination with carbon-based substances to obtain hybrid supercapacitors so as to increase the charge storing proportion of battery-type substances. The most effective method to obtain hybrid capacitors is to improve and increase rate performance and energy density. The most important and promising battery-type electrode materials are Ni and Co-based oxides. Their voltage ranges between 0 and 0.55 V. Hg/HgO can be used as alkaline electrolytes. In order to obtain a voltage window of 1.5V, they are mounted into hybrid SC devices with carbon-based materials (-1-0 V vs. Hg/HgO). As well as Ni and Co-based oxides, other important transition metal-basis substances like Cu and some binary TMOs can be used and they display excellent battery-type charge storage behavior [37]. Table 3.5 and 3.6 give the information about characteristics of supercapacitor' types, important parameters and comparison between supercapacitor and battery, respectively.

Table 3.5 Characteristics of Supercapacitor' types [41]

Types of Supercapacitors	**Charge duration [s]**	**Cycle life**	**Cell voltage [V]**	**Specific energy [Wh/kg]**	**Cost per kWh [USD]**	**Operating temperature [°C]**	**Self discharge per month [%]**
EDLC	1–10	1 000 000	2.7	3–5	~10 000	−40 to 65	60
Pseudo capacitance	1–10	100 000	2.3–2.8	10	~10 000	−40 to 65	60
Hybrid	100	500 000	2.3–2.8	180	Not known very good	−40 to 65	Not known very good

Table 3.6 Important parameters and differences between supercapacitor and battery [42]

Important Properties	**Supercapacitor**	**Battery**
Specific Energy (Wh/kg)	Between 1 and 10	10-100
Specific Power (W/kg)	Between 500 and 10000	smaller than 1000
Discharge Duration	Between seconds and minutes	Between seconds to minutes
Charge Duration	Between seconds and minutes	between 1 and 5 h
Coulombic Efficiency (%)	between 85 and 98	between 70 and 85
Cycle-Lifetime	>500000	nearly 1000

CHAPTER 4

THE USED MATERIALS IN FUEL CELLS AND SUPERCAPACITORS

4.1 The Used Materials In Fuel Cells

In fuel cells, cathode and anode materials have a great effect. Therefore, they must have important requirements like large electrical conductivity, sufficient electrocatalytic activity for fuel oxidation reactions, adequate mechanically strength to support the cell, and good porosity for efficient gas diffusion and transportation, thermal expansion suitability with other parts of fuel cells, good chemical stability in reducing environment and high temperatures.

4.1.1 Graphene

Many R&D groups and scientists have paid attention to the graphene because of good properties. These good properties contain high charge mobility of 230,000 $cm^2/V.s$, excellent thermal conductivity 3000 $Wm^{-1}K^{-1}$, 2.3 % absorption of visible light, strong mechanical strength of 130 GPa and large specific surface area of 2600 m^2/g. Therefore, graphene has become one of the most outstanding and preferable materials [43].

The selected material influence overall performance of the fuel cell. Graphene must have and provide some important properties like high conversion efficiency, large power delivery, low-cost, long life span and working safely.

Graphene can also be the best important allotropes of carbon and consists of sp^2-hybridized carbons. It is arranged and found in a 2D honeycomb lattice. One of the most important and outstanding property of graphene is that electrical and thermal conductivity of graphene are 10^6 Scm^{-1} and 3000 $Wm^{-1}K^{-1}$, respectively. High chemical stability and electrochemical activity provide that graphene can be used either an active metal-free electrocatalyst or a catalyst-support for fuel cells.

Table 4.1 Properties of graphene [43]

Optical Absorbance (absorption of visible light)	2.3 %
Electrical Conductivity	10^6 Scm^{-1}
Thermal Conductivity	3000 $Wm^{-1}K^{-1}$
Theoretical Specific Capacity	744 mAh/g
Specific Capacitance	550 F/g
Mobility of Charge	230000 $cm^2/V.s$
Breaking Strength	42 N/m
Young Modulus	1 Tpa
Density	<1 gcm^{-3} in 2630 m^2g^{-1}
Theoretical Specific Surface Area	2600 m^2/g

Table 4.1 presents the properties of graphene and these properties provide that graphene is the most preferable and useful material in fuel cells. It can also be used in future optoelectronics and photovoltaics instead of indium tinoxide (ITO) because of its high cost and brittle. In other words, graphene is extremely appropriate for the development of both energy conversion and energy storage.

Graphene is one of the most important carbon allotropes and has 2 dimensional structure. Carbon atoms are located in a hexagonal design and this design can also show similarity with chicken wire. Figure 4.1 illustrates the internal structure of the graphene.

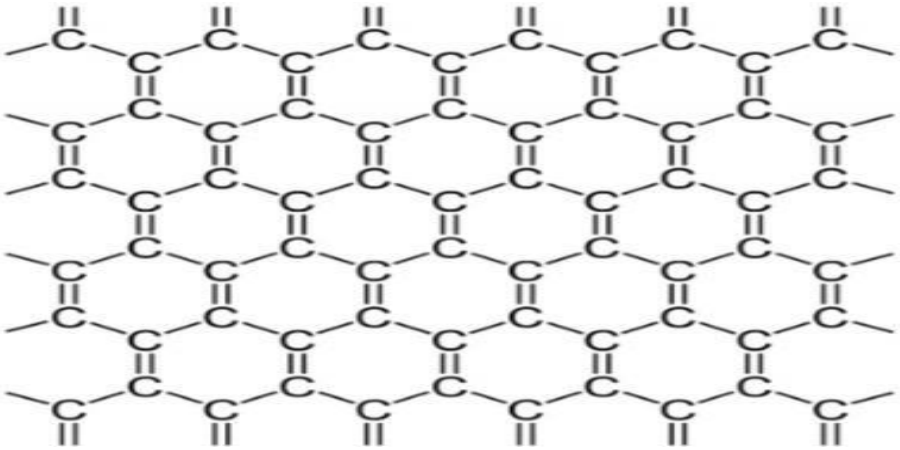

Figure 4.1 The structure of the graphene [44]

Graphene nanostructure contains an atom thick layer of graphite and the thickness of graphite is approximately 0.34 nm. In Figure 4.1, covalent bonds exist among carbon atoms. Owing to durability of the covalent bonds between carbon atoms, they develop the stability and tensile strength of the graphene. Graphene exhibits also larger electron mobility than other materials. Therefore, R&D groups have investigated and made an effort in order to improve and make use of this property in other applications.

The single layer of graphene contains sp^2 bonded carbon atoms and these carbon atoms can constructed and found within such a honeycomb appearance. This situation provides producing 3D bulk graphite. Graphite contains Van der Waals forces and these forces contribute to bond and connect the stack layers of graphene.

Figure 4.2 represents the electronic morphology and dislocations in graphene. One of the most effective ways of arranging and controlling graphene structure is to research electronic dislocations as it can be seen in the Figure 4.2. The improvement of nanostructured graphene basically depend on the movement of carbon atoms of the unit cell. Scientists carried out many experiments in order to obtain a nanostructured array with controlled shape, size, crystallinity and functionality. According to these informations, graphene can also be used and combined with a large number of inorganic structures in order to improve and increase their properties.

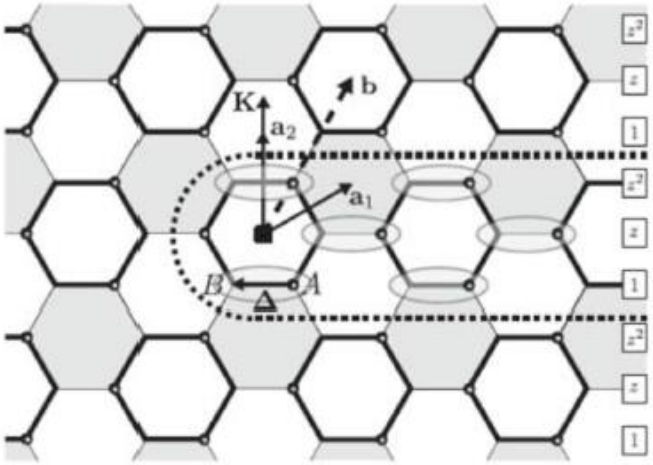

Figure 4.2 The electronic morphology and dislocations in graphene [43]

Graphene displays excellent electronic properties and contains Dirac points. In Dirac points, the conduction band and valence band keep in contact with each other as it can be shown in the Figure 4.3a. Both conduction band and valence band seems like smaller halves of a conical surface. Unoccupied conduction band is also known as π* band and occupied valence band is called π band. Main purpose of Dirac cones is to determine and obtain information about properties which take place in some electronic band structures. These structures are used to determine and express extraordinary electron transfer characteristics of substances such as graphene and topological insulators. When these substances possess energies which approach to the Fermi level, similarites have been shown between conduction and valence band in above and bottom halves of a conical surface. The point where both of these bands kept in contact with each other, is called Dirac points. Additionally, the another purpose of Dirac cones is to show relationship between energy and the two components of the crystal momentum k_x and k_y (Figure 4.3b). Because of these properties of graphene, it is one of the most outstanding intrinsic semiconductors. Intrinsic semiconductor acts also as massless relativistic particles that are called as Dirac fermions as it can be seen in the Figure 4.3.

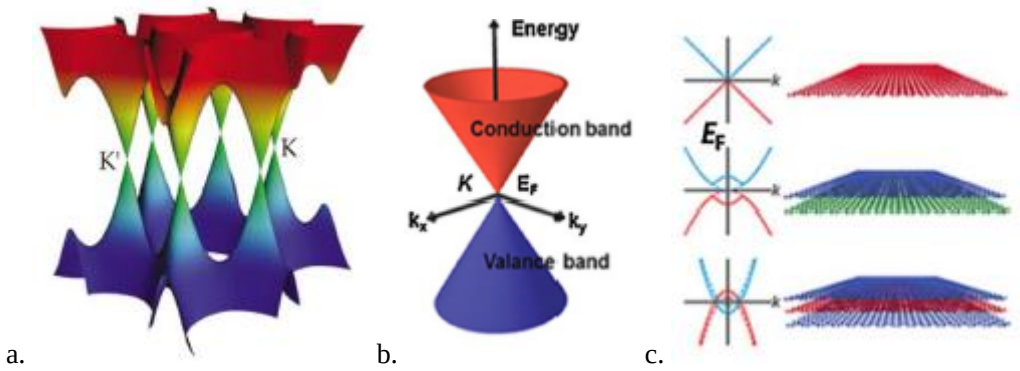

Figure 4.3.a.Valence band and conduction band keeps in contact with in K and K' points(Dirac points) b. The relationship between energy and crystal momentum near the Dirac points c. Fermi Energy levels, electrical and optical properties of different graphene layers [43]

Graphene presents also many charge mobility values at certain temperatures. For example, it displays the charge mobility of approximately $1.5*10^4$ $cm^2.V^{-1}s^{-1}$ at 300K

and approximately 6×10^4 $cm^2.(Vs)^{-1}$ at 4 K with charge concentration (both electron and hole) up to 10^{13} cm^2 [43].

Graphene is one of the best materials that conducts electricity and heat. In recent times, maximum thermal conductivity of monolayer graphene and supported graphene obtained 5000 W/(m.K) and 600 W/(m.K). There are also important methods about thermal conductivity in order to consistent, excellent results. Raman spectroscopy is one of the most important method and main purpose of this method is to determine and measure the thermal conductivity of graphene. Table 4.2 gives information about the thermal conductivity of graphene.

Table 4.2 Thermal conductivities of graphene by making use of Raman Spectroscopy [43]

Raman Specroscopy	Thermal Conductivity of Graphene w/(m.K)
2-5 μm diameter	4840 – 5300
1-5 μm diameter	3080 – 5150

Graphene can also be used as electrocatalysts. Fuel cells consist of two electrodes that are known as anode and cathode. The reduction of oxygen from air occurs at the cathode and the oxidation of fuels such as hydrogen, methanol and formic acid occurs at the anode. Noble metals like Pt(Platinum), Ru(Ruthenium), Pd (Palladium), Ni (Nickel) and Au (Gold) and their alloys are used as catalysts and to carry out reactions at the anode and the cathode in fuel cells. Pt is one of the widely utilized materials as catalyst in order to takes olace electrode reactions for low working temperature fuel cells. But, these noble metals have important disadvantages like high-cost, restricted reserve on earth, low reaction kinetics, leading to carbon monoxide poisoning. They prevent also diffusion of fuel molecules from anode to cathode and this situation leads to crossover effects. Carbon black is one of the most widely preferred support for fuel cells by virtue of its low-cost. Other non-carbon and carbon materials are also preferred and selected as catalyst backings that contain active porous carbon, CNTs, graphite and carbon aerogels. The most important and outstanding properties of these catalysts supports is to display excellent eletrical conductivity, strong and durable coupling with catalysts, good and high chemical and

electrochemical stability in the electrolysts, high surface for even dispersion of catalyst and low-cost.

Graphene is also most widely preferred and used material as catalyst. Many scientists have made an effort in order to obtain Pt catalyst hybrid with graphene. According to studies, catalytic activity was enhanced because of the larger implementation and activation of Pt on graphene sheets. Because of higher specific surface area of graphene sheets, good diffusion of Pt is provided. In addition to this, an important experiment is made about Pt/graphene catalysts in order to obtain and synthesize them with the help pf poly-diallyl-dimethyl-ammonium (PDDA). According to the obtained results, the PEM fuel cells display higher performance and better electrochemical stability. Because of the existence of PDDA, the catalytic activity has been enhanced with the help of good dispersion of Pt on the graphene.

Graphene is also used as electrolyte membrane. Proton exchange membrane (PEM) has a semi-permeable structure that is consisted of ionomer. Main purpose of this structure is to contribute to only protons to flow through. Additionally, this membrane has also importsnt properties like large thermal, mechanical and chemical stability, good tolerance to catalyst. Perfluorosulfonic acid membrane is the most preferable membrane of PEMs because of excellent conductivity, large mechanical strength and good chemical resistance but this membrane exhibit some important disadvantages like expensive, low conductivity at low humidity. It can also permit to flow methanol. In order to overcome this problem, researchers offered that graphene (widely GO(Graphene Oxide)) can be used in PEMs. GO exhibits outstanding properties like high surface area, excellent mechanical strength, good thermal stability, high proton conductivity and range operating temperature.

4.1.2 Perovskites Based Electrodes

Perovskite is one of the most outstanding materials for fuel cells because this material improves the kinetics of reactions in electrodes with temperature and is also low-cost. This material is also known as Calcium Titanium Oxide mineral that consists of $CaTiO_3$. This name is also used in order to classify the composites that possess the same type of crystal morphology as $CaTiO_3$ ($^{XII}A^{2+VI}B^{4+}X^{2-}{}_3$). Gustav

Rose found out Perovskites in 1839 in the region of Ural Mountains of Russia. The name of this mineral was given by Lev Perovski (1792-1856) who is one of the most important Russian mineralogists.

One of the most important advantage of perovskites is that they have been abundantly found in the Lower Mantle of Earth. Many investigation and R&D groups assumed that perovskites have found at the rate of 93% on earth. Furthermore, these materials exhibit also outstanding magnetic properties. These magnetic properties are related to the elements that is found in perovskites. On the other hand, perovskites contain also colossal magnetoresistance which stands for their electrical resistance is going to alter when they were positioned in the magnetic field.

Perovskites display some important physical properties like large absorption coefficient, superconductivity, charge ordering, colossal magnetoresistance, large thermopower, long-range ambipolar charge transport, low exciton-binding energy, large dielectric constant, ferroelectric properties. Therefore many scientists have paid attention to perovskites because of their excellent properties. Additionally, these materials have also a cubic structure. Their general formula is defined as ABO_3. In this formula, A and B stand for cations and Oxygen stands for the anions. The A cations can also be La, Sr (Strontium), Ca (Calcium), Pb (Lead) and these cations posess lower valances.Apart from lower valences, they have also larger size. The B cations can also be Ti (Titanium), Cr (Chromium), Ni (Nickel), Fe (Iron), Co (Cobalt), Zr (Zirconium) and they can occupate less space. When a comparison is made between A and B, A cation is greater than B cation. The coordination numeral of A is equivalent to 12 and the coordination numeral of B is equal to 6. A cation represents generally a transition metal. Figure 4.4 shows the structure of perovskites. As it can be seen in Figure 4.4b, A-site ion is located on the corner of the lattice and B are positioned in the center of the cube. These elements contribute to improve electrical conductivity.

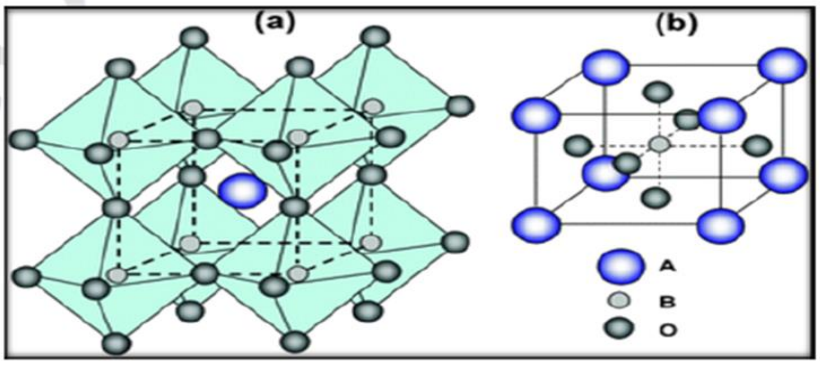

Figure 4.4 The structure of Perovskites based electrodes [45]

Table 4.3 represents also important properties of various Perovskites-based cathode materials. These datas are measured at 800 °C.

Table 4.3 Important properties of various Perovskites-based cathode materials [46] (σ_e = electrical conductivity (S/cm), σ_i = ionic conductivity (S/cm), D: Oxygen Diffusion Coefficient (cm^2/s), k: Surface Exchange Coefficient (cm/s))

Materials	σ_e, S/cm	σ_i, S/cm	D*, cm^2/s	k, cm/s	TEC ($\times10^{-6}$), K^{-1}
$Pr_{0,8}Sr_{0,2}Fe_{0,8}Co_{0,2}O_3$	76	0.0015			12.8
$Pr_{0,7}Sr_{0,3}Fe_{0,8}Co_{0,2}O_3$	171				12.4
La_2NiO_4	47		1.2×10^{-7}	1.7×10^{-6}	13.0
Pr_2NiO_4	94		1.2×10^{-7}	3.1×10^{-6}	13.6
$La_2Ni_{0.8}Co_{0.2}O_4$			9.8×10^{-8}	2.2×10^{-6}	11.3

4.1.3 Titanates Based Electrodes

Titanate is one of the inorganic compounds. There are also several kinds of titanium oxides and important properties of titanium oxides contain white, diamagnetic, high-melting, and insoluble in water. The most important point for preparation of Titanium Oxides is to provide high-temperature condition. In order to carry out this condition, tube furnaces can be utilized.

Energy conversion systems have occupied an important place for all of the energy systems. SOFC is one of the most important and outstanding energy system. Many investigation and research groups are making efforts in order to develop such systems. At the same time, they are discovering and making research novel and high-

quality electrode materials with developed properties. There are also several and various types of Titanates that are used as electrode materials in SOFC such as $CaTiO_3$ and $Sr_{1-3x/2}La_xTiO_{3-d}$. Additionally, an experiment that is related to these electrode materials, was made. According to the obtained results, there is a direct proportion between the value of conductivity and the content in the second composite. If the value of the conductivity enhances, the La content will enhance. The most outstanding anode materials in SOFC include $Sr_{1-3x/2}La_xTiO_{3-d}$, $Sr_{1-y/2-3x/2}La_xTi_{1-y}Nb_yO_{3-d}$ [45].

4.1.4 Apatite-Type Materials

Apetite has been one of the most significant members of phosphate minerals that compose of large concentration of OH^-, F^- and Cl^- that stand for hydroxylapatite, fluorapatite and chlorapatite, respectively. Its name was given by German geologist in 1786. Apatite has also been preferred as one of the most prominent minerals and is widely used in biological environmental systems. One of the most widely usage fields of apatite is in fertilizer. The main purpose of usage in fertilizer is to fabricate phosphorous. Figure 4.5 shows schematic diagram of internal structure of electrode materials; (a) perovskite, (b) double perovskite, (c) Titanates, and (d) apatite.

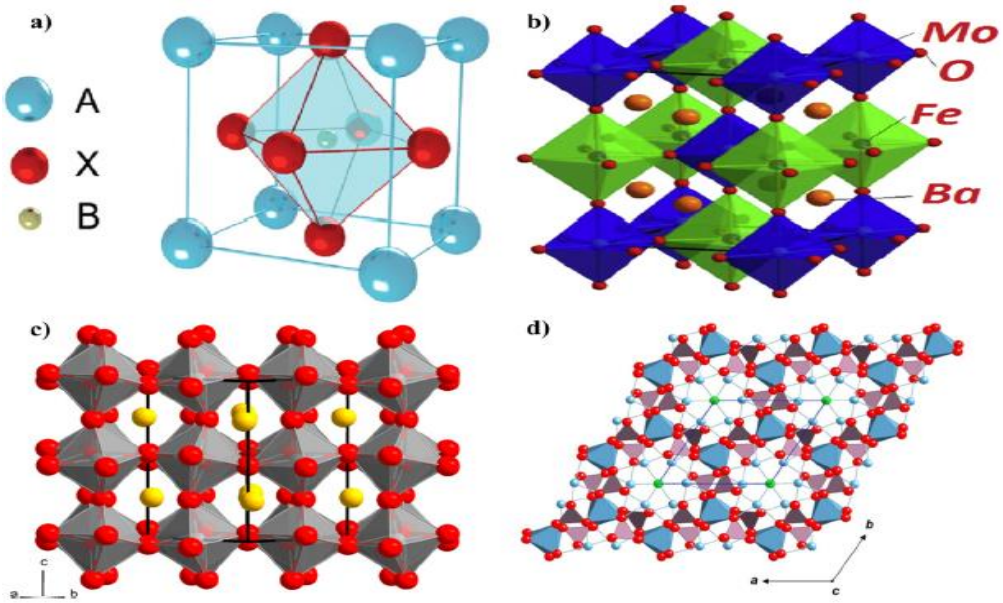

Figure 4.5 Schematic diagram of morphology of electrode ingredients; (a) perovskite (b) double perovskite (c) titanites (d) apatite. [45]

In addition to this, Table 4.4 gives information about comparisons for various morphologies which depends on anode materials for fuel cell.

Table 4.4 Comparison for various morphology based anode materials for fuel cell [45]

Anode	Material Type	Conductivity	Performance	Working Temperature
Perovskite	LSCF	200 +	1.2–1.5	550-850
	LSCM	0.053	0.70-0.80	650-800
	$La_{0.8}Sr_{0.2}Cr_{0.8}Mno_{0.2}O_3$	0.8-1.2	0.47–0.55	850-950
Double Perovskite	$Sr_2Mg_{1_x}Mn_xMoO_{6_\delta}$	0.42–0.65	-	650–1000
	$Sr_2FeNb_{0.2}Mo_{0.8}O_{6_\delta}$	0.4–0.6	0.38–0.45	550–700
Titanites	TiC_7N_3	-	-	600–1200
	$La_{0.2}Sr_{0.25}Ca_{0.45}TiO_{3_\delta}$	-	0.38–0.45	650–850
Apatite	$La_{10}Si_{5.5}A_{l0.5}O_{26.75}$	0.028	65–195	700–800
	$La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$	0.03–0.045	0.02–0.04	600–850

4.1.5 Porous Ni/YSZ Cermet

Cermet is a composite material and obtained by combining ceramic (cer) material with metal (met). The most important properties of cermet are high temperature resistance, durability, strength and hardness. The most widely used metals are nickel, molybdenum, and cobalt. Cermets contain generally less than 20% metal by volume. The metal can also be exposed to the plastic formation. These materials is one of the most outstanding and preferable materials as anode for high temperature SOFC. Because this anode material is low-cost and excellent electrical conductor. Additionally, it exhibits also chemically stable structure at high temperature and possesses large corrosion resistance to the fuel. Porous Ni/YSZ cermet exhibits closer TEC (thermal expansion coefficient) with that of YSZ electrolyte. Furthermore, the most important advantage of this material is that the porous structure contributes to carry out diffusion and permeation for fuel gas (Singhal and Kendall, 2003). The electrical conductivity of Ni/YSZ cermet anode depends on nickel content and size ratio between YSZ and Ni. Electrical conductivity is proportional to the nickel ingredient and size proportion. If nickel content and size ratio increase, the electrical conductivity will also increase [47].

This material is one of the most widely preferred anode materials in fuel cells owing to its low-cost, excellent chemical stability. Usage of only Ni particles leads to anode degradation. In order to prevent this problem, Ni particles are combined with YSZ (Yttria-stabilized zirconia). The YSZ particles form a groundwork that behaves as an inhibitor in order to hinder enhancement of the Ni powders. Additionally, TEC of Ni ($16.9*10^{-6}$ 1/K) has been higher than that of YSZ ($11.0*10^{-6}$ 1/K) as it was shown in the following table. Therefore, supplementation of YSZ provides that TEC of Ni/YSZ cermet approaches to those of fuel cell's constituents. Moreover, it enhances the ionic conductivty of the substance [47].

Table 4.5 Comparison of thermal expansion coefficient between Nickel and YSZ [47]

Materials	**TEC (K^{-1})**
Nickel	$16.9*10^{-6}\ K^{-1}$
YSZ	$11.0*10^{-6}\ K^{-1}$

4.1.6. Lanthanum Manganite ($LaMnO_3$)

This material is most widely used as cathode materials because of the excellent and valanced consideration of electrical conductivity, chemical reactivity electro-catalytic activity, and TEC. Lanthanum manganite is one of the most important inorganic compounds and a type of perovskites. The main reason of notation of $LaMnO_{3-\delta}$ is that $LaMnO_3$ possesses often Lanthanum vacancies and neutron scattering occurs. This cathode material exhibits also excellent conductivity. Table 4.6 presents properties of different types of Sr-doped Lanthanum manganite.

Table 4.6 Properties of Sr-doped Lanthanum Manganite [47]

	TEC ($x10^{-6}$ 1/K)	**σ_e (S/cm)**
$La_{0.6}Sr_{0.4}MnO_{3-\delta}$	13 (800)	130
$La_{0.7}Sr_{0.3}MnO_{3-\delta}$	12.8 (25-1100)	265 (947)

4.1.7. Cobalt-Based Electrodes

These materials exhibit also larger ionic and electronic conductivities than other materials. Additionally, these materials present also large thermal expansion coefficient. Sr-doped $La_{0.6}Sr_{0.4}CoO_3$ presents the highest electrical conductivity of $\sigma = 4.4 * 10^3$ Scm^{-1} [48]. Cobalt can enter the reaction with YSZ in order to produce insulating layers.

4.1.8. Yttria Stabilized Zirconia (YSZ)

This material has been one of the most commonly utilized electrolyte materials in fuel cells and a type of Fluorite-Structured Electrolytes. The most important and outstanding properties of YSZ is high oxide-ion conductivity at temperatures that are greater than 800 °C. In addition to this, YSZ exhibits also excellent mechanical and electrical characteristics. One of outstanding disadvantages of this electrolyte material is that it operates at high temperatures. This situation can sometimes restricts the usage of this material in several tradial applications of SOFC (Paściak et al., 2005). Figure 4.6 shows the crystal structure of the YSZ.

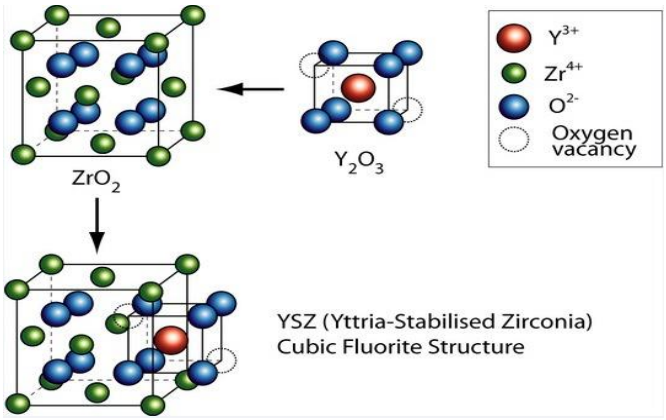

Figure 4.6 The crystal structure of the YSZ [49]

The thermal expansion coefficients are based on the modification of Zirconia as it is shown in the Table 4.7.

Table 4.7 Thermal expansion coefficients by depending on the modification of Zirconia [49]

Monoclinic	$7*10^6\ K^{-1}$
Tetragonal	$12*10^6\ K^{-1}$
Y_2O_3 stabilized	$10.5*10^6\ K^{-1}$

4.1.9 Sn-Based Oxides

M-doped SnO_2 is one of the most promising materials for fuel cells. This compound is obtained by doping SnO_2 with metal (M). SnO_2 (Tindioxide) is also called as stannic oxide and technological applications have commonly made use of SnO_2 like transparent conductors, chemical sensors, high-efficiency solar cells, and catalysts. Additionally, SnO_2 is also combined or doped with other elements in order to increase sensitivity, selectivity, stability, conductivity, and optical transmittance. SnO_2 is one of the most promising transition-metal dioxide combinations with rutile morphologies. Cassiterite can be known as tin oxide mineral and is the basic ore of tin [50]. As well as this, tin dioxide behaves as also an oxygen-deficient n-type semiconductor. Table 4.8 shows the most outstanding properties of SnO_2.

Table 4.8 Properties of SnO_2 (Tindioxide) [51]

Heat Capacity	52.6 J/(mol.K)
Density	$6.95\ g.cm^{-3}$ a 20°C $6.85\ g.cm^{-3}$ a 24°C
Solubility In Water	• Insoluble • Soluble in hot concentrated alkalis, acids
Magnetic Susceptibility	$-4.1*10^{-5}\ cm^3.mol^{-1}$
Crystal Structure	Rutile Tetragonal
Molar Mass	$150.708\ g.mol^{-1}$

Tindioxide is one of the most widely used materials as support material for low-temperature fuel cell catalysts. SnO_2 has been combined with Pt and Pd metals that has been used as supportive materials. Researchers have drawn attention to this supported material as catalyst in order to occur different chemical reactions. Chemical properties of SnO_2 contribute to be used it as a backing substance and contain its excellent ability of OH^- species at low potentials, inducement the electronic effect with Pt catalysts. These properties provide improvement the electrooxidation on Pt of CO and low molecular-weight alcohols, like methanol and ethanol. One of the most important drawbacks of SnO_2 is its low electrical

conductance and its conductivity must be increased although it is utilized as catalyst support in fuel cell. Furthermore, undoped tindioxide displays also 3.6 eV of bandgap with specific electrical resistance which is 10-10^6 ohm cm and has become one of the most outstanding bandgap semiconductors. Electrical resistivity which is knowns as specific electrical resistance, of SnO_2 is generally related to temperature and stoichiometry of the oxide. When SnO_2 was doped with Sb^{5+} (Antimony-Stibium) the electrical resistivity of SnO_2 was measured $10^{-2} – 10^{-3}$ Ωcm that is lower than undoped SnO_2 [50]. Table 4.9 presents briefly the electrical resistivity of undoped and doped SnO_2.

Table 4.9 Electrical resistivities of SnO_2 and Sb-doped SnO_2 [50]

Materials	**The Electrical Resistivity**
SnO_2	Between 10 and 10^6 Ωcm
Sb-doped SnO_2	Between 10^{-2} and 10^{-3} Ωcm

Pang and partners made an experiment about SnO_2. They obtained Ru-doping SnO_2 compounds or nanoparticles by making use of chemical precipitation and calcination method at the temperature of 550°C. According to obtained results, SnO_2 pieces which exhibit size of 20 nm as morphologic and in crystallite form, wasn't exposed to any changes after Ru was combined with SnO_2. In addition to this, Pt/Ru-SnO_2 was produced with the help of addition of Ru-SnO_2 with H_2PtCl_6 by reducing Pt precursor with $NaBH_4$. Pt presented particle which has size of 4 nm [50]. According to research of Safonova and partners, the inclusion of Pd, Ru and Rh contribute to improve the resistivity of SnO_2 films. As well as the study of Safonova and partners, Pang and partners shed light on the electrontransfer resistance (Rct) that reduces with the introduction of Ru. Table 4.10 shows the values of the electrontransfer resistance (Rct) on the Pt and Ru compound with SnO_2-graphite and Pt-SnO_2-graphite electrode materials, respectively.

Table 4.10 The electrontransfer resistance (Rct) of the Pt/Ru with SnO_2/graphite and Pt/SnO_2/graphite electrodes [50]

Materials	**Rct (Ω)**
Pt/Ru with SnO_2/graphite	4.92
Pt/SnO_2/graphite	6.28

Ru doping contributes to enhance the conductance of SnO_2. As well as improvement of electrical conductivity, it provides also development of the activity and the stability of Pt/ SnO_2. When a comparison is made for pristine SnO_2 particles, Ru may enhance the electrocatalytic activity of the Pt/ SnO_2 catalyst. One of the most important points of the combination of Ru with SnO_2 is that the reaction of RuOx with SnO_2 improves the production of hydroxyl types to make catalysation of the oxidation of toxical substances like (CO_{ads}) absorbed on the effective regions of platinum nanoparticles [50].

Additionally, the longtime cycle stability of the Pt/Ru-doping SnO_2/graphite electrode has been larger than Pt/SnO_2/graphite electrode [50].

SnO_2 possesses a surface area (<100m^2g^{-1}) that is smaller than that of reference Volcan XC-72. In order to utilize SnO_2 as a catalyst backing, SnO_2 must be synthesized with large surface area. There are also some important experiments and investigations that are related to the synthesis of SnO_2 with large surface area. BET surface areas that are higher than 100 m^2g^{-1}, were obtained by benefitting from several prominent techniques in the wake of calcination at the temperature which is from 300 to 500 °C [50]. Large surface area tin oxides that present good sintering resistance could produced by means of the hydrazine technique. Furthermore, large surface area that are larger than 200 m^2g^{-1}, were also formed by utilizing an adjusted Pechini method, making use of aqueous glyoxylic acid as disperser for Sn (IV) acetate.

SnO_2 NWs have also become outstanding materials for fuel cells. Nanowires (NWs) have become one type of the most outstanding one dimensional nanomaterials and exhibit also a large aspect ratio. They comprise of numerous materials and include solid cores. Saha and partners made an experiment about SnO_2 nanowires which were improved on fuel cell backings as catalyst supports for fuel cells. In order to improve gas permeability, NWs were deposited and grown on fuel cell backings and as a result of this process, 3D structure was obtained. Scientists got very important information about NW-based 3D structure like increased metal-support relation, improved mass transport in the electrodes for fuel cell's usages and enhancement of the usage of the noble metal catalyst. One of the most effective methods for SnO_2

nanowires is thermal evaporation method in order to grow on the fibres of a carbon paper [50]. Figure 4.7 presents SEM and TEM figures of SnO_2 nanowires by depending on this technique.

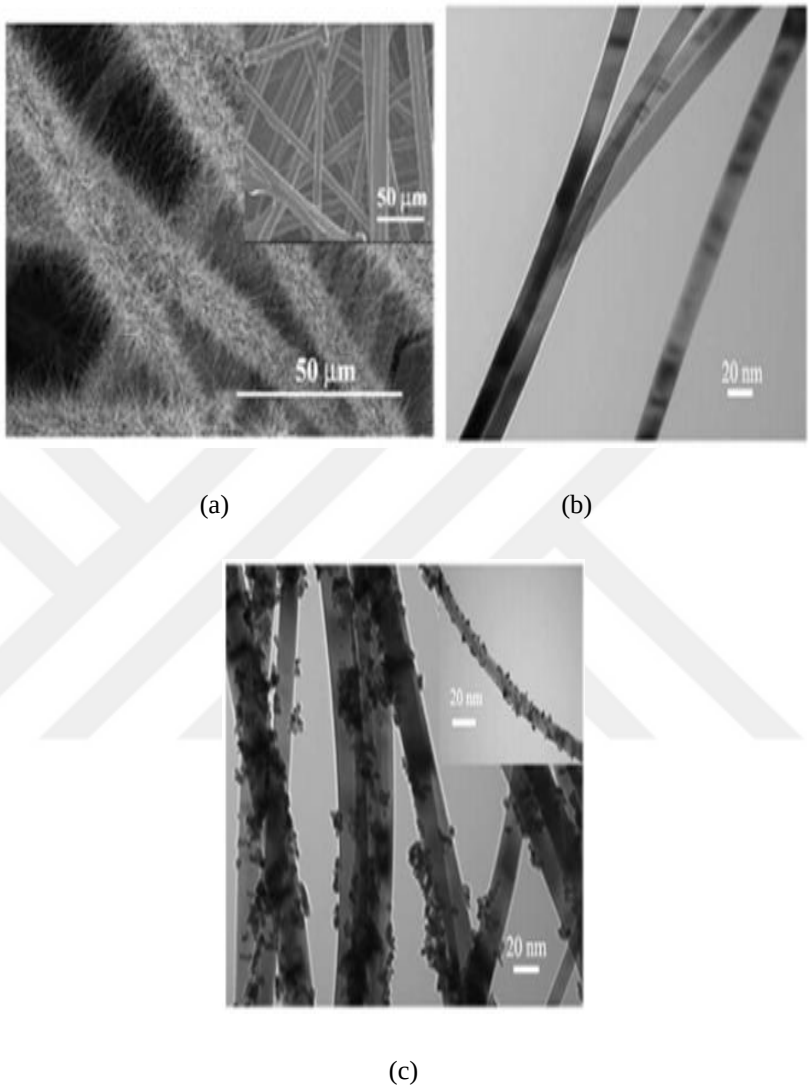

Figure 4.7 SEM and TEM appearances of SnO_2 NWs improved on carbon fibers of carbon paper with the help of thermal evaporation technique. (a) SEM illustration of SnO_2 NWs on fibers of carbon paper (50 µm). (b) TEM figure of SnO_2 NWs (20 nm). (c) TEM images of Pt nanoparticles on SnO_2 NWs (20 nm). [50]

Most important point is that the SnO_2 NWs was made chemically a pretreatment process with 5 Molar HNO_3 aqueous solution before the operation of metal nanoparticle coating was applied. This surface activation process gives rise to be formed oxide functional groups on the surface of the SnO_2 Nanowires. As it can be

seen in the Figure 4.7a, a thin layer of large density SnO_2 NWs significantly coats the surface of the carbon fibers within the carbon paper. In Figure 4.7b, TEM analysis explains that the NWs contain a straight line structure with a diameter of about 20 nm. Figure 4.7c displays the TEM image of the Pt nanoparticles that were electrochemically covered on the SnO_2 NWs. The length of SnO_2 ranges between 20 and 30 micrometer. In addition to this, Pt nanoparticles that possess a size of between 4 and 6 nm, could be seen remarkably on the surface of Nanowires. The main purpose of covering of Pt nanoparticles is to enhance electrical connection that takes place among the SnO_2 Nanowires and the carbon fibres. Pt/ SnO_2 Nanowires/carbon paper compound electrode presents larger electrocatalytic activities than standard Pt/C electrode for ORR and MOR. Furthermore, SnO_2 NW doped PtRu compound electrodes were obtained for methanol oxidation and displayed larger mass and specific activities within methanol oxidation than that of Pt-Ru catalysts covered on galssy carbon electrode. One of serious problems for the application of NWs to make catalysation for backings in PEMFCs and DMFCs whether these NWs are suitable material for the carbon paper in terms of excellent adhesion when actual fuel cell is worked. In order to overcome this problem, Saha and partners made outstanding studies that are related to the SnO_2 Nanowire and carbon paper combination electrode. They soaked the SnO_2 NW/carbon paper composite electrode into 0.1 Molar H_2SO_4 solution in 2 months timeframe and at 50°C. As a result of this experiment and investigation, they analyzed SEM examination. With the help of this examination, tha adhesion of large density NWs could be provided on the surface of carbon fibers [50].

4.1.10 Tungsten Oxide (WO_x)

Tungsten oxide can be used as backings in low temperature fuel cell's catalysts and acts as n type- semiconductor which exhibits bandgap ranging approximately from 2.6 to 2.8 eV. Additionally, WO_x displays several oxidation states like Tungsten (III) oxide, Tungsten (IV) oxide (Tungsten dioxide), Tungsten (VI) oxide (Tungsten trioxide), and Tungsten pentoxide and ranges from 2 to 6. This material can also be utilized in many applications like electrochromic, photocatalyst and gas-sensor applications. Table 4.11 presents the important properties of Tungsten Oxide (WO_x).

Table 4.11 Properties of Tungsten dioxide [52]

Properties	**The values for WO_2 (Tungsten dioxide)**
Molar Mass	215.839 $g.mol^{-1}$
Appearance	Bronze Solid
Density	10.8 $g.cm^{-3}$
Melting Point	1700°C
Solubility in water	Negligible
Magnetic Susceptibility	$5.7 * 10^{-5}$ $cm^3.mol^{-1}$
Crystal Structure	Distorted Rutile

Tungsten oxides show also excellent proton transfer due to the production of tungsten trioxide hydrates, that becomes one of the most important properties for fuel cell catalyst supports. In addition to this, the most promising advantage of Tungsten oxide support material is that it exhibits better thermal stable structure by depending on electrochemical oxidation circumstances than Vulcan XC-72R.

Niedrach and partners made a research that is related to combination Pt with Tungsten Oxides (WO_2, W_2O_5, and WO_3). Pt has also durable and strong structure against carbonmonoxide toxication when its catalytic oxidation takes place in fuel cells. According to observations of Kulesza and Fulkner, the electrocatalytic activity for methanol is increased owing to good diffusion of Platinum on WO_x. The main reason of the enhancement in the electrocatalytic activity of Pt in the existence of Tungsten Oxides was based on the convertion of WO_x to tungsten bronzes. In the following reactions, $H_{ads(adsorption)}$ that obtained from dissociation of CH_3OH is able to pour out the WO_x substrate [50].

$$WO_x + yPtH \rightarrow H_yWO_x + yPt \quad \textbf{(4.1)}$$

$$H_yWO_x \rightarrow WO_x + ye^- + yH^+ \quad \textbf{(4.2)}$$

According to these reactions, methanol eletrooxidation improves with the help of CO_{ads} varieties, and the excellent CO_{ads} tolerance with Pt–WO_x substances was obtained during the highest relation among Pt and WO_x. Pt must be diffused on the WO_x matrix in order to enhance WO_3 surface area.

Cui and partners made an experiment about synthesis of mesoporous WO_3 which displays good pore morphology. In order to obtain these mesoporous WO_3 support materials, they made use of mesoporous silica with 12-phosphotungstic acid as tungsten source. Additionally, Pt/WO_3 was also produced by making use of covering of H_2PtCl_6 on the mesoporous WO_3. Pt and WO_3 display also average size of approximately 6.5 nm - 6.2 nm, respectively. The obtained mesoporous WO_3 exhibits also the BET specific surface area of 86 m^2/g and the value of wall thickness approaches toward the spongy size of silica template (6.5 nm) [50]. Figure 4.8a and c represent TEM images which belongs to 15 wt% and 20 wt% Pt/WO_3, respectively.

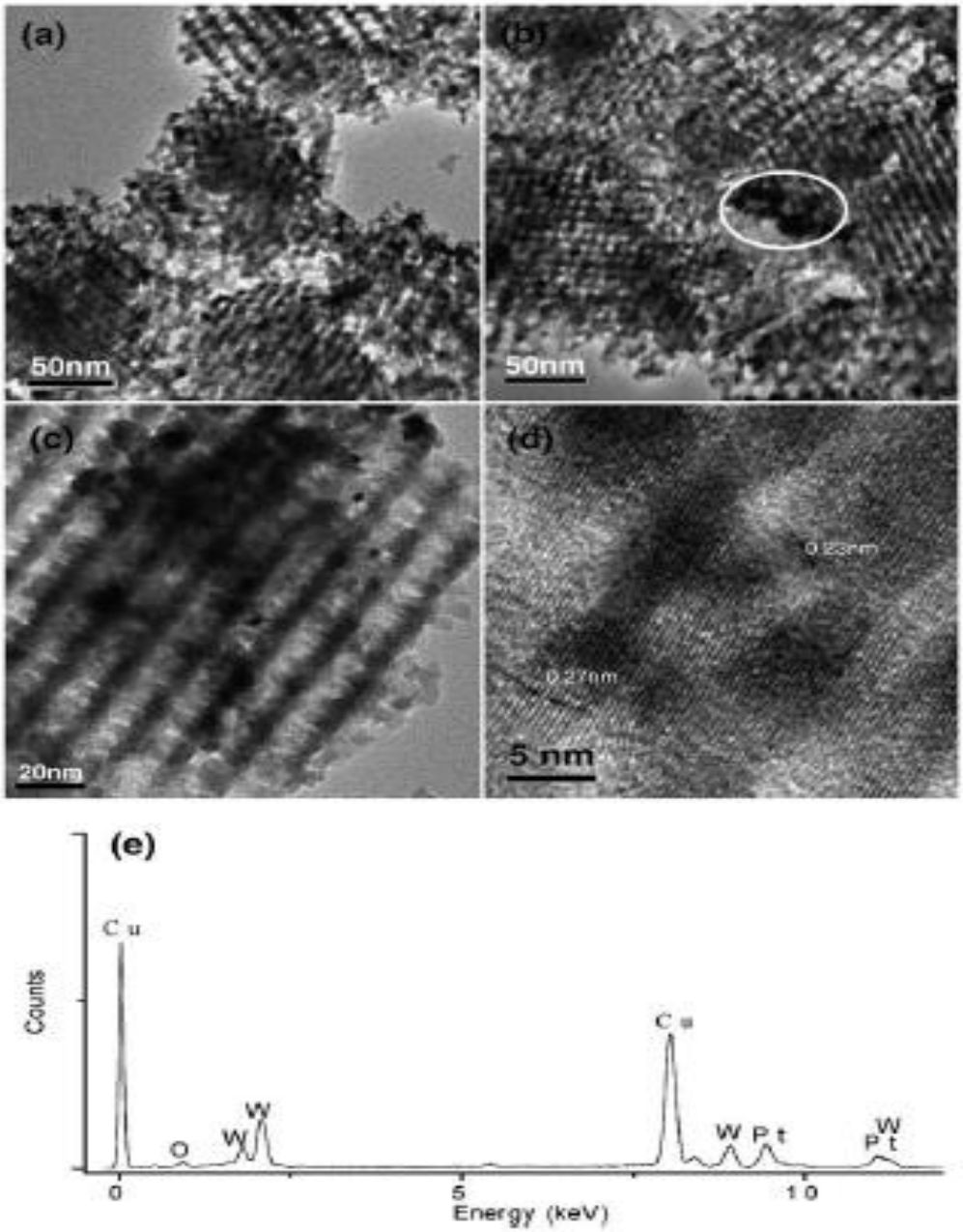

Figure 4.8 TEM images which belongs to meso-structured 15 wt.% Pt and WO_3 in (a, c), 20 wt.% Pt and WO_3 in (b); high-resolution TEM view in (d) and EDS form in (e) of 15 wt.% Pt and WO_3 [50]

According to these figures, Pt nanoparticles which was illustrated with intense points are diffused very good in the hole morphology of porous WO_3. Any very large particles or aggregerates could not be observed. But, several metal Pt nanoparticles can also be formed in exterior of mesopores WO_3 when amount of the Pt loading reaches to 20 wt% as it can be presented in the Figure 4.8b. In the Figure 4.8c**,** little

Pt nanoparticles can also be observed inside the holes of the mesopores WO_3 support. According to Figure 4.8d, there are two types of crystal lattice stripes. This figure is also known as the high-resolution TEM (Transmission electron microscopy). As it can be seen in this figure, d is equal to 0.23 nm which pertains to the Pt metal, the d = 0.27 nm pertains to WO_3 that provides a supportive evidence in order to certify the Pt granules locating in the pores of the backing. As Figure 4.8e is carefully analyzed and evaluated, better proof of Pt nanoparticles diffused. In this figure, Pt signals may also be simply observed by making use of EDS (Energy-dispersive X-Ray Spectroscopy). Pt/WO_3 exhibited good and large electrocatalytic activity into methanol oxidation and excellent electrochemical stability. When a comparison is made between Pt/WO_3 and Pt/C, 20 wt % Pt/WO_3 showed extremely larger the activity for methanol oxidation than that of commercial 20 wt % Pt/C catalysts. The increased electrocatalytic activity for methanol oxidation on Pt/WO_3 has been based on the improved catalytic effect and mesoporous morphology.

WO_3 nanorods have also preferred in fuel cells. Researchers and scientists have paid attention to the one dimensional (1-D) nanorods due to their excellent and common usage for a lot of novel applications. Since nanorods possess high specific surface areas, WO_3 which can exist in a nanorod form, can be preferred and used as an efficient support for fuel cells catalysts. Additionally, Rajeswari and partners carried out an experiment that is related to the synthesis of WO_3 nanorods by making use of pyrolysis of tetrabutylammonium decatungstate $((C_4H_9)^4N)^4W_{10}O_{32}$ at 450 °C. When pyrolysis is carried out at 450°C, surfactant species $((C_4H_9)^4N^+)$ is removed and the $W_{10}O_{32}$ is decomposed and this situation paves the way for production of pristine, unique crystalline WO_3 nanorods. The nanorods possess the dimensions which range between 130 and 480 nm, 18 and 56 nm mean length and width, respectively [50].

Maiyalagan and partners made efforts in order to synythesize tungsten oxide nanorods by utilizing infiltration or phosphotungstic acid ($H_3PW_{12}O_{40}$) solution into an Anodisc alumina membrane as a template. As well as $H_3PW_{12}O_{40}$, Platinum (Pt) nanoparticles had been coated on the nanorods with the help of an impregnation method. The diameter of the nanorods was measured nearly 200 nm and the size of the Pt nanoparticles ranges between 3 and 4 nm [50]. These studies took place in 1 M

H_2SO_4 and according to these studies, WO_3 nanorods display larger stability than that of stack WO_3. Pt doped WO_3 nanorods presented larger methanol oxidation efficiency than that of trading Pt and C combination catalyst twofold. As a result of these studies, Platinum supported on such nanorods contributes formation of more stable structure over several cycles in an electrochemical environment.

4.1.11 Sulfated Zirconia (S-ZrO_2)

Zirconia is one of the most prominent polymorphic materials that takes place in three temperature-based firms which include monoclinic or baddeleyte (between room temperature and 1170°C), tetragonal (between 1170 and 2370°C) and cubic (between 2370 and 2700°C). Zirconia is also known as Zirconium dioxide (ZrO_2) and a form of a white crystaline oxide of Zirconium. Table 4.12 displays important properties of Zirconia (ZrO_2).

Table 4.12 Properties of Zirconia (ZrO_2) [53]

Molar Mass	123.218 g/mol
Appearance	White powder
Density	5.68 $g.cm^{-3}$
Melting Point	2715°C
Boiling Point	4300°C
Solubility in Water	Negligible
Solubility	Soluble in HF, and hot H_2SO_4

Bandgap of the ZrO_2 is based on the phase (cubic, tetragonal, monoclinic or amorphous) and preparation methods with the voltage that ranges between 5 and 7 eV. When zirconia is combined with anions such as sulfate, zirconia contributes to produce a highly acidic or super-acidic catalyst that presents excellent catalytic activity in many reactions. Sulfated zirconia (SO_4^{2-}(ZrO_2,S-ZrO_2) is a type of a crystalline solid acids that involves monoclinic and tetragonal phases. Additionally, Sulfate zirconia presents also a high Hammelt and strength H_o of -16.03 that contributes to make it a strongsuper acid. As well as Sulfate zirconia, Nafion possesses only approximately -12. According to obtained results between the stability of sulfated materials and temperature in the existence of methanol and H_2O,

Sulfated Zirconia contains a large efficacy at temperature of 300°C. In other words, it shows large proton conductivity with the help of large atomic ratio of S/Zr. When the ratio of S/Zr was equal to 0.35, the S-ZrO_2 had proton conductivity of 5.10^{-2} $S.cm^{-1}$ at 60-150°C. In addition to this, S-ZrO_2 displays also a large hydrophilic structure. These properties lead to be preferred S-ZrO_2 as an excellent candidate as backing material for fuel cell catalysts. Owing to large proton conductivity, the existence of the changed electrolyte ionomer in PEMFC electrodes can restrict the usage of S-ZrO_2 as catalyst backing. The reduction of ionomer could give rise to prevent enhancement of the gas dispersion and water transmission. Moreover, usage of Pt provides also important benefits. So, Platinum particles which were covered in the small pores could be provided in small contact with a proton conductor. As a consequence of this process, the low usage of Platinum is provided. Due to large hydrophilicity of S-ZrO_2, it can contribute to increase the cell performance under a small relative moisture. On the other side, acid sites can also be formed over the surface in small pores and this situation enables the combinationof Platinum with S-ZrO_2. By depending on this situation, Suzuki and partners, made an experiment about this combination in order to use in PEMFC. They can make use of S-ZrO_2 powdered (according to reference [50] 80 m^2/g) as a backing material [50]. This material can be found at the market. Pt was coated on S-ZrO_2 with the help of ultrasonic spray pyrolysis. The amount of Pt was 53 wt% in the Pt/S-ZrO_2. The following figures represents the SEM and reflected electron appearances of the S-ZrO_2 and Pt/S-ZrO_2 particles.

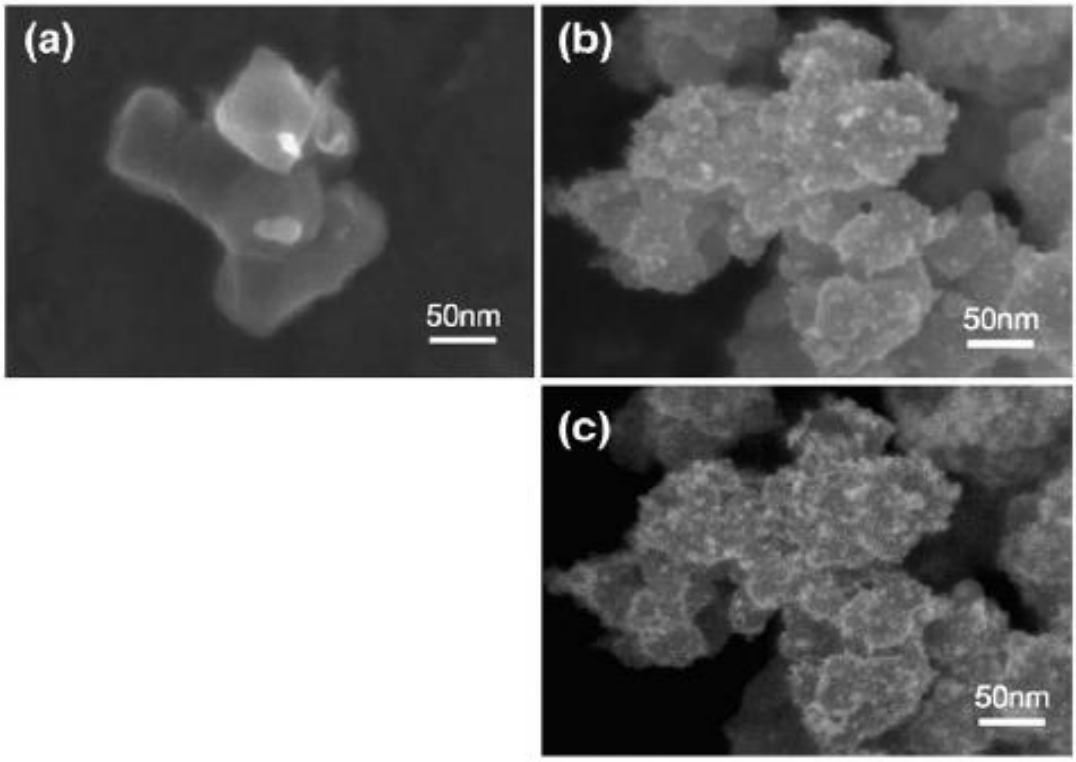

Figure 4.9 Pt particles have been encoloured with white in COMPO figure. (a) Scanning Electron Microscopy appearance for Sulfated Zirconia. (b) SEM appearance for Pt doped S–ZrO_2. (c) reflected electron view for Pt doped S–ZrO_2 [50]

Figure 4.9a displays SEM (Scannig Electron Microscopy) of S–ZrO_2 with the particle size of 50nm. Figure 4.9b exhibits the SEM appearance of Pt/S–ZrO_2 and according to this figure, largely diffused nanoparticles can also be seen on the Pt/S–ZrO_2. Figure 4.9c represents the composition image (COMPO) of Pt/S–ZrO_2 and the nanoparticles were Platinum. As it can be seen in these figures, Pt is largely diffused on the S–ZrO_2 surface as nanoparticles. When a comparison is made between Pt/S–ZrO_2 and Pt/C in terms of the PEMFC efficiency by depending on the electrocatalytic activity, the PEMFC performance of the Pt/S–ZrO_2 cathode has become smaller than the Pt/C in the existence of Nafion ionomer. Main reason of this situation is that the gradient of the voltage and current graph for the Pt doped S–ZrO_2 showed similarity to Pt/C in the great current density which ranges between 1.5 and 2.5 A/cm^2. Additionally, any high IR loss was not observed. On the other side, the cell efficiency of Pt doped S–ZrO_2 cathode has become larger than Pt/C without the existence of Nafion ionomer. Because absence of Nafion ionomer gives rise to

reduce the proton conductivity in the catalyst layer. Therefore, the cell efficiency was reduced in cathodes in the absence of Nafion ionomer. But, the reduction of the cell efficiency on the Pt doped S–ZrO_2 became lower than the Pt/C. In spite of the fact that the voltage reduction of Pt/C at 1 A/cm^2 had been equal to about 0.22 V, the reduction of Pt doped S–ZrO_2 had been equal to 0.10 V. The proportion of the cell voltage reduction for Pt doped S–ZrO_2 became 16% that is smaller than 33% for Pt/C [50]. According to this information, Pt doped S–ZrO_2 backing enabled sufficient protons for production of high current and the ingredient of the ionomer within the catalyst layer can be decreased by making use of S–ZrO_2 as the support material.

One of the most important points about the proton conductivity of the proton exchange membranes is the water content. Humidification and saturation of the reactant gases can give rise to reduce water content and as a result of this situation, proton conductivity of the membranes decreased. The decrease of the membrane thickness contributes to occur easily water back dispersion which occurs between the cathode and the anode, and this situation does not have a great effect on decreasing of the proton conductivity of the working membrane. But, thinner membrane leads to improve the reaction crossover. Therefore, the cell performance can be decreased and the membrane quickly be degraded. In order to overcome this drawbacks, Uchida and partners suggested the utilization of self-moisturizing membranes with largely diffused nanometer-sized Pt and a hygrpscopic oxide (TiO_2).

4.1.12 Silicon Dioxide (SiO_2)

This material is also called as Silica that is a type of Silicon Oxide with a chemical formula of SiO_2. One of the most outstanding advantage of SiO_2 is its hardness since the ancient times. Because of this property, it can be preferred and used in fuel cells and other applications. Sand contains significantly amounts of silica in many parts of the world. Table 4.13 gives important properties of SiO_2.

Table 4.13 Properties of SiO_2 [54]

Molar Mass	60.08 $g.mol^{-1}$
Appearance	Transparent solid (Amorphous) White/Whitish Yellow (Powder/Sand)
Density	2.648 g/cm^3 for α-quartz 2.196 g/cm^3 for amorphous
Melting Point	1713°C for amorphous
Boiling Point	2950°C
Susceptibility of magnetic	$-29.6*10^{-6}$ $cm^3.mol^{-1}$
Conductivity of thermal	1.4 $W.m^{-1}.K^{-1}$ (amorphous)

Silica can also be converted into silicon with the help of reduction with Carbon. SiO_2 displays also several different crystalline forms as well as amorphous forms. Apart from stishovite and fibrous silica, whole crystalline forms include tetrahedral SiO_4 elements which are connected with each other by unexclusive vertices in various regulations.

Seger and partners carried out an experiment about SiO_2 and obtained silica which was supported with Pt as cathode material in PEMFCs. This research group produced a good diffused catalyst surface with low conductivity loss by managing the ratio of Platinum to silica. At small Pt concentration (Pt:SiO_2 proportion of 1:1 and 2:1), Platinum was equally diffused [50]. With the help of this good diffusion, an interconected particle network is provided. In order to evaluate resistance and voltage losses that are produced by the existence of silica in the fuel cell, the current interruption method was utilized. According to the obtained results, the Pt/SiO_2 combinations displayed losses of resistance that show similarity to trading Pt-black material. By depending on outcomes, the silica support can not provide any important enhancement for total resistivity. This system shows also losses that originated from the polarization and researcher are making efforts in order to hinder these effects. Additionally, the Pt and SiO_2 combination material at the 2:1 proportion presented maximum power densities.

4.2 The Used Materials In Supercapacitors

The selection of electrolyte plays an important role on supercapacitors and the electrolye must have the following properties;

- The ionic size and type,
- The ion and solvent concentration and interaction,
- The potential window.

4.2.1 Activated Carbon (AC)

This material can be used in EDLC (Electrical Double Layer Capacitors) as electrode. Because they have great surface area, excellent electrical properties and low-cost. AC are produced from many substances that include a large carbon content like coal, coconut shells and wood. AC contains the powerful physical adsorption forces and the largest volume of adsorbing porosity. Moreover, it can also possess a surface that is larger than 1000 m^2/g. This material can also be obtained by making use of physical or chemical activation method with the usage of many carbon-based substances like wood coal shell. The physical activation method is based on the amelioration of carbon precursors at a large temperatures (between 700 and 1200 °C) by making use of oxidation gases such as vapour, carbon dioxide and air. Chemical activation provides that the treatment of carbon precursors occurs at a low temperature by making use of activating agents like sodium hydroxide, KOH, zinc chloride and phosphoric acid. Additionally, Activated Carbon exhibits various physiochemical properties with good improved surface area that reach to 3000 m^2/g by making use of activation methods and the used carbon precursors. There are three types of porous structure of Activate Carbon and these structıres are produced from activation processes. Porous structure of AC contain micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) [55]. Many R&D (Research and Development) groups made an effort in order to analyse the correlation among specific capacitance and specific surface area of AC and according to this study, a difference and incompatibility sre found between them. Possessing a large specific surface area of approximately 3000 m^2/g leads to produce a relatively small capacitance. This situation expresses that all pores does not have a great effect during charge accumulation. Table 4.14 shows the

specific capacitances of Activated Carbon in different electrolytes. This table presents that different electrolytes play a great role on the capacitance performance of AC. According to this table, the specific capacitance in aqueous electrolyte is larger than the specific capacitance of organic electrolytes.

Table 4.14 Specific capacitances of Activated Carbon in different electrolytes [1]

Electrolytes	**Specific capacitances of AC (F g^{-1})**
Aqueous	100 - 200
Organic	50 - 150
Aqueous (with KOH-treated AC)	160 - 225

4.2.2 Carbon Nanotubes (CNTs)

These materials play great and important role in the science and enginering of carbon materials. CNTs are tubes that consisted of carbon with diameters typically measured in nanometers. They exhibit also outstanding properties like high electrical conductivity, excellent porosity morphology, perfect mechanical and thermal stability and good electrical properties. In addition to these properties, they exhibit also excellent tensile endurance and thermal conductivity due to their nanostructure and durableness of the bonds among carbon atoms.

Carbon nanotubes have been the most durable substances in terms of tensile strength and elastic modules because of the covalent sp^2 bonds that are produced between the individual carbon atoms. Catalytic dissipation of several hydrocarbons and managing various parameters have become most important production methods of carbon nanotubes. By making use of these methods, nanostructures can also be produced in various conformations and their crystalline structure can also be controlled. Moreover, CNTs possess also mesopores which are interconnected. This situation contributes to form a continous charge diffusion that makes use of accessible surface area.

CNTs are consisted of graphitic walls that are assembled in near one-dimensional cylinders in Figure 4.10. The long 1-D structure of CNT s exhibits good mechanical properties and hinders also the scattering of electrons. Furthermore, highly ordered CNT arrays possess important surface area and this situation presents high porous

area for electron storage. By making use of morphology and purity, the specific capacitance of CNTs is between 15 and 200 $F.g^{-1}$ [1].

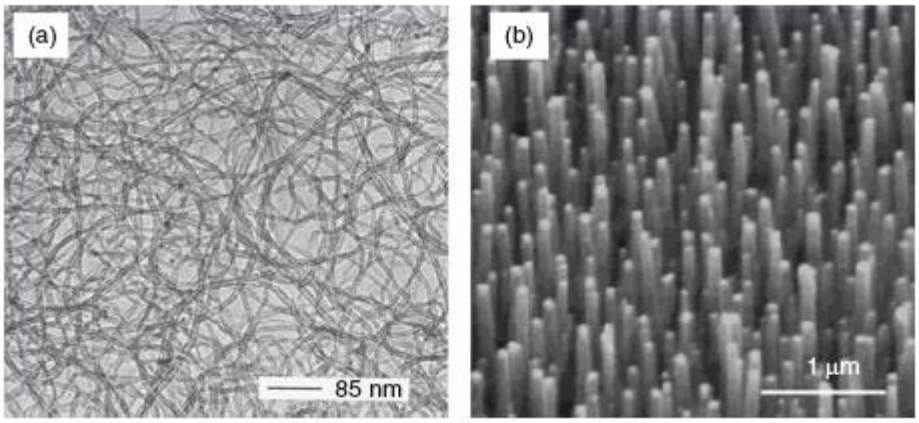

Figure 4.10. (a) Transmission electron microscope (TEM) image of carbon nanotubes. (b) Scanning electron microscope (SEM) image of a carbon nanotube. [1]

CNTs can also be divided into two groups; single-walled carbon nanotubes which can be abbreviated SWCNTs or multi-walled carbon nanotubes which can be abbreviated MWCNTs. Table 4.15 gives the properties of CNTs.

Table 4.15 The properties of CNTs [56]

	Properties
Density For A Solid	1.3 to 1.4 $g.cm^{-3}$
Specific Strength	48,000 kN·m/kg
Strength (Individual CNT shells)	100 gigapascals (15,000,000 psi)
Electric current density (metallic nanotubes)	4×10^{9} $A.cm^{-2}$
Thermal conductivity (an individual SWNT)	3500 W/(m·K)

4.2.3 Conducting Polymers (CPs)

These materials have been used as electrode material owing to their cheapness and simple production. They exhibit also more excellent conductivity and higher capacitance than carbon-based electrode materials. Conducting polymers can make use of different electrode configurations like *n/p type configuration*. N-doped and p-doped electrodes stand for negatively charged and positively charged electrodes, respectively. Conducting polymers present large energy and densities with the help of these configurations.

Conducting polymers are one of the most important organic polymers that conduct electricity. One of the most outstanding advantage of conducting polymetrs is their processability. They make use of reduction/oxidation process in order to provide storage and deliver charge. During occurrence of oxidation process, ions will be sent to the polymer back bone. During reduction process, they are going to return to the solution. In addition to this, reduction/oxidation process in conducting polymers leads to form a mechanical tension that restricts the stability through several charge-discharge cycles.

Conducting polymers provide the conduction of electricty via a conjugated band matrix. They display also larger energy density than metal oxides and contain reversible Faradaic redox capabilities. Polyaniline, polypyrrede and polythiophene are the most important types of conducting polymers. CPs that have nanoarchitectures have also large surface area and good porosity and thsese properties contribute to obtain excellent performances due to their intrinsic conduction, large surface to volume ratio and surface interactions at the nanoscale.

When CPs interact with the doping ions, the capacitance will increase and improve. One of the most important points is the fast charge/discharge nature of supercapacitors. This situation leads to affect negatively the polymer structure through swelling and cracking that decreases the polymers' overall life cycle. In order to increase the life cycle, CPs are combined with carbon supports. Zhou and partners made a reseach on syntheziation of polyaniline (PANI) and they obtained a capacitance of 609 F/g. Additionally, according to the research of Wang and their partners, capacitance of graphene oxide (GO)-doped PANI (531 $F.g^{-1}$) is greater than PANI only (216 $F.g^{-1}$) [57, 58]. Figure 4.11 shows the chemical structures of some conductive polymers (CPs).

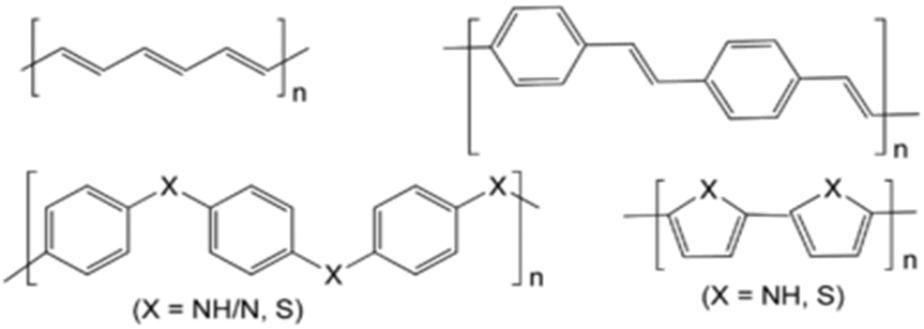

Figure 4.11 - Chemical structures of some conductive polymers [57]

4.2.4 Aqueous Electrolyte

This electrolyte material has been one of preferable and useful electrolyte materials in supercapacitors because of its low-cost and abundance. H_2SO_4, KOH, and potassium chloride are the most preferred aqueous electrolytes. Table 4.16 gives some important characteristics of various types of electrolytes.

Table 4.16 Characteristics of various types of electrolytes [1]

Electrolyte	Density (g/cm^3)	Resistivity (Ω cm)	Cell Voltage (V)
KOH	1.29	1.9	1
Sulfuric Acid	1.2	1.35	1
Propylene Carbonate	1.2	52	2.5–3
Acetonitrile	0.78	18	2.5–3
Ionic Liquids	1.3–1.5	125 (25◦C) 28 (100◦C)	3.25-4

Aqueous electrolyte exhibit usually excellent conductivity (e.g., 0.8 S cm^{-2} for 1M H_2SO_4 at temperature of 25°C). Aqueous electrolytes are classified into alkaline, acid, and neutral solutions. The main purposes of electrolytes in supercapacitor technology is to prevent leakage, increase capacitance and provide easy handling. In order to achieve these purposes, aqueous electrolytes can be arranged and modified by adding and combining different gels with these electrolytes in order to obtain an excellent stable electrolytic system. Wang et al. soaked polyacrylamide gel (PAM-G) into a aqueous solution of 6 Molar KOH for approximately 60 h and they obtained electrolytic system with perfect cycling stability, rate capability, and great specific capacitance (196 F/g at Galvanostatic charge discharge 1 A/g) [58].

4.2.5 Ionic Liquids (ILs)

ILs consist of solvent-fee molten salts in liquid form at room temperature that is because of their low melting temperatures. They are the most preferable and useful electrolyte materials because they are nontoxic and nonflammable and present also the widest voltage vindow (0 to 3-5 V), lack of thermal or chemical instability (Galinski, Lewandowski, and Stepniak, 2006). These electrolytes have also large chemical and thermal stab ilities with wide working voltage ranges. The most important point is that ILs can also be heated up to 300°C and any vaporization does not occur (Burke, 2007). But, the most outstanding obstacle of ILs is the insufficient ionic conductivity when a comparison is made with other two types of electrolytes. One of the most effective way of increasing the conductivity is to heat ILs to 125 °C [1].

4.2.6 Organic Electrolyte

Supercapacitors make generally use of organic electrolytes like acetonitrile and propylene carbonate due to their wide working voltage windows (0 to 2.2 - 2.7 V). This voltage range contributes to increase the energy density to the standard of commercial demand. Additionally, acetonitrite is the most preferable than propylene carbonate. The main reason of this is that acetonitrite carries one third of ionic resistivity of propylene carbonate. But, the most important disadvantage if acetonitrite is its flammability and toxicity. In addition to this, organic electrolytes lead also to form aging (i.e. degradation) of carbon electrodes. The decomposition of organic electrolyte have a negative effect the pores of the electrodes because this decomposition decreases also both the capacitive performance and cyclic stability (Azais *et al*., 2007) [1].

Figure 4.12 shows the effects of distinct electrolytes on energy density and specific capacitance.

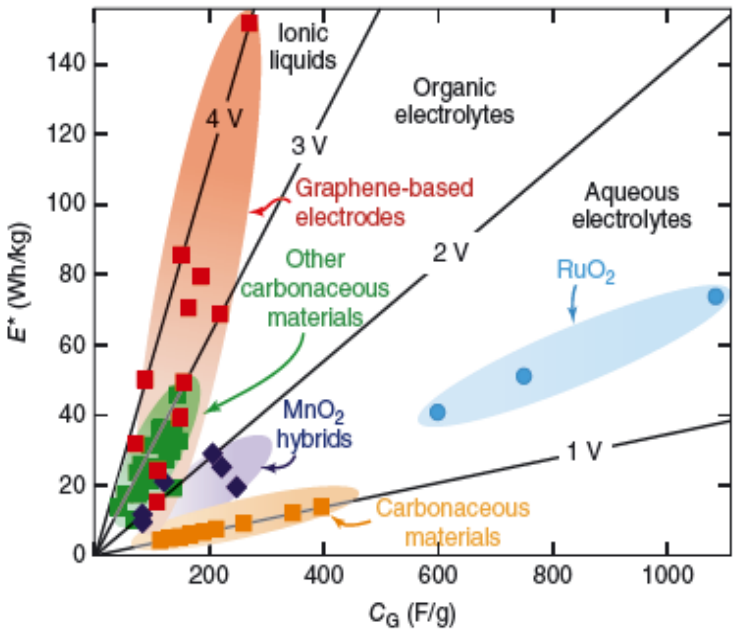

Figure 4.12 The correlation amidst energy density and specific capacitance (Electrochemical Supercapacitors for Energy Storage and Conversion) (2015) [1].

4.2.7 Transition Metal Oxides (TMOs)

These materials provide an important option for supercapacitors owing to their high specific capacitance and low resistance. These properties can contribute to fabricate supercapacitors with great energy and power. Thus, supercapacitors can be more useful and preferable. There are many forms of metal oxides like Nickel oxide (NiO), ruthenium oxide, Manganese oxides, iridium oxide are the most important, popular and useful metal oxides for supercapacitors. The main advantages of metal oxides are low-cost and utilization of milder electrolyte. TMOs have become one of the most outstanding and popular members and candidates of electrochmically active materials for the future applications and generations of supercapacitors because of their good and high electrochemical performance.

Manganese Oxide is a type of transition metal oxides (TMOs). In recent times, many scientists have drawn attention to the manganese oxide as an electrode material due to the good physical and chemical properties. This compound can be also used in a lot of mechanisms like biosensor, energy storage, molecular absorption, catalysis and

ion replacement. Manganese oxide is an important electrode material owing to its low-cost, environmental friendliness, great and excellent capacitive performance in aqueous electrolytes. However, there are also important disadvantages of Manganese Oxides like low conductivity (10^{-5} – 10^{-6} $S.cm^{-1}$), high dissolubility within alkaline or neutral electrolyte [37]. Table 4.17 gives the specific capacitances of different Manganese oxide materials.

Table 4.17 Specific capacitances of different Manganese oxide materials [37]

Materials	**Specific Capacitance (F g^{-1})**
Li-$Mn_{1-x}Ru_xO_2$	360 F g^{-1}
MnO_2@GCs@MnO_2	390 F/g at a current density of 0.5 A/g within 6 Molar KOH electrolyte
Hollow MnO_2 Nanospheres	299 F g^{-1} at 5 mV s^{-1}
Mn_3O_4	261 F g^{-1}
The MnO_2 Electrode	178 F /g at 5 mV/s

Ruthenium oxide (RuO_2) has been a prominent type in TMOs and an inorganic compound. Additionally, it is the most preferred and used electrode substance in virtue of their great and excellent conductivity, superb thermal stability. They have also long life cycle and good reversibility. The following reaction represents the energy storage mechanism of RuO_2 [37].

$$RuO_2 + xH^+ + xe^- = RuO_{2-x}(OH)_x \ (0 < x < 2) \quad \textbf{(4.3)}$$

Table 4.18 presents the specific capacitances of different types of RuO_2 like anhydrous RuO_2, hydrated RuO_2.0.5 H_2O, and amorphous RuO_2.

Table 4.18 Specific capacitances of different types of RuO_2 [37]

Material	**Specific Capacitance (F/g)**
Anhydrous RuO_2	24
Hydrated RuO_2.0.5 H_2O	342
Amorphous RuO_2	1580

4.2.8 Graphene and CPs (Conducting Poymers) Composites

These composites have become the most outstanding materials for supercapacitors. CPs comprise of one (C-C) and two (C=C) carbon bonds which display electrical conductive structure via a conjugated bond basis. CPs exhibit also large theoretical specific capacitances and large charge mobilities. Therefore, CPs have become and preferred as excellent pseudocapacitive materials in order to construct supercapacitors with larger energy densities when a comparison was made between the conventional carbon-based EDLCs and CPs pseudocapacitors. However, the most important disadvantage of CPs is that their stability is very low when they confront with long cycle. When charge and discharge operations take place, continuous insertion and de-insertion of ions lead to be obtained volumetric changes such as swelling, shrinkage, and even cracking [59]. As a consequence of this situation, the specific capacitance decreases suddenly. Hence, supercapacitors which benefit from CPs, can not fulfill the requirements of application. So as to avoid this problem, researchers and scientists have made efforts for combination graphene with CPs. rGO (Reduced Graphene Oxide) contributes to enhance the stability and capacitance retention of CPs.

Graphene and PANI Composites have become one of the most preferable candidates for supercapacitors. PANI (Polyaniline) is a type of conducting polymers and has become one of the most preferable and useful electrode substances for supercapacitors because of its low-cost, excellent stability, great pseudocapacitance, and simple synthesis. One of the most important points is that PANI requires protons in order to occur regularly charge/discharge processes. Therefore, it benefits from an acidic or a protonic solution, a protonic ionic fluid as an electrolyte, during its usage as the energy storage material. So as to solve the low mechanical cycle ctability of PANI, graphene forms framework of this combination (graphene/PANI). When synthesis process of this combination carries outi the graphtic material contributes also to ameliorate environment for PANI growth. There are also important synthesization methods of nanostructured PANI/graphene composites like templating, electrochemical polymerization, and chemical polymerizaiton methods.

Wu and partners researched and made an experiment about these composites. As a result of this experiment and study, they fabricated a combination of CCG and PANI nanofibers by means of a simple vacuum filtration process. The main purpose of the usage of CCG is to obtain electrodes which can also be necessary for energy conversion in solar cells and storing such as batteries, capacitors as well as industrial catalysis, chemical and bio-sensing systems. Polymer composites have also benefitted from CCG. One of the most outstanding advantages or purpeses of CCG is that it contributes to ameliorate and improve mechanical and electrical properties of energy storage devices [60]. According to obtained results of Wu's study, G-PNF_{30} displays also mechanically stable structure and good flexibility. Due to its this property, several desired structure can also be produced. This material consists of generally 44% CCG ($5.5*10^2$ S/m) which is approximately 10 times that of a PANI-NF film [61]. Figure 40 exhibits the comparative "IR drop". The another figure shows also CV curves of supercapacitors which depend on G-PNF_{30}, as-forming PANI-NF, and CCG layers. This figure indicates that there is a rectangular area with two redox peaks and this area gives rise to change in oxidation states of PANI. According to Figure 4.13, the CV of uncontrolled CCG presents the true quasi-rectangular area property for double layer capacitance. According to results obtained, PANI-NFs exhibits low cyclic stability by decreasing 29% after 800 cycles were completed at 3 Ag^{-1}. One of the most outstanding properties of G-PNF_{30} is that a symmetric supercapacitor device which is obtained from G-PNF_{30} film, displayed a specific capacitance of 210 Fg^{-1} at 0.3 Ag^{-1}. This value can not be compared with the theoretical capacitance of PANI (nearly 2000 Fg^{-1}) [59].

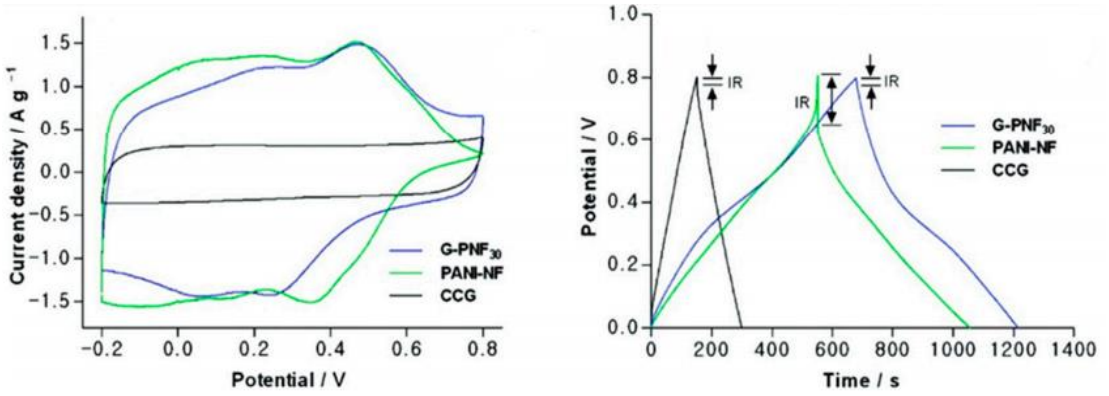

Figure 4.13 IR drop and CV curves of G-PNF_{30}, as-forming PANI-NF, and CCG plates [59]

Wu and partners fabricated a 3D porous PANI-rGO composite gel. The rGO sheets which were coated by PANI molecules contribute to generate an excellent porous network so as to occur the ion transport. One of the most important points for supercapacitors is that the ion transport must be necessarry for an electrode. Several tests were made on this obtained material. According to these tests, this substance showed a large specific capacitance which was measured 808 F/g (5157 mF/cm^2) at a great current density of 53.33 A/g (377.4 mA/cm^2) [59].

There are also many studies and developments in the electrochemical performance of graphene/PANI combination which could be improved for adjusting the morphology and increasing the surface area. According to reference [59], a research was made on the GO/PANI composite and stated that dissimilarities in Graphene oxide concentrations cause formation of distinct constructions for the GO/PANI combination with several electrochemical actions. Additionally, Li and partners created graphene/PANI nanocompounds with the help of reduction of GO with hydrazine in the existence of distinct quantities of PANI nanoparticles. The PANI particles may hinder graphene sheet agglomeration in order to enhance the surface area of the ending nanocompounds. By regarding of results obtained, the rGO/PANI combination displayed large surface area of 891 m^2/g. Moreover, the specific capacitance of the substance had also obtained as 257 F/g at 0.1 A/g in 1 Molar H_2SO_4 [59].

Graphene and PPy Composites are also one of the best alternatives for supercapacitors. Polypyrrole (PPy) has been the most outstanding CPs due to its large electrical conductivity, excellent mechanical properties, simplicity of preparation and cheap. Many energy storage devices have benefitted from PPy like supercapacitors, batterries. But, the most important disadvantage of PPy is its stability like PANI. In order to overcome this drawback, many researchers and scientists offered the obtainment of PPy/carbon composites. They generated this composite material. By depending on obtained results, graphene/PPy composites may significantly increase the electrochemical performance when supercapacitors present superior mechanical properties.

In recent times, Shu and partners produced flexible graphene/PPy nanofiber films [59]. There are also several types of tihs composite like G-PPyNF1, G-PPyNF2. The following figures give the relationship between current (Ag^{-1}) and Voltage (V) of G-PPyNF1 and G-PPyNF2. According to Figure 4.14, G-PPyNF1 which displays a large graphene proportion, exhibited a rectangular CV form even at 400 mV/s. Additionally, this composite substance presented also a specific capacitance which was measured as 161 F/g at 0.5 A/g within 1 Molar Li_2SO_4 with 80% retention after 5000 cyclings were completed [59].

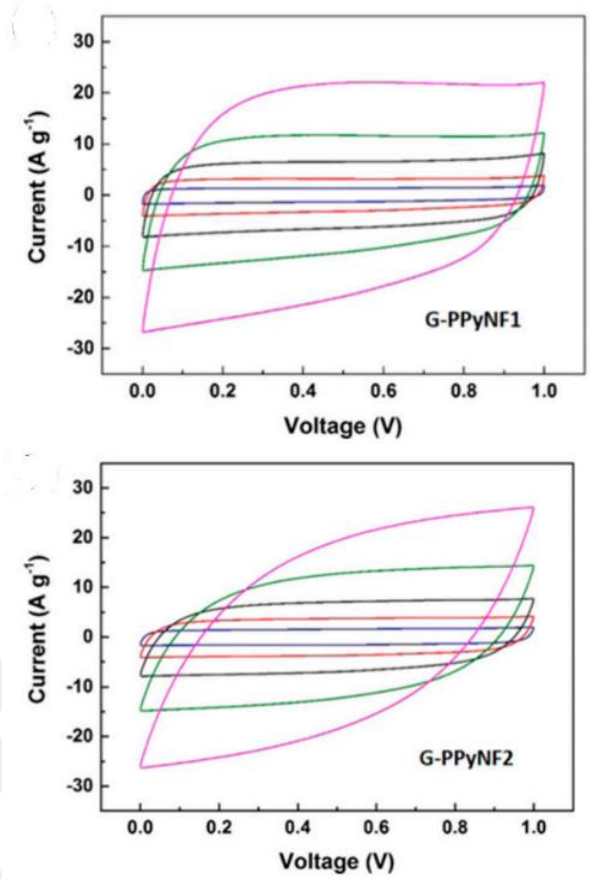

Figure 4.14 Relationship of current (Ag^{-1}) and voltage (V) between G-PPyNF1 and G-PPyNF2 [59]

Agglomeration and restacking of graphene sheets have become a great issue for both researchers and scientists during fabrication process of these composites. In order to abstain from this problem, researchers and scientists have made use of sulfonated graphene and N-doped graphene for the synhesization of these composites. When a comparison is made between pure graphene and the sulfonated graphene (SG), the sulfonated graphene exhibits a high electrical conductivity. Therefore, researchers have combined PPy with SG and obtained an excellent conductive material which was fabricated by making use of interfacial polymerization. According to the obtained results, this composite material present a specific capacitance of 360 F/g at 1A/g within 1 Molar H_2SO_4 [59]. Lai and partners made a research about N doping of the graphene network and expressed that the N doped graphene system might not contribute to develop electrical features. However, this graphene network could provide the uniform growth of PPy on both sides of the graphene.

So as to improve the electrochemical properties, the morphology and structure of composites must be controlled. Zhu and partners made an experiment which is related to this controlling process. So, they achieved transformation of morphologically the characteristic of "cauliflower" appearance of PPy into a homogeneous nano-sheet morphology composite with the help of adjustment of the graphene content [59]. This structure contributes to be obtained a more accessible surface area in order to adsorb electrolyte ions and decrease ion and charge transport ways. This produced composite substance possessed great capacitance of 255.7 Fg^{-1} at 0.2 Ag^{-1}, and 199.6 F/g at 25.6 A/g within 3 Molar KCl. Table 4.19 shows datas of this composite material.

Table 4.19 Capacitance at two different current values in 3 M (Molar) KCl [59]

Capacitance (F/g)	Current (A/g)
255.7	0.2
199.6	25.6

Additionally, capacitance retention was obtained 93% after 1000 cycles had completed at different current densities.

There are also outstanding experiment and studies which are based on graphene and PPy composites. One of the most important studies is that core/shell types structures which contribute to enhance and develop the properties of composites. Qi and partners made a research about this topic and produced a core/Shell tubular structured, graphene nanoflake-coated, PPy nanotube (GNF/PNT) hybrid for all-solid-state flexible supercapacitors [59]. The Graphite Nanofiber (GNF) coating offers many promising advantages for supercapacitors. These advantages include that it contributes to efficiently protect and acts as the electron transport way. With these advantages, the quantity of GNF covering must be controlled. As well as this, the capacitance of whole composite must also be adjusted and optimized. By depending on obtained results, a flexible all-solid-state symmetric supercapacitor devices which makes use of GNF/PNT, presented an areal capacitance of 128 mF/cm^2 at 1.8 mA/cm^2, by depending on energy density of 11.4 $\mu Wh/cm^2$ at a power density of 720 $\mu Wh/cm^2$. In addition to these values, cyclic stability was also excellent, with 80%

capacitance retention after 5000 cycles were completed. Table 4.20 displays the areal capacitance at various important values [59].

Table 4.20 Areal capacitance at various important values [59]

Areal Capacitance	**Under these conditions**	
	Current	1.8 $mAcm^{-2}$
128 $mFcm^{-2}$	**Energy Density**	11.4 $\mu Whcm^{-2}$
	Power Density	720 $\mu Whcm^{-2}$

Many researchers and scientist have paid attention to hydrogels and aerogels owing to their high surface areas and outstanding mechanic characteristics. Accoring to reference [59], researchers created HGPAs with 3D hierarchical morphology by providing freze-drying graphene and PPy combination. This created material had an interconnected and balanced 3D porous system. Additionally, Polypyrrole nanoparticles have homogeneously been provided its embedding within the aerogel by hindering agglomeration of holey graphene nanosheets. A HGPA electrode which presents a mass proportion of PPy : HGO = 0.75, displayed large specific capacitance of 418 F/g at a current density of 0.5 A/g, excellent rate capacity (80%) at current densities which ranges between 0.5 and 20 A/g. Furthermore, this electrode material exhibited also excellent cycling efficiency (74%) after 2000 cycles were achieved in 1.0 M KOH aqueous electrolyte. The hierarchical morphology and excellent relation which takes place between PPy nanoparticles and HG nanosheets have play key role on the electrochemical efficiency.

According to reference [59], researchers fabricated a graphene and PPy hydrogel so as to provide its usage in flexible solid-state supercapacitors by benefitting from a simple heating approach [59]. This composite material exhibits also a porous structure which contributes to be formed more electrochemically active surfaces in order to ocur the adsorption/desorption of electrolyte ions and to be more flexible. According to the obtained results, this composite material showed a specific capacitance which was obtained as 363 F/cm^3 at a current density of 1 mA/cm^3 and a capacitance retention of 98.6% after 12000 cycles were achieved. Table 4.21 represents the specific capacitance of this material in various conditions.

Table 4.21 The specific capacitance of graphene/PPy hydrogel in various conditions [59]

Specific Capacitance	**In these conditions**	
	Current density	1 $mAcm^{-3}$
363 Fcm^{-3}	**Capacitance retention**	98.6%
	Cycle	12000

Graphene and Poly (3,4-ethylenedioxythiphene) (PEDOT) Composites have also been preferred and used in supercapacitors. PEDOT has been the best conducting polymer. The synthesizaiton of this conducting polymer is based on polymerization of the 3.4-Ethylenedioxythiphene (EDOT) monomer. PEDOT displays several benefits like excellent electrical conductivity, high pseudocapacitance, low toxicity, simple treatability [59]. Due to these advantages, several researchers and scientists have paid attention to the PEDOT. One of the most important disadvantages of PEDOT is its insoluble. So as to overcome this disadvantage, water soluble PSS can be used as the charge-balanced dopant.

PEDOT presents generally a specific capacitance which ranges between 70 and 130 Fg^{-1}. This value is based on the polymerization method which was used. Additionally, changing or differing morphology, processing parameters, and electrolyte solutions have played a vital role on determining the electrochemical performance of PEDOT for supercapacitor's usage fields. When a comparison was made between PEDOT and other CPs, PEDOT displays high cyclic stability in the oxidized state [59]. Alvi and partners formed G-PEDOT nanocomposites. According to the obtained results, this nanocomposite material presents a specific capacitance which was measured 304 F/g in 2 M HCl and 261 F/g within 2 M H_2SO_4 at 10 mV/s. Table 4.22 represents the specific capacitances of G-PEDOT in various solutions.

Table 4.22 The specific capacitances of G-PEDOT in various solutions [59]

Specific Capacitances (F/g)	**Solutions**
304 Fg^{-1}	2 M HCl
261 Fg^{-1}	2 M H_2SO_4

The mounting and usage of hydrogels have become one of the most excellent and effective amethods so as to fabricate graphene/PEDOT composites with perfect

electrochemical properties. Zhou and partners obtained a graphene and PEDOT hydrogel with good mechanical efficiency and large conductivity with the help of in situ polymerization. These research group explained that a large ingredient of carbonyl groups within Graphene Oxide leads to be produced a high quantity of PEDOT stacks. By virtue of their uniform and intensive microstructure, this composite material displayed an excellent electrical conductivity of 0.73 S/cm and a specific capacitance of 174.4 F/g. In addition to this, it showed also a high compressive fracture stress whic was produced 29.6 MPa and a module of nearly 2.1 MPa at 10 rad/s [59]. Table 4.23 represents the significant properties of this composite material (graphene/PEDOT hydrogel).

Table 4.23 Significant properties of graphene/PEDOT hydrogel [59]

Electrical Conductivity	0.73 Scm^{-1}
Specific Capacitance	174.4 Fg^{-1}
Compressive Fracture Stress	29.6 MPa

In recent times, many researchers and scientists have also utilized several metal oxides in order to combine them with graphene/PEDOT composites. As a result of this process, ternary composites are produced. The main purpose of these composites is to improve the specific capacitance. The enhancement of the specific capacitance depends on significantly the addition of metal oxides. As well as this enhancement of the specific capacitance, graphene contributes to also increase the electrical conductivity. Additionally, the combination of graphene with PEDOT can provide production of 3D system morphology which contributes to occur ion transfer and improve specific surface area [59].

4.2.9 Graphene and Organic Molecules

As it was mentioned above, many researchers and scientists have paid attention to graphene/CP composites because of their excellent properties for supercapacitors. Since recent years, organic molecules have combined with graphene in order to use supercapacitors. This combination presents also pseudocapacitance. The main purpose of organic molecules in supercapacitors is to provide modification of graphene for electrode materials. As well as this property, they have also exhibited

performance. Organic molecules offer also important advantages like low-cost, excellent pseudocapacitance, and flexibility. Thanks to these advantages, batteries, supercapacitors, and other significant energy storage devices can also benefit from these organic molecules.

Figure 4.15 is called Ragone plot. According to this figure, supercapacitors (SCs) which are called as electrochemical capacitors, took part in a important position. Main reason of this is that supercapacitors have higher energy density than conventional electrostatic capacitors. They possess also higher power density and quicker power delivery than batteries [6]. Ragone plot has been the most important plot in energy storing. The main purpose of usage of this plot is to compare the energy density and power density of distinct energy storage devices. Additionally, this plot displays also the energy stored per unit mass (Specific Energy - Wh/kg) and deliverable power unit mass (Specific Power – W/kg) [4]. David V. Ragone is the person who discovered and improved this plot.

$$\text{Specific Energy} = (V*I*t)/m \quad \textbf{(4.4)}$$

$$\text{Specific Power} = (V*I)/m \quad \textbf{(4.5)}$$

V: Voltage (V)
I: Electric Current (A)
t: time (s)
m: mass (kg)

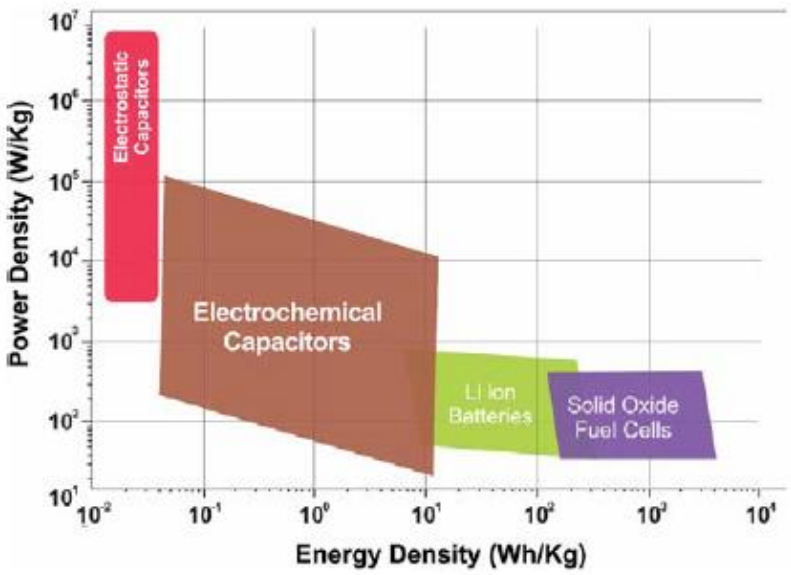

Figure 4.15 Ragone plot of several energy storage devices [37]

Supercapacitors have also great potential to use in the hybrid vehicles (according to reference [57]). Additionally, significant elements influence the electrochemical performance of supercapacitors (SCs). These factors consist of the physicochemical characteristics of electrode substances, the choice of electrolyte, and the voltage range of electrodes (according to reference [57]). In order to enhance the electrochemical performance of supercapacitors, pne of the most preferable methods is to develop novel and high quality electrode materials. The main purpose and function of these materials is to contribute to increase the electron transfer and ion diffusion. Figure 4.16 shows the annually improvement of new electrode substances for enhancement of the electrochemical performance of supercapacitors. According to Figure 4.16, carbon materials are the most preferable, useful and popular electrode materials for supercapacitors by virtue of their large surface areas that store charges by making use of physical adsorption of ions on the material surface [37]. In other words, charges accumulate on the surfaces of the electrodes. This kind of supercapacitors that have charge storing mechanism, possesses a low energy density (<10 $Whkg^{-1}$). There has also been many studies in order to increase the energy density of supercapacitors. These studies involve replacement of carbon materials by making use of electrochemically active substances or the hybridization of carbon materials with the help of electrochemically active materials. When a comparison is

made between active materials and carbon materials, electrochemically active materials are able to have more energy storage capacity than carbon materials because of their faradaic charge transfer and the electrochemical process [37].

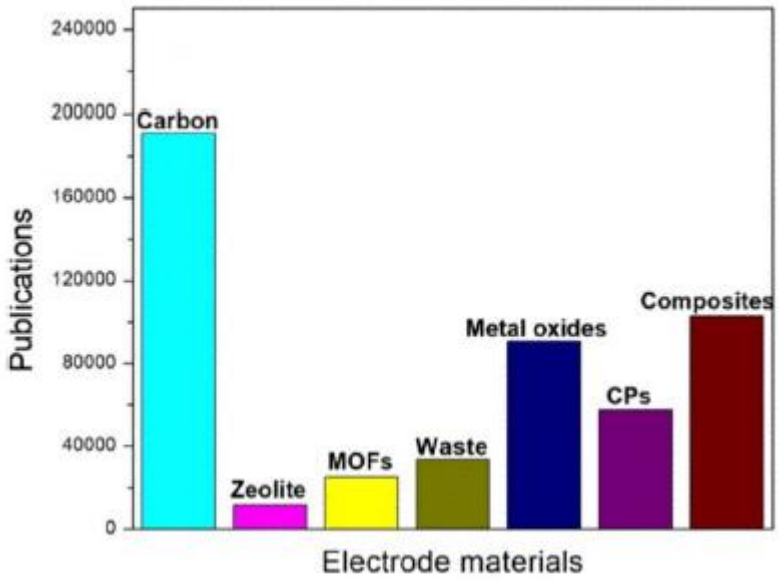

Figure 4.16 Annually development of supercapacitor electrode materials [37]

CHAPTER 5

APPLICATIONS AND ADVANCES OF FUEL CELLS AND SUPERCAPACITORS

5.1 Applications of Fuel Cells

Fuel cells have been used in many applications like space program, backup power systems, transportation applications, stationary and portable applications etc.

5.1.1 Backup Power Systems

The main purpose of these systems is to supply power during the power failure. These systems can also make use of fuel cells in many sizes and benefit from hydrogen as a fuel source. One of the most outstanding advantages of backup fuel cells is their commercialization that is more faster than other fuel cells. Backup power systems involve computer mechanisms, fabrication facilities, houses and power distribution units. The PEMFC is the most preferable type of fuel cells for backup power applications. Additionally, several fuel sources can also be used as fuel sources like compressed hydrogen, liquid hydrogen. One of the most important tools for backup power applications is an electrolyzer systems because of its hydrogen production. Another promising advantage of electrolyzer system is utilization with electricity that is generated from solar panels, a wind source, a nuclear source or the local power company [62].

5.1.2 Transportation Applications

These applications can also benefit from fuel cells and contain cars, autobuses, utility transport vehicles, scooters and bicycles. In the following parts, each of these vehicles is going to be mentioned.

Fuel cells provide a lot of opportunities for automotive applications. R&D groups and scientists made efforts in order to improve and use fuel cells for transportation applications for a long time. The main reason of usage of fuel cells is their low or

zero emissions. Fuel cells can meet the entire power of these vehicles or also be utilized for start-up. Fuel cell is utilized as the secondary power source. The working temperature of the automotive fuel cell ranges between 60 and 80°C owing to the usage of the polymer membrane that restricts the temperature to below 100°C [62]. Figure 5.1 gives parts of an automobile which use fuel cell.

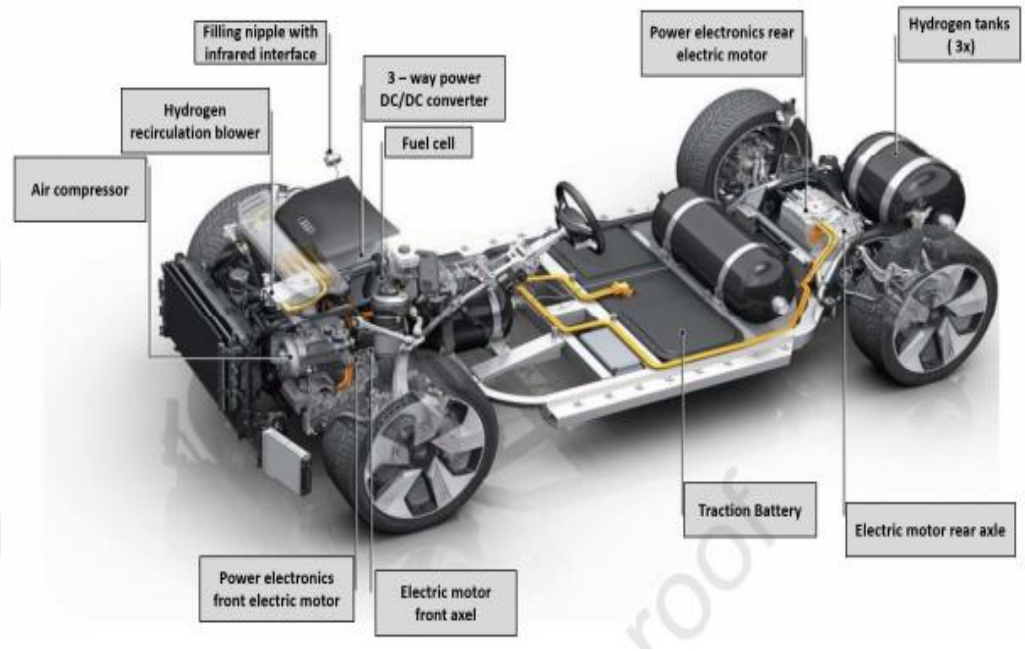

Figure 5.1 Automobile application of fuel cells [63]

One of the most outstanding examples of automobile application is NECAR4 as it is mentioned in the fuel cell mechanism. Figure 5.2 shows NECAR4.



Figure 5.2 NECAR4 [64]

Buses can also benefit from fuel cells in order to meet their energy demands. When a comparison is made between automobiles and buses, the differences between these vehicles are the power demands, space usability, working conditions, and refueling regions in terms of fuel. Buses make use of more energy than automobiles because of their large weight and area as well as their continuous stops and starts. Additionally, on-board buses can simply store a large amount of hydrogen due to the existing area of a autobus [62].

Buses which make use of fuel cells, display more excellent properties than diesel buses because of their low or zero emissions. These vehicles play an important role on heavily populated and polluted cities. Several bus producers have made important investigations and studies in order to obtain fuel cell buses in the 1990s. Buses can also make use of compresses hydrogen as fuel source such as fuel cell automobiles. Fuel cell buses have been used for a long time in many cities like British Columbia, Amsterdam, Hamburg, Luxemburg, Stuttgart etc [62].

As it can be seen in Figure 5.3, there are four hydrogen tanks. Hydrogen is stored in these four hydrogen tanks. These tanks are connected to the fuel cell system and fuel cells convert hydrogen and oxygen into the electricity and water. As it was mentioned in the chapter part of the mechanism of fuel cells, as long as hydrogen tanks are provided for many applications, fuel cell provides electricity production. In this system, Li-ion batteries can also be used in order to store excess electricity.

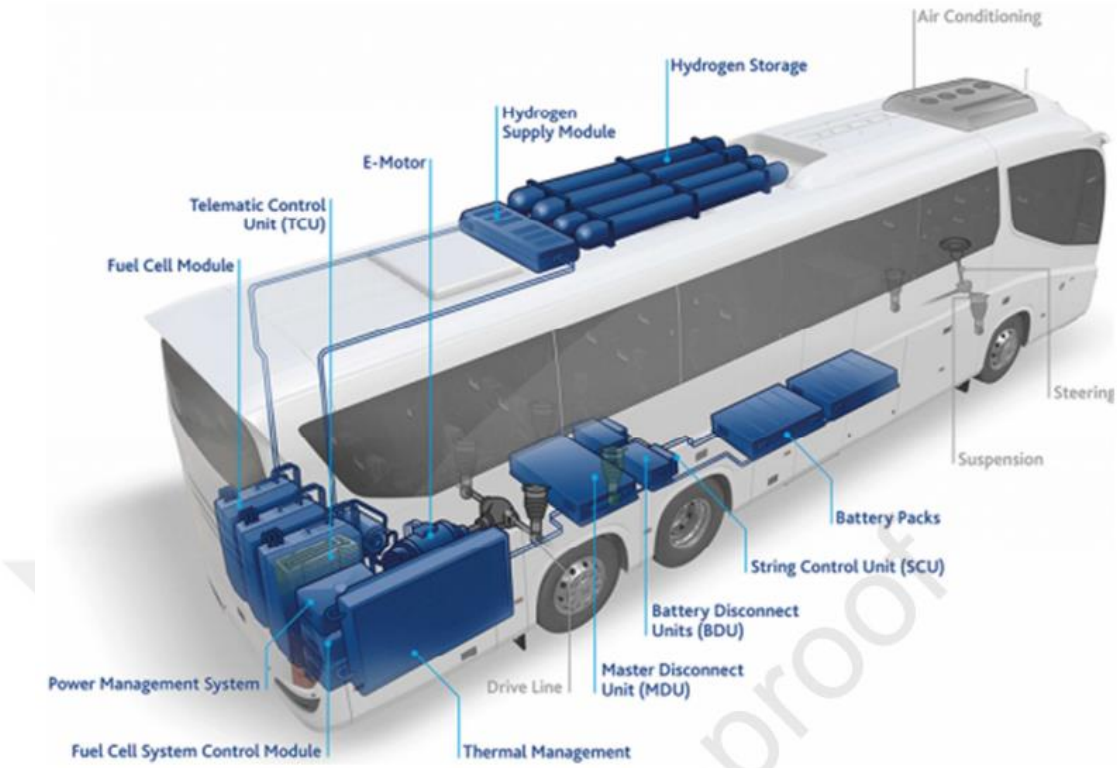

Figure 5.3 Bus applications of fuel cells [63]

Fuel cells have accomodated themselves to utility vehicles in recent years. In the first years, utility vehicles make use of lead-acid batteries that give rise to increase the maintenance and charging time. In order to overcome this problem, these vehicles started to use fuel cells. Fuel cells exhibit low-cost, low maintenance, and more usabilities for tranportation applications [62]. Additionally, they do not also produce any emissions. Utility vehicles which use fuel cells, involve forklifts, golf cars, airport movers, wheel chairs. The first fuel cell was improved in the beginnings of 2000s for utility vehicles. The most preferable fuel cell types for utility vehicles contain the PEMFCs, DMFCs, and AFCs. Utility vehicles which is powered by fuel cells, make use of compressed hydrogen, methanol, metal hydrides, and sodium bororhydrideas fuel sources.

Environmentalist people and persons who inhabit in over-populated countries, utilize bicycles as transportation vehicles. These vehicles provide also important benefits for environment like zero emissions and no environmental pollution. Fuel cells can be combined with these vehicles. However, hydrogen storage have become in important

problem for these vehicles. Therefore, researchers and scientists have made many investigations about metal hydrides and electrolyzers for the last decade.

In the beginnings of 2000s, many producers improved their first fuel cells in order to use them in scooters and bicycles. Methanol and zinc can be used as fuel sources for these vehicles. The most useful fuel cell types for scooters and bicycles are the PEMFCs, DMFCs, and Zinc-Air Fuel Cells (ZAFCs) [62].

5.1.3 Stationary Power Applications

These applications have significantly benefitted from fuel cells for over twent years. The fuel cell selection have become one of the most important points. Fuel cells have been used as primary power source for these applications. These applications provide also power for our houses and are not combined with the grid. One of the most important advantages of these applications is the usage as supplemental power. Additionally, hybrid power mechanisms may also draw on fuel cells. In other words, fuel cells can be combined with solar cells, capacitors, or other significant energy storage mechanisms and contribute to produce power. They may act as auxiliary power system or power generator during power failure in order to produce power. Furthermore, these systems can also make use of supplement power sources for peak periods. Therefore, batteries can also be combined with supercapacitors and this combination has generally become significant supplement power sources.

Several producers started to evaluate their power facilities in the years of 1990s. In contrast to fuel sources for fuel cell types, these producers utilize generally natural gas as fuel source. As well as natural gas, propane, compressed hydrogen, bio-gas, methanol, oil-based fuels are the most widely preferred and used fuel sources. Additionally, stationaty power applications make use of the PEMFCs, SOFCs, MCFCs, AFCs, and PAFCs. The major countries are the United States, and Japan in terms of the number of fuel cell power facilities [62].

5.1.4 Space Applications

Fuel cells were also used in the space program in the 1960s and 1970s like AFC-Apollo, and polymer electrolyte fuel cell (PEFC-Gemini). Figure 5.4(a,b) and Figure 5.5 represent the fuel cells for space applications like Apollo and Gemini program.

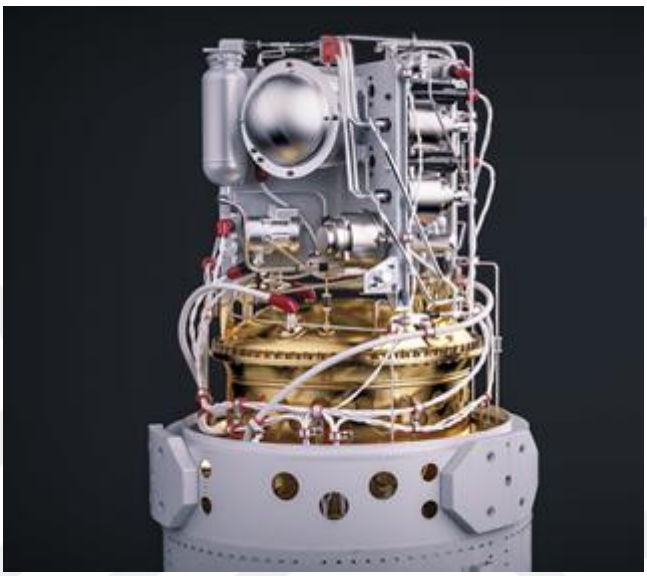

Figure 5.4a. Alkaline fuel cell for apollo space program [65, 66]

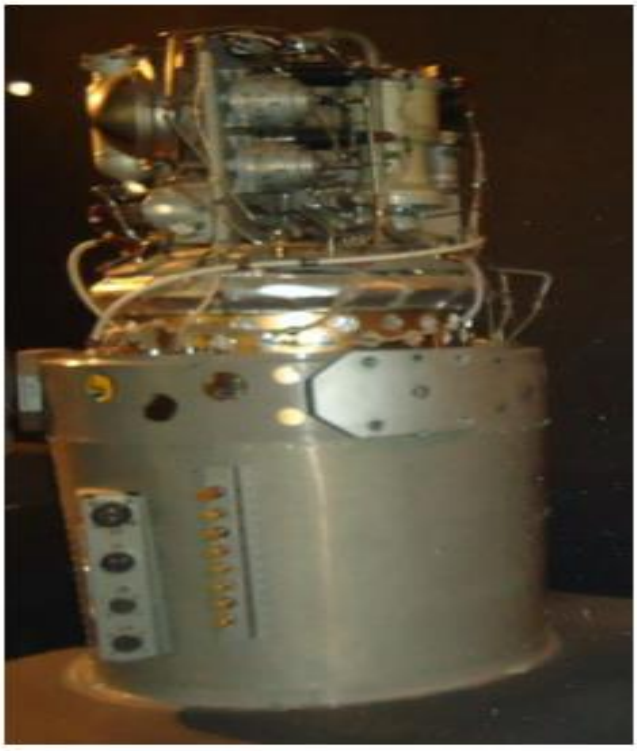

Figure 5.4b. Alkaline fuel cell for apollo space program [65, 66]

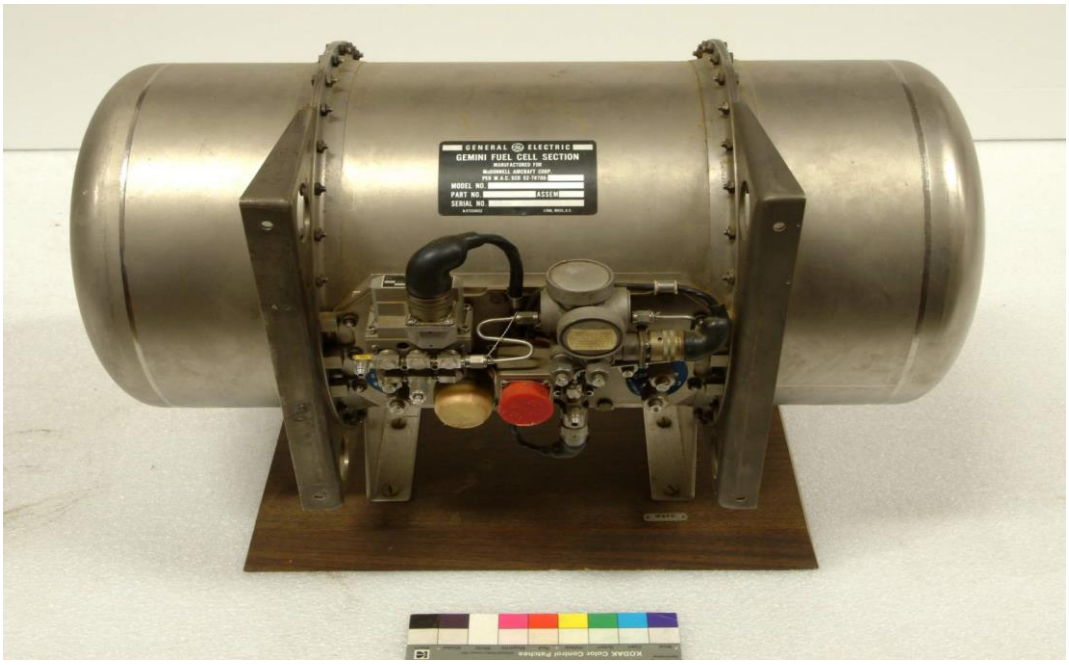

Figure 5.5 Polymer electrolyte fuel cell for Gemini space program [67]

Figure 5.6 represents a schematic diagram for space applications of fuel cell. This figure is also known as *regenerative fuel cell system*. The main purpose of the usage of this system is to provide power or energy demand and drinking water for spacecraft or space applications. This system is obtained by combining the fuel cell with electrolyzer. As it can be seen in Figure 5.6, this system works in a closed loop and contains two different stack which are called as fuel cell and electrolyzer. Connection of these stacks is provided by three storage tanks (hydrogen, oxygen and water). The working principle for space applications of this system can be explained as the following: First of all, three possible approaches have been used which are known as discharge method, charge method and idle mode. In discharge approach, fuel cells make use of hydrogen and oxygen which is made storage within the tanks, in case of power (energy) and drinking water demand of spacecraft. As a result of this process, the generated water can be stored in the water tank. In charge approache, hydrogen and oxygen tanks must be filled. This filing process is provided by benefitting from water (H_2O) tank with the help of electrolyzer which contributes to separate H_2O into hydrogen and oxygen. In idle approache, any stack does not work but fuel cell meet energy or power demand for the spacecraft. In this mode, tanks are completely filled with hydrogen and oxygen. Additionally, researchers and scientists paid attention to several important factors for this system [66].

- Thermal controlling expedients in order to decrease mass,
- Water adjustment under space circumstances,
- Quick answer for power procurement,
- Inactive mechanism project to obstruct treatment and setbacks [66]

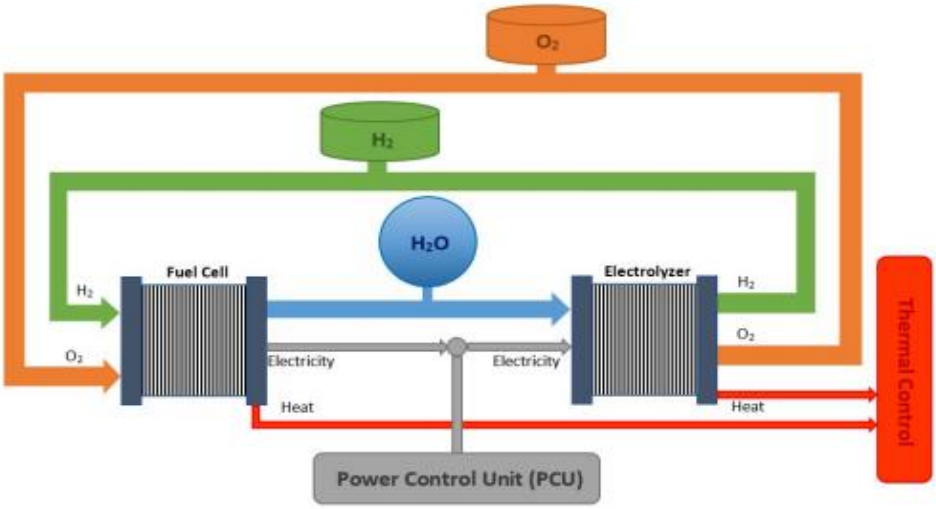

Figure 5.6 Schematic diagram of regenerative fuel cell system in space utilizations [66]

Fuel cells provide good contributions for the space programs. The main purpose of usage of fuel cells in space programs are to meet the requirements of drinking water and energy. NASA have also significantly benefitted from fuel cells and made studies on improvement of fuel cells for space applications. As an example, the rocket motors of every shuttle consumed approximately 500,000 gallons of refrigerated liquid hydrogen during flight NASA has also paid attention to safety in order to prevent explosion of hydrogen tanks or other hydrogen storage materials [68].

5.1.5 Portable Applications

These applications have occupied an important place in our lives. As it is known, many portable devices use usually electrochemical batteries. Disposable batteries have become the basic power supply for portable devices such as flashlights, MP3 player and displayed their own disadvantages like non-rechargeable, high-cost because of their more usage. Rechargeable batteries exhibit more preferable and useful batteries than disposable batteries. Rechargeable batteries make use of Nickel-Cadmium, Nickel-Hydride and Lithium-ion batteries. Many electronic and technological devices benefit from batteries such as notebooks, MP3 players, mobile phones. One of the most outstanding drawbacks for batteries is the elapsed time for recharging process. So as to avoid this drawback, people start to use another power

supply. Therefore, mini fuel cells are preferred as a basic power supply. These fuel cells have provided larger currents for a long time in order to be operated portable devices or applications. Fuel cells exhibit higher energy density than lithium ion batteries and this property contributes to be utilized them for much longer times. Many governments financed such these system for decreasing air pollution and consumption of hydrocarbon fuels or fossil fuels [69].

Fuel cells have also been utilized in portable applications which ranges between 25 W and 5 kW. The main purpose of utilization of fuel cells in these applications is to decrease noise and emissions and improve device working time as well as energy efficiency. Portable applications involve generally computer, camera, mobile phone, and cordless tools. Notebooks and mobile phones can akso make use of DMFCs and H_2-PEFCs as power supply in the power range between approxiamtely 5 W and 75 W. Many manufacturers produced notebooks which benefits from fuel cells like Toshiba, Samsung, NEC. Many researchers and scientists have made progress about utilization of Li-ion batteries in many applications like Panasonic NCR 18650B, 691 WhL^{-1}, 266 $Whkg^{-1}$). Portable applications have not commercially been available very much. However, several electronic devices have existed at markets such as MiniPak Charger (Horizon), Powertrekk (myFC), and Upp Fuel Cell (Intelligent Energy). These devices include usually PEFCs:2-5 W, 5 V USB. Furthermore, the price of these devices is between $100 and $230. These devices weigh also between 120 and 235 g and benefits from H_2-catridges which depend on Metal Hydride (MH) and water activated NaSi as fuel source [70].



Figure 5.7 Portable applications of fuel cells [71]

5.1.6 Military Applications

These applications have significantly beefitted from fuel cells. Since the improvements of fuel cells, research and development (R&D) groups have paid attention to the usage of fuel cells in military and other applications. In addition to this, US Navy's Bureau of Ships (Electronic Division) provided financial support in order to studies of General Electric on fuel cells for military applications [69]. The main purpose of utilization of fuel cells in military applications is to provide power sources for military devices or tools like command centers, forts, radar stations, telecommnications installations by building fuel cell power plants. Land forces and soldiers have carried a lot of equipment like communication tools, night vision devices during combat or other important situations and these devices have also made use of fuel cells. In this case, one of the most outstanding points is that fuel cells must have low-volume and weight. Fuel cells must also opereate under difficult and real conditions in military applications and processes regardless of depending on conditions like weather, day and night. They must also display a durable structure so as to achieve faulty manipulations.

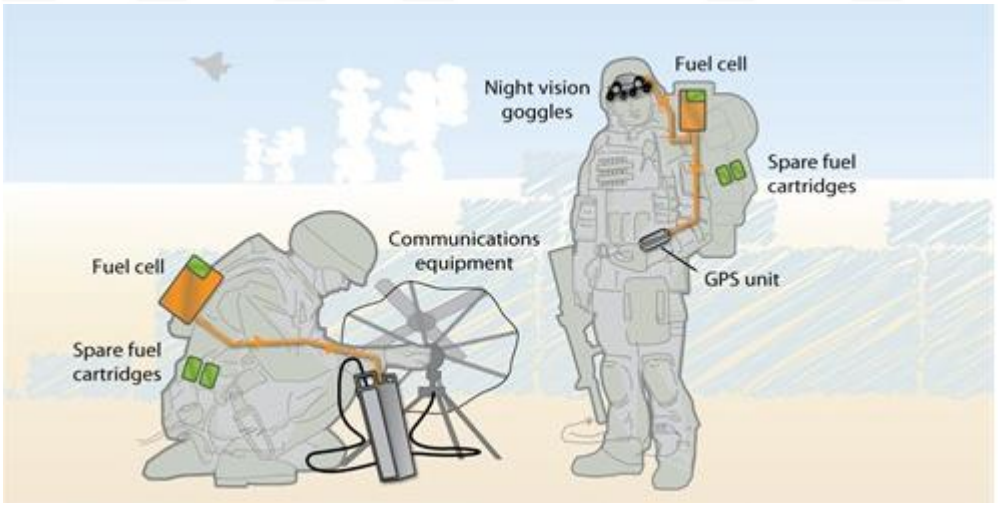

Figure 5.8 Military applications of fuel cells [72]

5.2Applications of Supercapacitors

5.2.1 Applications of Consumer Electronics

Consumer electronics include personal digital assistants (PDAs), GPS, portable media players, hand-held devices, laptop computers, photovoltaic systems etc. Supercapacitors can provide power for these devices. For example, Supercapacitors supply power for photographic flashes in digital cameras and for LED flashlights and their charge time is also very short such as 90 seconds. Additionally, many portable speakers can also use supercapacitors as power supplement. In same portable electronic devices, fluctuations can also ocur and supercapacitors overcome this problem and stabilize these fluctuations [73].

5.2.2 Grid Power Buffer Applications

These applications like electric vehicles (EVs), hybrid electric vehicles (HEVs), air conditioning systems, and advances power conversion systems give rise to form current fluctuations and harmonics. As a result of these fluctuationsi undesired voltage fluctuations and power oscillations are generated on the grid. Power oscillations can also create many problems like decreasing of the efficiency of the grid, voltage drops in the common coupling bus, and significant frequently fluctuations in whole system. In order to achieve this drawback, supercapacitors may be used as an interface that takes place between the load and the grid. They behave as a buffer between the grid and the large pulse power that are produced from the charging station [73].

5.2.3 Low-Power Equipment Power Buffer

These equipments contain generally RAM (Random-access memory), SRAM (Static Random-access memory), microcontrollers and PC cards. Supercapacitors contribute to decrease the effects that are obtained from short power interrotions and large current peaks.

One of the most outstanding points about supercapacitors is the combination uninterruptible power supplies (UPS) with them. This combination contributes to

decrease the cost per cycle and prolong battery life. Additionally, supercapacitors can also be used as backup power for actuators in wind turbine pitch systems. In the event of breakdown of main supply, blade pitch can also be managed [73].

5.2.4 Voltage Stabilizer

Supercapacitors can play an important role on stabilization of voltage instabilities for power cables by behaving as inhibitors. Wind turbines and solar cells mechanisms can be significantly affected by weather conditions like gusting or clouds and as a result of this situation, power fluctuations may also be created. In such cases, supercapacitors are going to prevent this drawback. Additionally, supercapacitors can also be located along the power lines so as to consume reactive power and improve the AC power factor in a lagging power flow circuit. This situation will contribute to be used effectively them in order to generate power [73].

5.2.5 Microgrids

Microgrids make use of clean, sustainable and renewable energy resources such as wind, solar so as to provide energy themselves. The power generation from renewable energy sources depends on weather conditions. In some cases, energy or power demand can be high and these energy sources can not meet this demand. In order to solve this problem, supercapacitors can be combined with microgrid systems. Supercapacitors provide significant benefit for microgrid because microgrid systems generste usually DC power and supercapacitors can benefit from this power in both DC and AC applications.

Supercapacitors can also generate voltage buffer in order to meet for fast changing power loads because of their large and discharge rate through an active control system. Voltage buffer is an important electronic circuit factor and the main purpose of this factor is to isolate the input from the output and to produce no voltage or a voltage that is presented as the input voltage. In addition to this, this factor can also stabilize the voltage from input to output. If the voltage is buffered, this situation is provided by making use of an inverter in order to convert DC power into AC power

to the grid. One of the most impoertant points about supercapacitors is that they cannot make frequency correction [73].

5.2.6 Energy Harvesting

Supercapacitors have become one of the most reliable and suitable energy storage devices for energy harvesting systems. Energy harvesting is also called as power harvesting and one of the most outstanding processes. In energy harvesting systems, energy is obtained from external or renewable energy sources such as solar panels, wind turbines, thermal power plants etc. and is converted into electrical energy in energy storage device [73].

5.2.7 Street Lights

Supercapacitors can also be utilized in street lights. In these applications, supercapacitors are combined with a solar cell power source and LED lamps. Japan has made prominent studies about Street lights and one of the most known cities that makes use of this combination is Sado City. First of all, supercapacitors start to store energy that is produced from solar anels and deliver energy or power to LED lamps. As a result of this process, supercapacitors can compensate the energy for Street lights overnight [73].



Figure 5.9 The combination of supercapacitors and solar cell in street light [73]

5.2.8 Medical Applications

Hospitals and health care services occupy an important place in our lives and consume a high quantity of energy. Supercapacitors and other important energy storage devices have played an important role during power failure. Defibrillators have been extremely affected by this negative situation. In order to hinder this drawback, defibrillators can benefit from supercapacitors. Supercapacitors can provided power 500 Joules so as to make the heart beat and continue the heart back into sinus rhytm by shocking [73].

5.2.9 Transport Applications

In aviation applications, many prominent aerospace systems manufacturers started to make use of supercapacitors in order to deliver power to actuators for doors and evaluation slides that are utilized in airliners. Diehl Luftfahrt Elektronik GmbH company have carried out inportant studies about this application. Airbus 380 have become one of the most outstanding examples for this application [73].

Military applications or institutions can also draw on supercapacitors in their own systems and supercapacitors must need large specific power in order to utilize radar antennae, laser power supplies, military radio communications, avionics exhibitions and instrumentation, backup power for airbag deployment and GPS-guided missiles and projectiles [73].

Automotive industry can benefit from supercapacitors as a power supply. Toyota presented prominent automobiles that drew on supercapacitors. Toyota’s Yaris Hybrid-R concept car is one of the most known Toyota’s models that uses supercapacitors in order to obtain from supercapacitors. The another important manufacturer is PSA Peugeout Citroën that benefit from supercapacitors in automative applications. In this application, supercapacitors contribute to increase automobile’s velocity or acceleration as part of its stop - start fuel-saving system. In Mazda’s i-ELOOP system, energy storage process occurs in a supercapacitor when the automobile starts to slow down. This automobile utilizes also supercapacitors in order to provide its own power during stopping of engine via the stop - start system.

Maxwell Technologies explains that supercapacitors display many advantages or benefits. Maxwell Technologies is one of the most important American developers and producers in San Diego, California. Their studies and productions are based on energy storing devices and power distributing products in many applications like transportation, renewable energy mechanisms, auxiliary power, electronic apparatuses. Additionally, they asserted that more than 20000 hybrid buses benefit from supercapacitors in order to contribute to enhance acceleration or velocity of automobiles or other vehicles, especially in China. China started also to make use of supercapacitors in their own trams in 2014 and their recharge time is 30 seconds [73].

Railway applications like railroad locomotives with diesel-electric transmission can also utilize supercapacitors as a secondary power source or supply. The basic working principle of supercaoacitors in this application is based on capture the breaking energy of a full stop and transfer the peak current in order to operate the diesel engine and provide enhancement of acceleration or velocity the train. The another important purpose of supercapacitors contribute to stabilize line voltage. Supercapacitors are usually preferre and used in this application because they need low maintenance and provide great advantages for the environment. Additionally, they can enable up to 30% energy saving for the railway vehicles by relying on the driving mode. The selection of both supercapacitors and materials in supercapacitors play a great role for railway applications [73].

5.2.10 Energy Recovery

In recent years, air pollution, global warming and greenhouse gases emissions have become the most outstanding problems. Many companies and manufacturers have made significant productions in order to reduce these problems. Furthermore, the usage of supercapacitors in these applications contributes to decrease energy consumption and global warming. The main purpose of energy recovery is to provide decreasing the amount of input energy to the system [73].

5.2.11 Hybrid Electric Vehicles (HEVs)

Many R&D groups and scientists have researched and studied about HEVs. Moreover, they made efforts for electric vehicles (EVs) so as to combine batteries with supercapacitors. According to these studies, they managed to decrease signigficantly fuel consumption from 20% to 60% with the help of recovery of brake energy in EV sor HEVs. Supercapacitors have better properties than batteries like quick charge, wide temperature range, their excellent and stable electrical properties, and longer lifetime. Since 2013, important automative producers have fabricated and improved prototypes that maje use of supercapacitors rather than batteries so as to increase driveline efficiency. The Mazda 6 can be given as an example for this expression. Thus, this car contributes to decrease the fuel consumption up to 10% [73].

CHAPTER 6

MARKET ANALYSIS OF FUEL CELLS AND SUPERCAPACITORS AND COMPARISON RESULTS

6.1 Energy Storage Comparison of Storage Devices Regarding Various Materials

6.1.1 Comparison of The Used Materials in Fuel Cells Regarding Various Properties

Table 6.1 and Figure 6.1 give the list of the electrical conductivities of the used materials in fuel cells. The electrical conductivities of several materials were given in the used materials in fuel cells. The rest of them was added on this table. According to this table and figure, graphene displays a higher electrical conductivity than other used materials in fuel cells.

Table 6.1 Electrical conductivities of the used materials in fuel cells [43, 45, 46, 48, 74-81]

Materials	Electrical conductivities (S/cm)
Graphene	10^6
$Pr_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$	76
La_2NiO_4	47
Pr_2NiO_4	94
$La_{0.8}Sr_{0.2}Cr_{0.8}Mno_{0.2}O_3$	0.8 – 1.2
LSCM	0.053
LSCF	200
$Sr_2Mg_{1-x}MnxMoO_{6-\delta}$	0.42 – 0.65
$Sr_2FeNb_{0.2}Mo_{0.8}O_{6-\delta}$	0.4 – 0.6
$La_{10}Si_{5.5}A_{10.5}O_{26.75}$	0.028
$La_{0.6}Sr_{0.4}MnO_{3-\delta}$	130
$LaMnO_3$	83 S/cm at 800 °C
Cobalt Based Electrodes ($La_{0.6}Sr_{0.4}CoO_3$)	$4.4*10^3$
Silicon dioxide	10^{-12}
SnO_2 Nanowires	0.46 $\Omega^{-1}cm^{-1}$ = 2.1739 S/cm
WO_3 (Tungsten Oxide)	$8*10^{-6}$ $\Omega^{-1}cm^{-1}$ = $1.25*10^5$ S/cm
Ni/YSZ	1000
Sulfated Zirconia (S-ZrO_2)	$4*10^{-2}$ S/cm at 70 °C
	$8*10^{-3}$ S/cm at 150 °C
Indium Tinoxide	$1.3*10^4$
4.5 Yttria Stabilized Zirconia (YSZ)	$2.96*10^{-6}$ S/cm at 400 °C

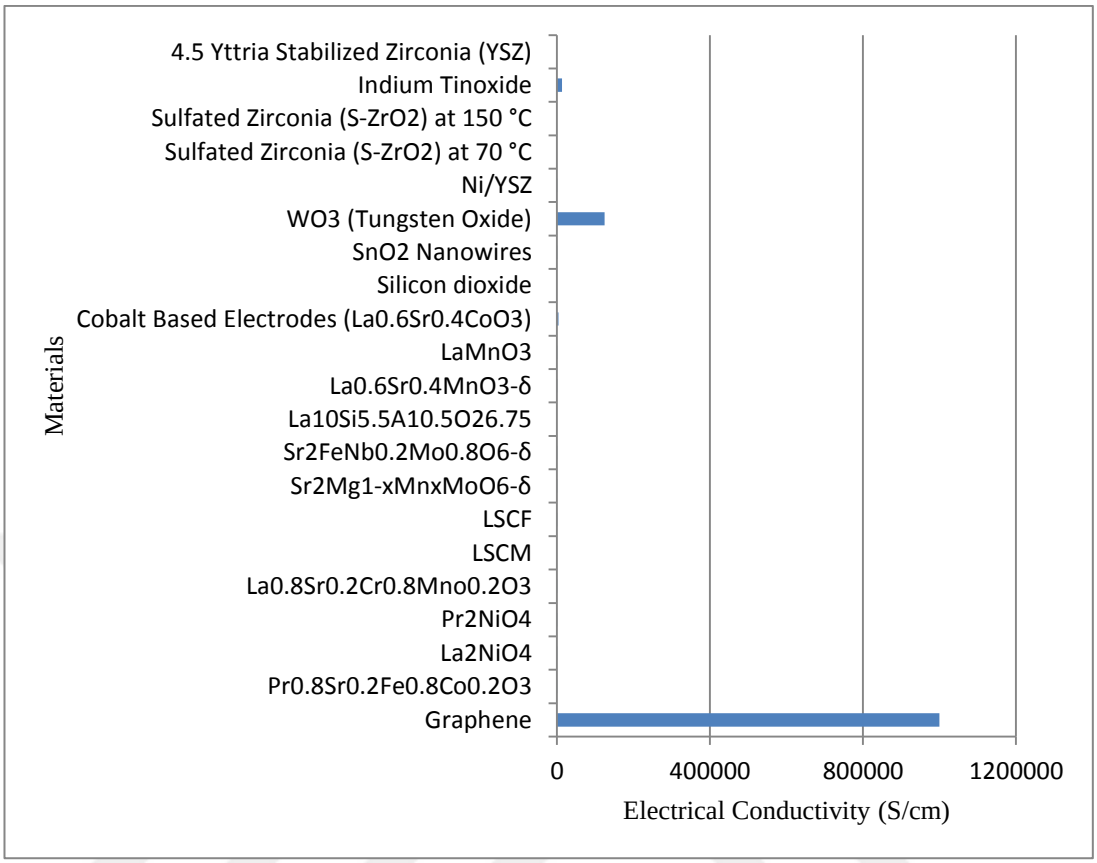

Figure 6.1 The illustration of electrical conductivities of the used materials in fuel cells [43, 45, 46, 48, 74-81]

Table 6.2 Thermal conductivities of the used materials in fuel cells [43, 54, 82-90]

Materials	Thermal Conductivity ($Wm^{-1}K^{-1}$)
Graphene	3000
Sr- doped Lanthanum Manganite (Lanthanum Stronium Manganite – LSM ($La_{1-x}Sr_xMnO_3$)	0.191 $Wm^{-1}K^{-1}$ at x = 0.1
	0.198 $Wm^{-1}K^{-1}$ at x = 0.2
	0.199 $Wm^{-1}K^{-1}$at x = 0.3
SiO_2 Silicon dioxide (SiO_2) (Amorphous)	1.4
Tungsten Oxide Thin Films (WO_3)	1.63
WO_2/WO_3 Films	1.28
Tin Oxide (Sn-based Oxides)	40
Cobalt based Oxides ($LiCoO_2$)	5.4
7 YSZ	2.2–2.9
$BaTiO_3$ (type of titanates)	2.65
La_2NiO_4 (type of perovskite)	5.96 (W/(mK)) at 325 K
40% porous Ni/YSZ	4
Zirconia	21.2276 $Wm^{-1}K^{-1}$ at 298 K (which was obtained from thermal conductivity equation)
	26.31 $Wm^{-1}K^{-1}$ at 359 K

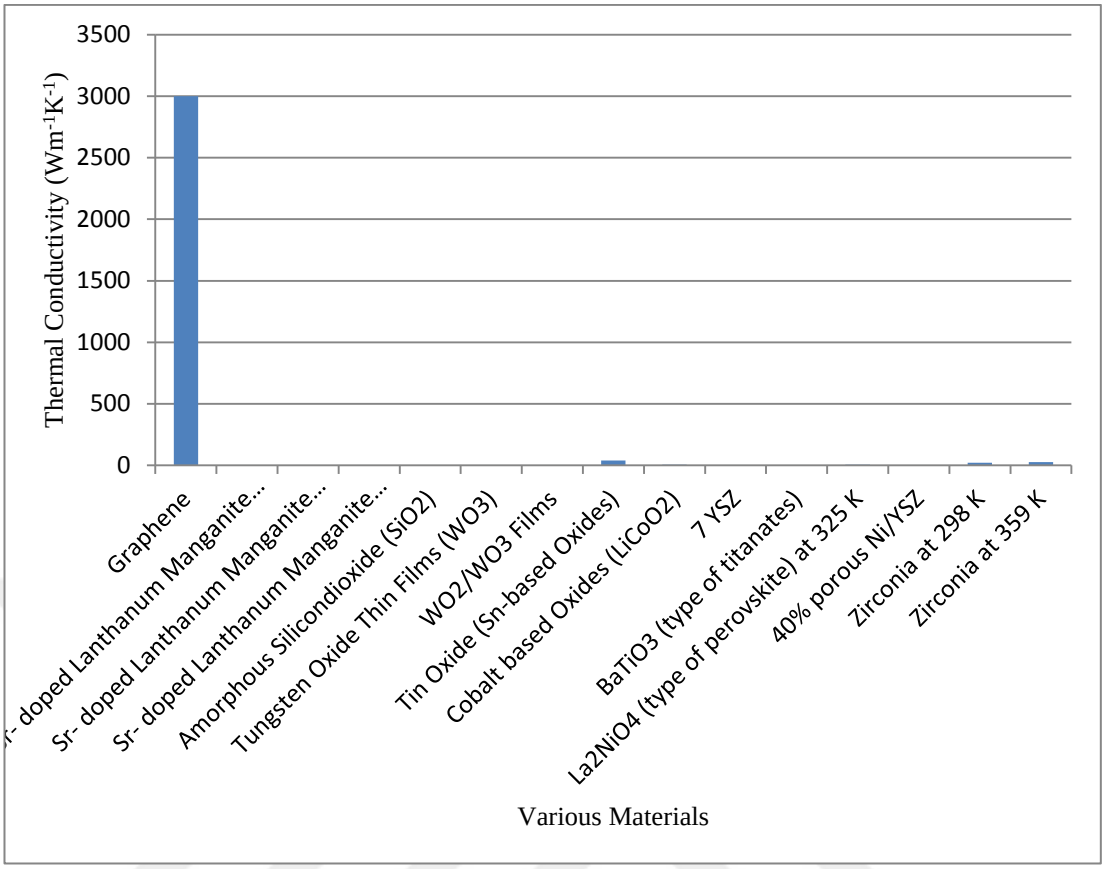

Figure 6.2 The relationship between the used materials in fuel cells and their thermal conductivities ($Wm^{-1}K^{-1}$) [43, 54, 82-90]

Table 6.2 and Figure 6.2 display the thermal conductivities of the used materals in fuel cell. For Zirconia, there are two different thermal conductivity (k) values. One of them was calculated at 298 K by making use of the following formula [89]:

$$k=8.8527+7.0820*10^{-3}T+2.5329*10^{-6}T^{2}+2.9918*10^{3}T^{-1} \quad \textbf{(6.1)}$$

$$k=8.8527+7.0820*10^{-3}(298)+2.5329*10^{-6}(298)^{2}+2.9918*10^{3}(298)^{-1}=21.2276$$

$$(Wm^{-1}K^{-1}) \quad \textbf{(6.1a)}$$

According to reference, thermal conductivity depends significantly on temperatures and thermal conductivity of 40% porous Ni/YSZ is around equal to 4 $Wm^{-1}K^{-1}$ [88].

The main reason of the given thermal conductivity difference between WO_3 thin films and WO_2/WO_3 films is a larger thermal resistance at the interface which is

positioned between WO_2 and WO_3 films as a result of mismatch of phonon state [82].

Table 6.3 Thermal expansion coefficients of the used materials in fuel cells [46, 47, 91-100]

Materials	Thermal Expansion Coefficients (TEC) (K^{-1})
$Pr_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$	$12.8*10^{-6}$
$Pr_{0.7}Sr_{0.3}Fe_{0.8}Co_{0.2}O_3$	$12.4*10^{-6}$
La_2NiO_4	$13*10^{-6}$
Pr_2NiO_4	$13.6*10^{-6}$
$La_2Ni_{0.8}Co_2O_4$	$11.3*10^{-6}$
$BaTiO_3$	$10.8*10^{-6}$ at 350 °C
Nickel	$16.9*10^{-6}$
Yttria Stabilized Zirconia (YSZ)	$11.0*10^{-6}$
Ni/YSZ with 25% porosity	$12.48*10^{-6}$
$LaMnO_3$	$11.2*10^{-6}$
$La_{0.6}Sr_{0.4}MnO_{3-\delta}$	$13*10^{-6}$
$La_{0.7}Sr0._3MnO_{3-\delta}$	$12.8*10^{-6}$
Indium Tin Oxide (ITO)	$7.26*10^{-6}$
Graphene	$-3.75*10^{-6}$
Tungsten Oxide	$4.5*10^{-6}$
Amorphous Tungsten Oxide	$12*10^{-6}$
Silicon dioxide (SiO_2)	$0.75*10^{-6}$
Lithium Cobalt Oxide ($LiCoO_2$)	$1.3*10^{-5}$
Hydroxyapetite	$13.9*10^{-6}$
Zirconia (ZrO_2)	$9.5*10^{-6}$

In Table 6.3, the thermal expansion coefficient of Zirconia is equal to $9.5*10^{-6}$ 1/°C = $9.5*10^{-6}$ 1/K. This value was obtained from thermal expansion conversion [101].

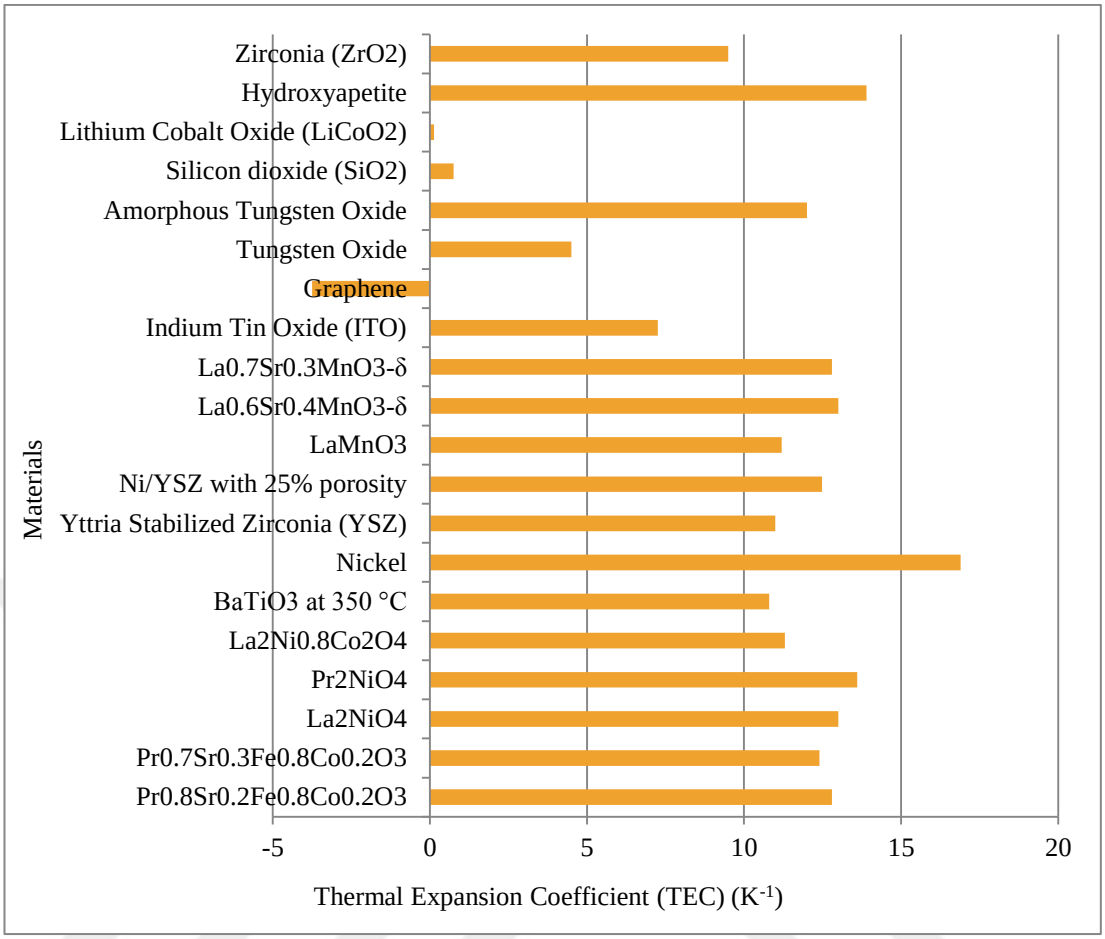

Figure 6.3 Thermal expansion coefficient (TEC) of the used materials in fuel cells in terms of 10^{-6} (1/K) [46, 47, 91-100]

In Figure 6.3, the thermal expansion coefficient of Hydroxylapetite is equal to $13.9*10^{-6}$ (1/°C). By making use of conversion table, it is $13.9*10^{-6}$ (1/K) [101].

Table 6.4 Specific surface area of the used materials in fuel cells [43, 102-113]

The Used Materials In FuelCells	Specific Surface Area (m^2/g)
Graphene	2600
Lanthanum Manganite ($LaMnO_3$)	42.6
Strontium Titanate Particles	5 – 10
Hydroxyapatite	100 m^2/g during 1 year period
Nickel	156.94
Yttria Stabilized Zirconia (YSZ-800: code)	81.8
Yttria Stabilized Zirconia (HYSZ-0: code)	319.2
NiO/YSZ Composite Powder	14.7 m^2/g with the help of BET analysis
Cobalt-based Oxides (Nickel-Cobalt Oxides)	438.3
LSCF (Lanthanum Strontium Cobalt Ferrite): Type of Perovskite	14
TiO_2 Particles (T33)	33.3
TiO_2 Particles (T174)	174.5
SnO_2	37
SiO_2	175 - 225
Sulfated-Zirconia (S-ZrO_2)	120 m^2/g at 600 °C
	147.5 m^2/g was obtained in the experiment

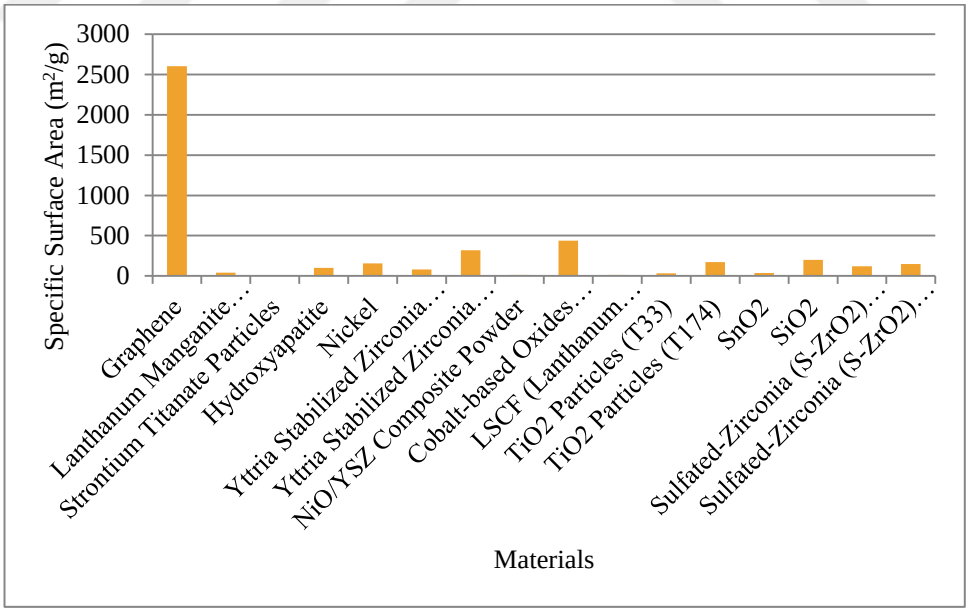

Figure 6.4 The illustration of specific surface area of the used materials in fuel cells [43, 102-113]

6.1.2 Comparison of The Used Materials in Supercapacitors Regarding Various Properties

Table 6.5 Specific capacitances of the used materials in supercapacitors [1, 37, 57, 58, 114,115]

The Used Materials in Supercapacitors	Specific Capacitances (F/g)
Activated Carbon (AC)	100-200 (in aqueous electrolyte)
	50-150 (in organic electrolyte)
	160-225 (in aqueous electrolyte with KOH-treated AC)
Carbon Nanotubes (CNTs)	Between 15 and 200 F/g
PANI (type of Conducting Polymers)	216
Activated Carbon – Carbon Nanotubes composite material in H_2SO_4 electrolyte	205
Biomass-derived carbons in organic electrolyte	146
Biomass-derived carbons in the Ionic Liquids	224
Graphene Oxide (GO) – doped PANI	531
Li-$Mn_{1-x}Ru_xO_2$	360
MnO_2@GCs@MnO_2	390 F/g at 0.5 A/g within 6M KOH electrolyte
Hollow MnO_2 Nanospheres	299 F/g at 5 mVs^{-1}
Mn_3O_4	261
MnO_2 electrode	178 F/g at 5 mVs^{-1}
Anhydrous RuO_2	24
Hydrated RuO_2.0.5H_2O	342
Amorphous RuO_2	1580
G-PNF_{30}	210 Fg^{-1} at 0.3 Ag^{-1}
PANI – rGO Composite Gel	808 F/g at 53.33 A/g
rGO/PANI	257 F/g at 0.1 A/g in 1 Molar H_2SO_4
Sulfonated Graphene/PPy	360 F/g at 1 A/g within 1 Molar H_2SO_4
Graphene-PPy	255.7 Fg^{-1} at 0.2 Ag^{-1}
	199.6 F/g at 25.6 A/g
G-PEDOT	304 Fg^{-1} within 2 M HCl
	261 Fg^{-1} within 2 M H_2SO_4
Graphene/4,4'-oxydianiline	612 Fg^{-1} at 5 mVs^{-1}

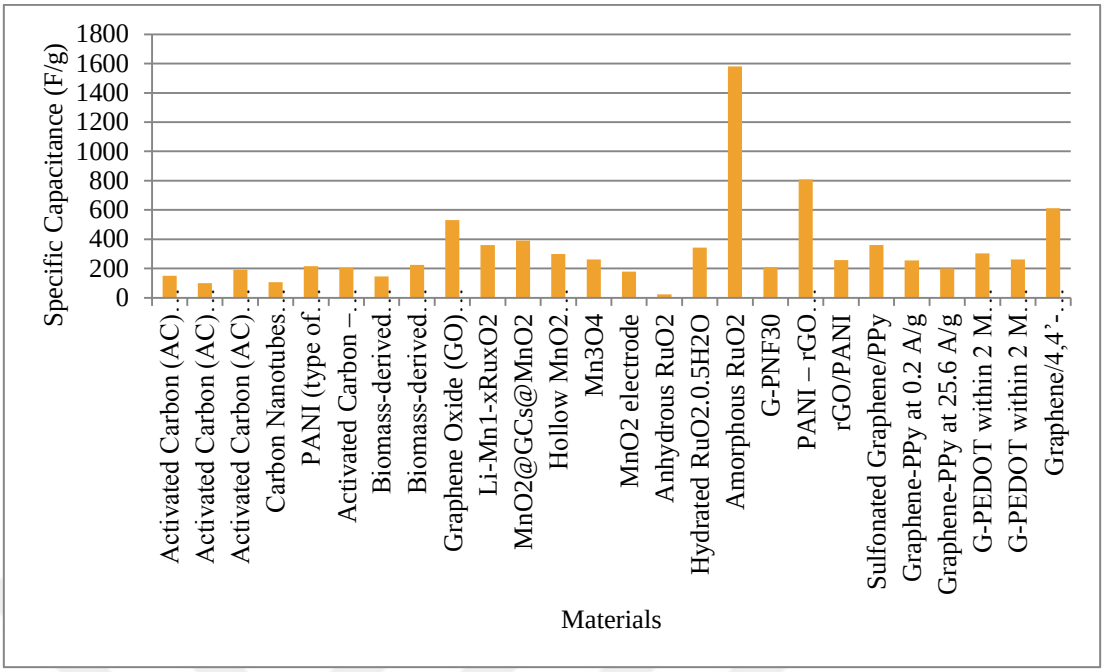

Figure 6.5 Specific capacitance of the used materials in supercapacitors in terms of F/g [1, 37, 57, 58, 114,115]

Table 6.6 Thermal conductivities of the used materials in supercapacitors [56, 116-124]

The Used Materials In Supercapacitors	Thermal Conductivity ($Wm^{-1}K^{-1}$)
Carbon Nanotubes (CNTs)	3500
Activated Carbon (AC)	0.3 at 4.5 K
	6.3 at 300 K
Conducting Polymers (CPs)	between 1 $Wm^{-1}K^{-1}$and 20 $Wm^{-1}K^{-1}$
Aqueous Electrolyte (Sulfuric Acid Concentrated)	0.5 $Wm^{-1}K^{-1}$
Ionic Liquids (ILs)	between 0.12 $Wm^{-1}K^{-1}$ and 0.2 $Wm^{-1}K^{-1}$
Organic Electrolyte (Acetonitrile)	0.2501 $Wm^{-1}K^{-1}$ at 298 K
	0.2070 $Wm^{-1}K^{-1}$ at 303 K
Single Crystalline Ruthenium Oxide (RuO_2) with electrical conductors like Cr and Pt	50
Single Crystalline Ruthenium Oxide (RuO_2) with La	1
GNPs/PPS (Graphene Nanoplatelets/Polyphenylene Sulfide)	4.414
Pure PANI	0.5
PANI with 50wt % GNP	3.3
PDMS/TS-rGO-PPy (Polydimethylsiloxane/Towel-Gourde Sponge – Reduced Graphene Oxide – Polypyrrole)	0.249

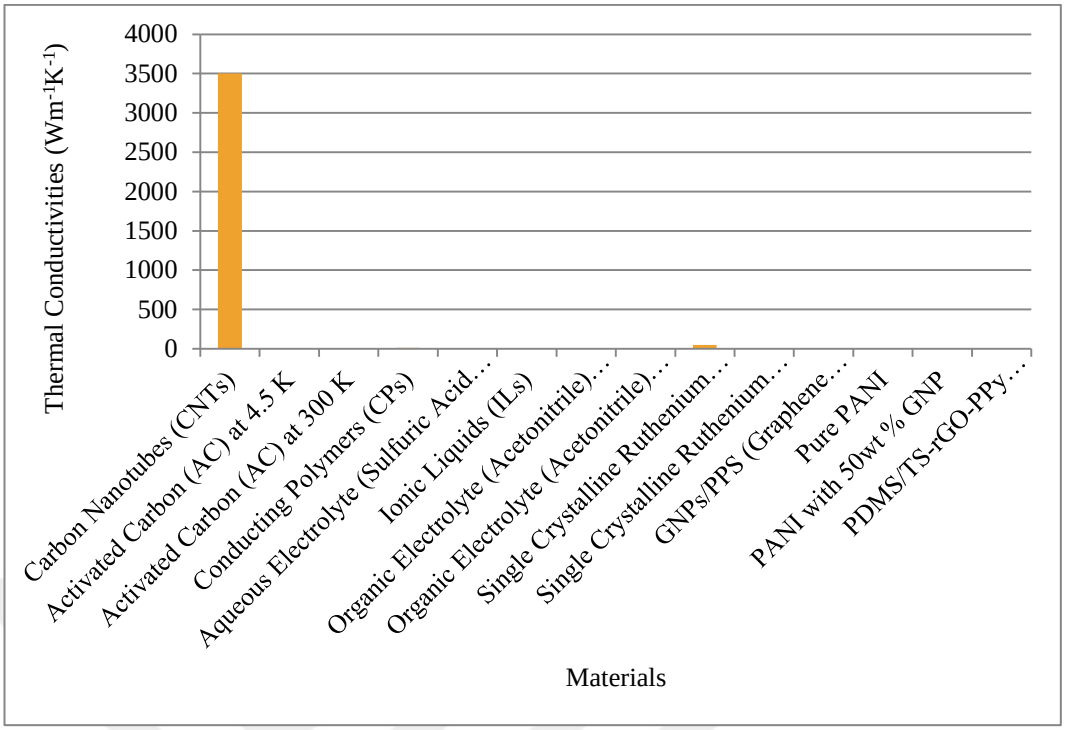

Figure 6.6 Thermal conductivities of the used materials in supercapacitors in terms of ($Wm^{-1}K^{-1}$) [56, 116-124]

In Table 6.7, the specific surface area of propylene carbonate is equal to 103.8 m^2/g and it was obtained from Gallosilicate zeolite (Ga-Silicate-1).

Table 6.7 Specific surface area of the used materials in supercapacitors [55, 125-133]

The Used Materials in Supercapacitors	Specific Surface Area (m^2/g)
Activated Carbon (AC)	3000
Carbon Nanotubes (CNTs)	948
PANI (Type of Conducting Polymers)	33.6
Activated Mesoporous Carbons with KOH (Aqueous electrolyte)	1118
Propylene Carbonate	103.8
Carbon Aerogels with 35 % mass ratio of Ionic Liquids	2309
α - MnO_2	96
Crystalline RuO_2	120 m^2/g at 350 F/g
Graphene PANI Composites	891
PPys@ GA (Polypyrrole Nanospheres @ Graphene Aerogel)	686

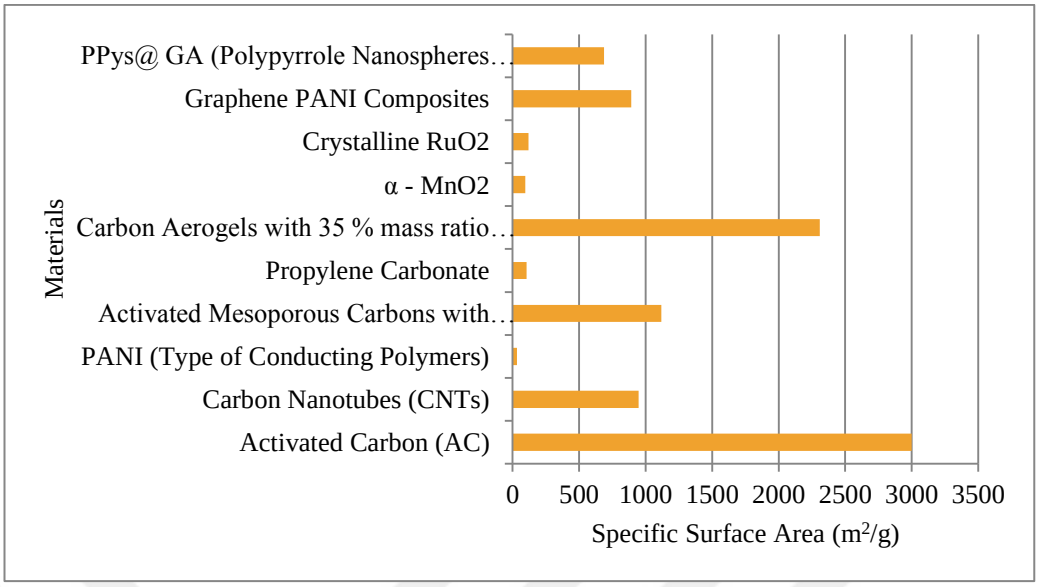

Figure 6.7 The illustration of the specific surface area (m^2/g) of the used materials in the supercapacitors [55, 125-133]

Table 6.8 The electrical conductivities of the used materials in the supercapacitors [37, 134-143]

The Used Materials in Supercapacitors	Electrical Conductivities (S/cm)
Activated Carbon (AC) with KOH	0.0352
Carbon Nanotubes (CNTs)	10^5
Undoped Conducting Polymers (CPs)	10^{-6}
Aqueous KOH	$540*10^{-3}$
EMIM – BF_4 (type of Ionic Liquids)	$1.355*10^{-3}$
Acetonitrile (type of organic electrolyte)	$33*10^{-3}$ S/cm at concentration of 12.348 mol/dm^3 of [BMIm] [Br]
Manganese Oxide (MnO_2)	10^{-5}
Ruthenium Oxide (RuO_2)	10^5
PEDOT:PSS/PU/ionic liquid	8.8×10^{-5}
Graphene/PANI	$8.07*10^{-2}$
PAN(PolyAcrylonitrile/NH_4NO_3(Ammonium Nitrate)/Propylene Carbonate (80 mol % PAN, 20 mol % NH_4NO_3, and 0.02 mol % PC)	$7.48*10^{-3}$ at 303 K

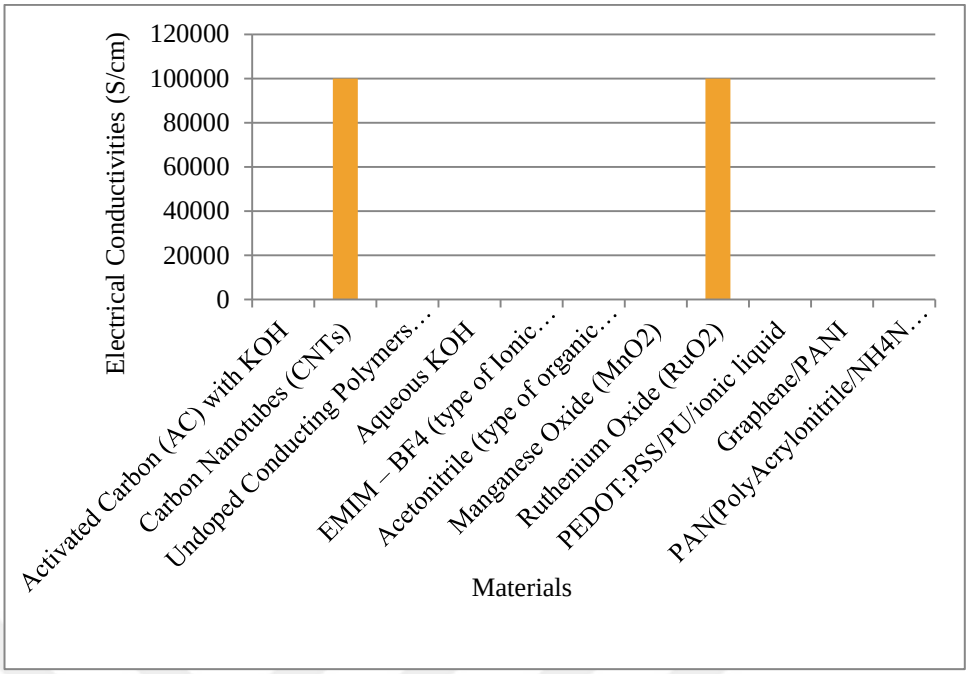

Figure 6.8 The illustration of electrical conductivities (S/cm) of the used materials in the supercapacitors [37, 134-143]

In Table 6.8, the electrical conductivity of RuO_2 is equal to 10^5 $ohm^{-1}.cm^{-1}$. As it is known that, electrical conductivity can be defined as the inverse of the electrical resistivity. Ohm.m is known as the SI unit of the electrical resistivity. [144]. As a result of this conversion, the electrical conductivity of RuO_2 is equal to 10^5 S/cm.

6.2 Market Analysis of Storage Devices

6.2.1 Market Analysis of Fuel Cells

Fuel cell market analyzes and evaluates global fuel cell and hydrogen projects. These projects contain business and financial projects, federal businesses, comparisons of many market sectors for fuel cells which are based on transportation, stationary power and consumer electronics. Fuel cell market made progress in 2016 as well as the developments of hydrogen energy storage, transportation of hydrogen, enhancement of fuel cell's performance and efficiency [145].

Honda, Toyota and Hyundai made outstanding studies and researches which are related to fuel cell electric vehicle (FCEV) and hydrogen refueling stations. According to the fuel cell technologies market report 2016, 92 more hydrogen

refueling stations have been put into practice in 2016. 45 of these stations are located in Japan and 20 of them are placed in California. These stations in Japan and California constitute 70% of the new-opening hydrogen stations in 2016. Many leading companies made sales of fuel cells in Europe [145].

By depending on many reports and results, fuel cells market generally prevails in 3 applications which are known as stationary power, transportation and portable power [145]. Hospitals, hotels, homes, schools can be regarded as the stationary power applications [146].

The Figure 6.9 gives the relationship between years and the number of fuel cell systems. According to Figure 6.9, nearly 62000 fuel cell systems were sent to every place of the world. The Figure 6.10 displays the relationship between the total power in terms of Megawatts (MW) and years. By looking at Figure 6.10, there is a significant difference between 2015 and 2016. According to Figure 6.10, the most remarkable increasing can be seen in transportation sector. The main reason of this situation is that Japan, Korea and other powerful countries pay attention to light-duty vehicles, buses, automobiles etc. The Figure 6.11 shows the distribution of fuel cells from country to country in terms of both applications and Megawatts (MWs) [145].

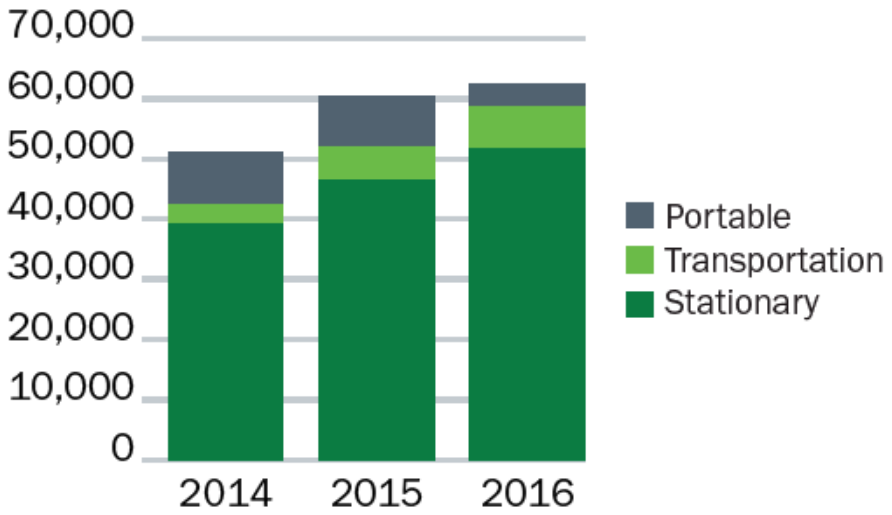

Figure 6.9 The relationship between number of fuel cell systems and years for 3 applications [145].

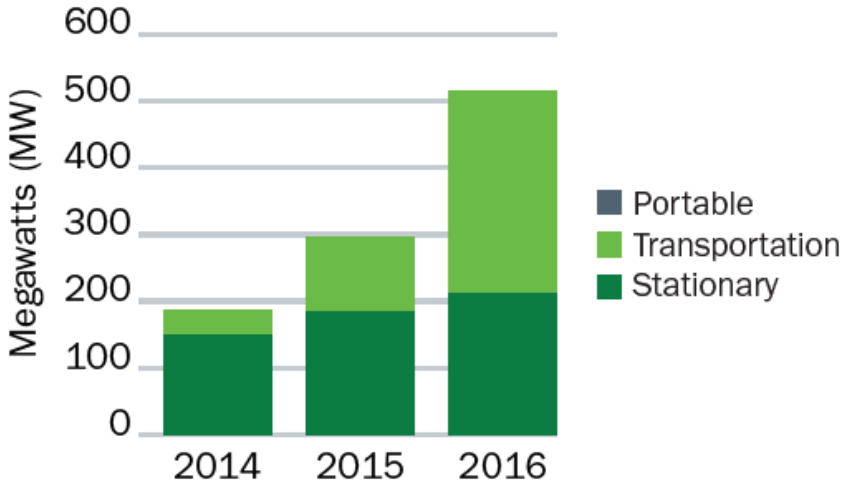

Figure 6.10 The relationship between total power and years for 3 applications [145]

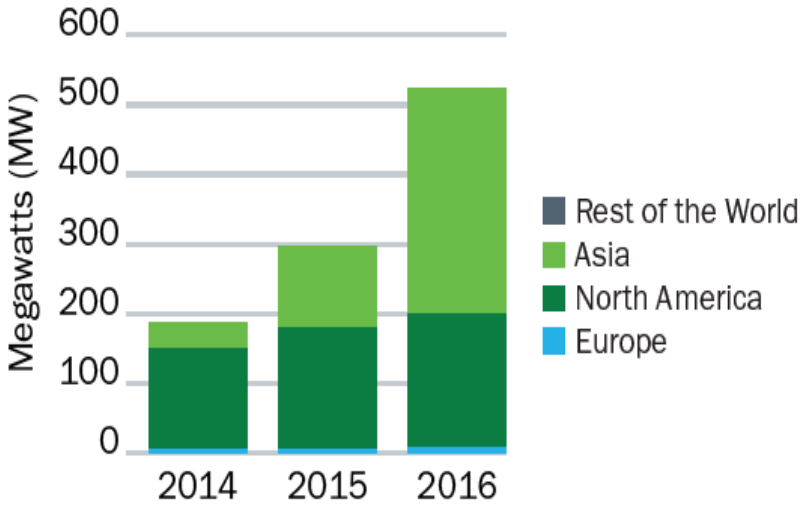

Figure 6.11 The distributions of fuel cells from country to country in terms of applications and Megawatts (MWs) [145]

By depending on the report which obtained Figure 6.11, China has become one of the most prominent countries which requires the most fuel cells. In addition to this, a small increase can also be observed in stationary fuel cell applications. This situation indicates that sustainable studies and operations were made about these applications [145].

Table 6.9 exhibits gross revenue (GR) and cost of revenue (COR) of several foremost companies which make research about fuel cells and invesment for fuel cells. These companies fabricate also fuel cells for many applications. By looking at Table 6.9, information can be attained about financial data of these companies. Additionally, many companies and researchers can also obtain company expansions, industry investment, acquisitions and profits by making use of this table. Apart from these measurements and data, Table 6.9 provides us also an evaluation of venture capital (VC), private equity (PE), and other important investment activity which involve equity and stock offerings in order to enhance capital [145]. Venture capital can be defined as a type of private equity and fund. With the help of it, investors can establish their companies which will continue long-term studies. It includes many financial-based terms like investors, financial establishments and banks [147]. Private equity (PE) is also known as alternative investment and includes capital which is not given on a public exchange. It composes of investors and their funds which can be invested in privated institutions or public establishments [148]. Private equity can also pay attention to purchasing processes of them. The basic reason for selecting these companies is that they are directly involved in and pay attention to fuel cell production. In addition to this production, these companies deal with trade of fuel cells. Gross revenue can be defined as the money which is obtained by all of a company's workings in the course of a certain period. After gross revenue was calculated, deductions for expenses are determined. As well as gross revenue, cost of revenue has become a significant role on the fuel cell market. The cost of revenue is defined as the total working expenses which are directly based on the goods sold and services supplied, like selling and marketing performances. These performances are directly proportional to sale. As it can be clearly seen in Table 6.9, gross revenue of Ballard Power Systems exhibits an increase of $28.8 million in 2016 as compared to the this revenue of 2015. The main reason of this increasing is improvements of the market. As well as gross revenue, cost of revenue of the same company displays an enhancement of $14.6 million in 2016 as a comparison was made with this revenue of 2015 [145].

Table 6.9 Comparison of gross revenue (GR) and cost of revenue (COR) of several companies in different years [145].

Companies	2016		2015		2014		2013		2012	
	GR	COR	GR	COR	GR	COR	GR	COR	GR	COR
Ballard Power Systems (Canada)	85,27	61,086	56,46	46,49	68,721	58,475	61,251	44,49	43,7	36,3
FuelCell Energy (U.S.)	108,25	108,61	163,08	150,3	180,293	166,57	187,66	180,54	120,6	120,1
Hydrogenics Corp. (Canada)	28,99	22,995	35,86	29,89	45,548	34,33	42,413	30,352	31,7	26,45
Plug Power (U.S.)	85,928	81,982	103,29	113,18	64,23	69,092	26,601	37,849	26,108	40,463
Ceres Power (UK)	1,113	14,026	324	12,476	1,224	10,128	523	13,255	226	18,48
SFC Energy AG4 (Germany)	44,04	30,794	47,31	34,083	53,631	37,97	32,413	22,49	31,26	18,497

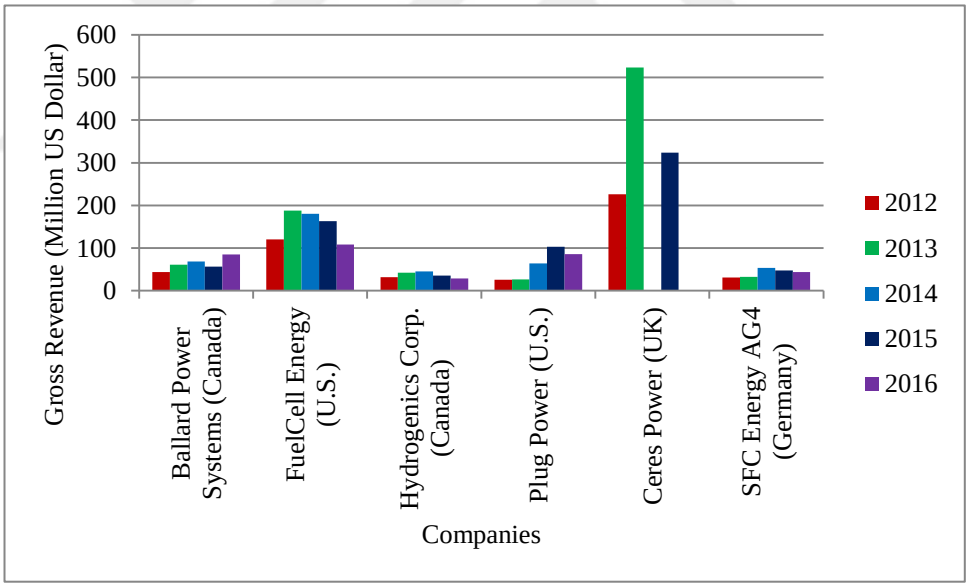

Figure 6.12 Gross revenue of the several companies in different years [145]

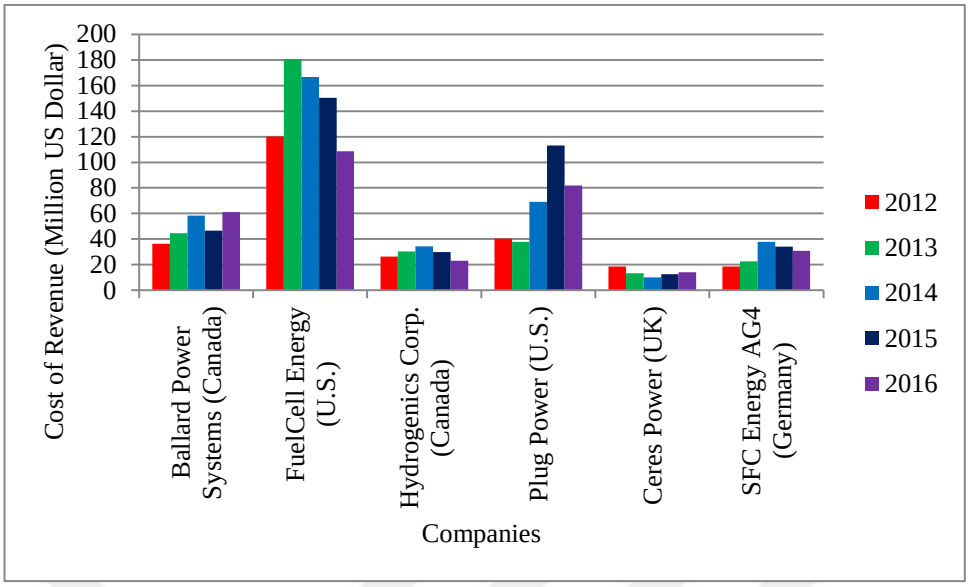

Figure 6.13 Cost of revenue of the several companies in different years [145]

As both gross revenue and cost of revenue were carefully analyzed and evaluated, a decreasing of $54.8 million was observed in 2016 for Fuel Cell Energy Company in terms of gross revenue as it was compared with the gross revenue of 2015 for the same company. POSCO Energy which is an prominent partner of Fuel Cell Energy, presented greater revenue than the revenue of the Fuel Cell Energy Company and this situation caused this decreasing for Fuel Cell Energy Company. These revenues depend on module sales. As it was looked at the cost revenue of Fuel Cell Energy Company between 2015 and 2016, a decreasing of $41.7 million could be observed in 2016 as compared with 2015 [145].

Hydrogenics cooperation has become one of the most outstanding companies which makes research about fuel cells in Canada. According to this table, the decreasing value in gross revenue is equal to $6.9 million in 2016. Decreasing in the electrolyzer sales for energy storage devices and industrial mechanisms and transportation of specific important projects in 2015 gave rise to this revenue decreasing [145].

Plug Power Company has played a vital role on the improvements of the both fuel cells and fuel cells markets. As it can be seen in the Table 6.9, the decreasing of the gross revenue which is equal to $17.4 million, was observed in 2016 as compared to 2015. The main reason of this decreasing is that fuel cell mechanisms or systems

were slightly less sold. Power Purchase Agreements (PPA), services transportation of the fuel cells to customers and infrastructure possess high share on this decreasing gross revenue [145].

As it can be observed in the Table 6.9, Ceres Power exhibited an increasing of $1.5 million in 2016 in terms of cost of revenue as compared with the same revenue in the year of 2015 [145].

SFC Energy AG4 has become one of the most remarkable companies which carries out studies about fuel cells in Germany. According to Table 6.9, a decline of 3.5 million was observed in the revenue of this company in 2016 as compared with revenue in 2015. Because high sales were not took place to the Oil & Gas segment. By depending on the report of this company, good sales in the security and industry department did not succeed in the increasing of the revenue for this company [145].

Table 6.10 shows the Research and Development expenditures for significant fuel cell companies in several companies in different years. Table 6.11 gives the comparisons between the companies in terms of total assets and liabilities for different years [145].

Table 6.10 The R&D expenditures for important fuel cell companies in several countries for different years [145].

Companies	2016	2015	2014	2013	2012
Ballard Power Systems (Canada)	19,827	16,206	14,294	17,117	19,273
FuelCell Energy (U.S.)	20,846	17,442	18,24	15,717	14,354
Hydrogenics Corp. (Canada)	3,576	4,07	3,284	2,566	4,452
Plug Power (U.S.)	21,177	14,948	6,469	3,121	5,434
Ceres Power (U.K.)	10,588	9,146	7,138	7,19	13,205
SFC Energy AG4 (Germany)	4,148	5,806	4,53	5,4336	4,257

Table 6.11 Comparisons between assets and liabilities of several companies in years [145].

Companies	2016 Assets	2016 Liabilities	2015 Assets	2015 Liabilities	2014 Assets	2014 Liabilities
Ballard Power Systems (Canada)	183,446	61,903	161,331	49,717	127,949	48,715
FuelCell Energy (U.S.)	342,137	167,884	277,231	122,62	280,636	122,33
Hydrogenics Corp. (Canada)	49,273	38,891	59,368	39,12	47,555	32,079
Plug Power (U.S.)	240,832	146,122	209,456	83,567	204,181	44,715
Ceres Power (U.K.)	10,081	3,103	20,685	4,084	10,084	3,726
SFC Energy AG4 (Germany)	33,793	20,454	35,889	19,331	47,256	19,667

According to the fuel cell market report which was written in 2015, more than 60000 fuel cells which can produce higher than 300 MW, were dispatched all over the world in 2015. Figure 6.14 exhibits all shipments of fuel cells all over the world by depending on applications in terms of Megawatts (MW) in 2015 [149].

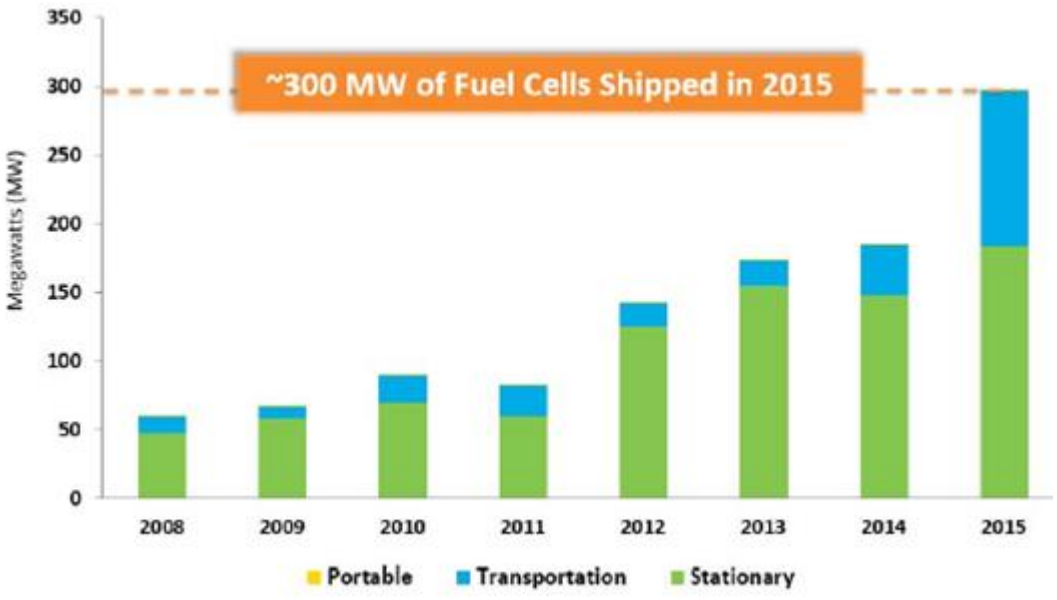

Figure 6.14 Relationship between shipments and years by depending on Megawatts [149]

As it can be clearly seen in Figure 6.14, there is a significant increase between 2014 and 2015. As a comparison was made between these two years by looking at this

figure, approximately 60%-65% of increase can be observed. This outstanding increase is based on many elements [149].

In the stationary applications, commercial and next generation fuel cell mechanisms contribute to improve the power output. As well as this, customers or end-users are generally making use of larger systems. Many companies or manufacturers both in the USA and in Korea are building high Megawatts (MW) fuel cell power plants. Fuel cell companies and producers are making exportations these fuel cell mechanisms to Korea. As it can be clearly shown in Figure 6.15, there is a 20% enhancement in fuel cell mechanisms shipments throughout the world in terms of application in 2015 as compared to 2014 [149].

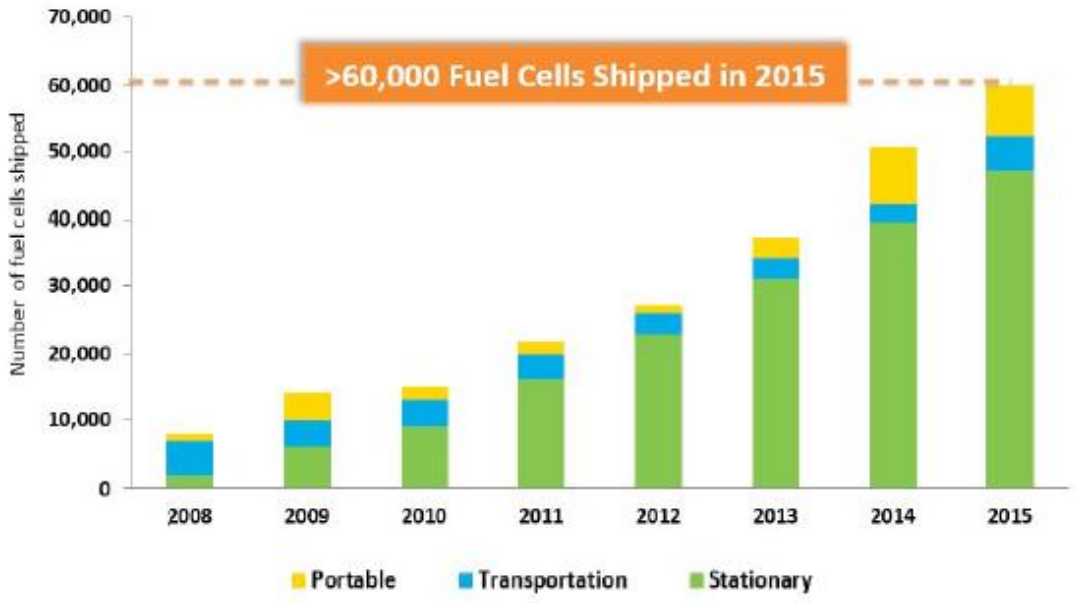

Figure 6.15 Distribution by years of fuel cell mechanisms shipments throughout the world [149]

The name of “ENE-FARM” was given as the first fuel cell in the world so as to be used in homes in Japan. The basic working principle of this type of fuel cell is that it separates hydrogen from Liquified Petroleum Gas (LPG) and then hydrogen enters the reaction with oxygen in the air in order to produce electricity as well as heat and water. ENE-FARM can generate electricity power which is between 0.3 and 1 kW

[150]. Additionally, the sales of ENE-FARM residential fuel cell mechanisms provide improvement of the fuel cell market [149].

Figure 6.16 gives the relationship between power output in Megawatts and locations by depending on years. As this figure could carefully be analyzed and evaluated, North American fuel cell companies and producers make shipment of higher than 150 MW in the whole world [149].

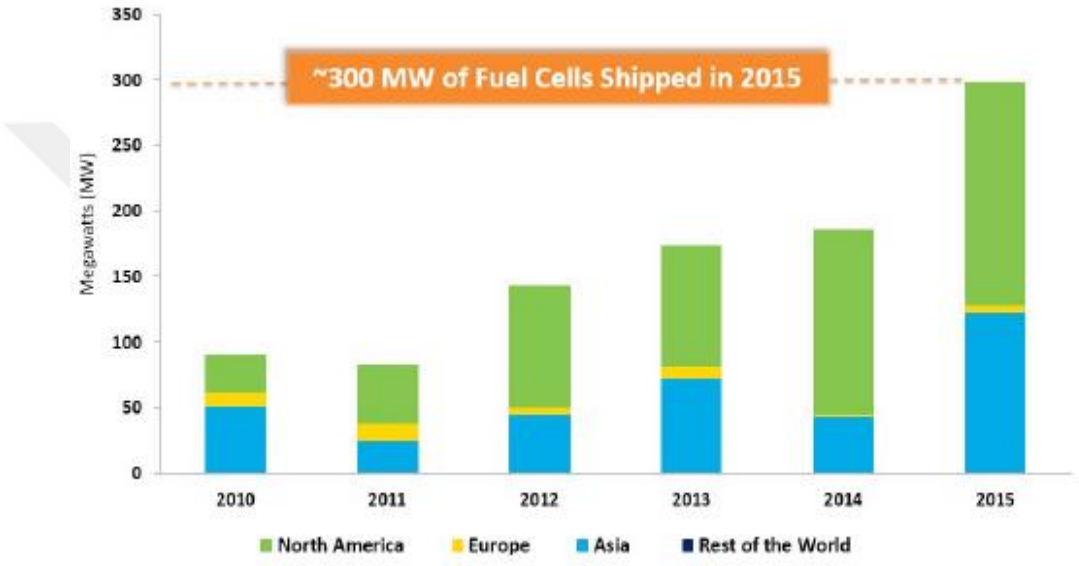

Figure 6.16 Comparisons by years in continents throughout the world [149]

According to the report which was written in 2015, Asian countries doubled shipments in 2015 as compared with the shipments in 2014. In other words, the shipments under 50 MW were carried out in 2014 and higher shipments than 100 MW were achieved in the year of 2015. This expression is based on the shipments which was made for fuel cell electric vehicles (FCEVs) by Hyundai and Toyota. Additionally, it also makes combination with stationary fuel cells which are obtained by Japan (Ene-Farm) and Korea (POSCO Energy) [149].

Business and financial projects and movements contribute to gain information about monetary data or values of fuel cell and hydrogen companies or manufacturers. Apart from financial services, business services have played key role on the fuel cell

market. These activities or services contain generally company expansions, industry investment, and obtainments and procurements [149].

By depending on the fuel cell market report 2015, fuel cell and hydrogen companies and producers improved their business performances by means of combinations with other businesses or obtainments and procurements. These important business performances are tabulated in Table 6.12 [149].

Table 6.12 Businesses performances of companies by means of combinations with other companies [149]

Company	Acquired	Transaction Value	Notes
Ballard Power Systems (Canada)	Protonex Technology Corporation (U.S.)	$30 million	They estimated debts of Protonex Technology and paid them.
Intelligent Energy (U.K.)	Société Bic S.A. (France)	$15 million	They bought all types of fuel cells of Société
NEL ASA (Norway)	H_2 Logic (Denmark)	NOK300 million ($35.7 million)	They signed an agreement so as to manage H_2 Logic company which is an important producer of hydrogen fueling stations.
	Rotoboost H_2 AS (Norway)	N/A	They bought all shares of Rotoboost H2 AS.
Plug Power (U.S.)	HyPulsion (France)	$11.47 million	They made an agreement with Axane which is auxiliary instution of Air Liquide, in order to buy the rest 80% of Hypulsion. Hypulsion was established under leadership of Plug Power nad Air Liquide in 2012.
SolidPower GmbH (Germany)	Ceramic Fuel Cells Limited GmbH (Australia)	N/A	They took charge of all assets and employees of Ceramic Fuel Cells which went büst in 2015.
Toray (Japan)	SolviCore (Germany)	N/A	Toray bought 50% shares of Umicore and Solvay with SolviCore
UQM Technologies (U.S.)	Roush Performance Products (U.S.)	N/A	They gained fuel cell compressor services from Roush company.

Furthermore, other important producers and companies developed their business activities in 2015 as the following [149]:

- PowerCell Sweden which makes studies improvement of fuel cell, built an independent department in Germany.

- ElectroPower Systems is an outstanding company which is based on hydrogen energy storage in Italia. This company established a department in San Francisco, California.

- Fuel Cell Energy expanded their fuel cell production which is going to enhance the size of its Connecticut production factory and its production capacity.

Table 6.13 exhibits disclosed top venture capital (VC) and private equity (PE) investments in companies which are based on fuel cell production in 2015. Table 6.13 represents also the disclosed investments. As well as these investments, there are also undisclosed investments which were carried out in 2015 [149].

As it can clearly be seen in Table 6.13, total $143.7 million investments were made for fuel cells. Three main companies which made investments for fuel cells are given in Table 6.13 [149].

Table 6.13 Disclosed top venture capital (VC) and private equity investments in companies [149]

Company	Amount (million US$)
Credit Suisse AG (Switzerland)	130.0
Emerald Technology Ventures AG (Switzerland)	13.3
350 Investment Partners LLP (U.K.)	0.4
TOTAL	$143.7

CreditSuisse AG is a banking and finance company whose headquarter is located in Zurich, Switzerland [151]. Credit Suisse AG made $130 million investment for fuel cells in U.S. SOFC manufacturer Bloom Energy in 2015 [149]. Emerald Technology Ventures has become one of the most prominent investment company for various technological companies in Switzerland [152]. This firm makes investments in Elcomax GmbH company which makes studies about fuel cells in Germany. As it can be shown in Table 6.13, Emerald Technology ventures $13.3 million of investment for fuel cells [148]. The another outstanding company is 350 Investment Partners LLP in the United Kingdom (U.K). The main purpose of this company is to control and regulate Venture Capital (VC) investments for several companies [153]. As Table 6.13 was carefully analyzed and evaluated, investment of $0.4 million was

made for another fuel cell company which is known as ACAL Energy, Ltd [149]. Furthermore, 350 Investment Partners LLP company made another investment in ACAL Energy which generate fuel cells. In fact, 350 Investment Partners LLP company carried out three investment in February, August and September. The investment value of 350 Investment Partners LLP company was $0.4 million in February as it was mentioned above. In addition to this value, $0.03 million was invested in the same company in August by 350 Investment Partners. The another important investment took place in September [149].

InvenCapital which is located in Germany, has a great effect on determination of fuel cell market and made investment in Sunfire GmbH which has been one of the most significant high-temperature fuel cell improver in Germany. Moreover, Ardica Technologies which has become one of the most outstanding micro fuel cell companies in the USA, increased their investment up to $1.1 million in September 2015 [149].

Table 6.14 represents the most remarkable fuel cell investors and countries between 2000 and 2015. According to Table 6.14, 5 investors which show the most enhancement of their investments, are CreditSuisse in Switzerland, Kleiner Perkings Caufield&Byers in the USA, Superannuation Fund in New Zealand, New Enterprise Associates in the USA and Mobius Venture Capital Inc in the USA. As Table 6.14 was analyzed and evaluated, it can be clearly observed that U.S. has been one of countries which carried out the largest increasing investment in this period. This investment value is equal to $794.9 million. Furthermore, in the light of the values from Table 6.14, Switzerland lifted to the second place with the help of its overall investment of $299.8 million. U.K. which is placed in the third place, followed Switzerland in terms of total investment with $245.1 million [149].

Table 6.14 Ten venture capital and private equity investors and countries for fuel cells [149]

Top Ten Fuel Cell Investors		Top Ten Countries with Highest Levels of Private Investment in Fuel Cells	
Company	Amount (Million US$)	Country	Total All VC and PE Investment (Million US$)
Credit Suisse (Switzerland)	266.2	U.S.	794.9
Kleiner Perkins Caufield & Byers (U.S.)	105.7	Switzerland	299.8
Superannuation Fund (New Zealand)	100.0	U.K.	245.1
New Enterprise Associates (U.S.)	71.0	Singapore	113.0
Mobius Venture Capital, Inc. (U.S.)	68.2	New Zealand	100.0
GIC Pte. Ltd. (Singapore)	63.0	Canada	73.8
GSV Capital Corp. (U.S.)	54.2	Germany	42.5
DAG Ventures LLC (U.S.)	54.2	Sweden	23.6
Rolls-Royce Holdings PLC (U.K.)	50.0	Russian Federation	21.0
Enertek Services Pte. Ltd. (Singapore)	50.0	Denmark	20.0
Subtotal (top 10 only)	$882.5	Subtotal (top 10)	$1733.7

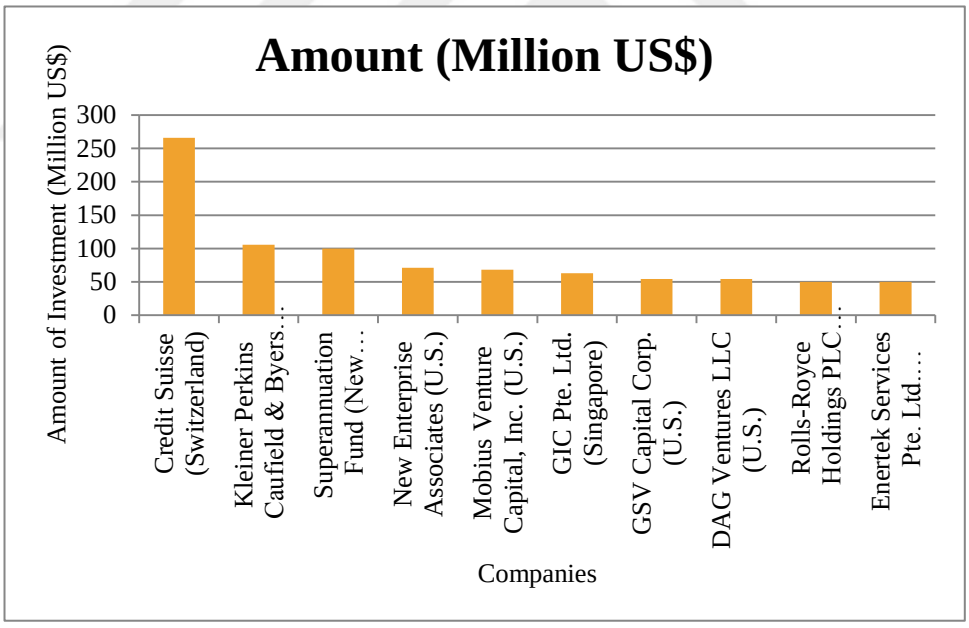

Figure 6.17 The relationship between the companies and their investment values in terms of million $US [149]

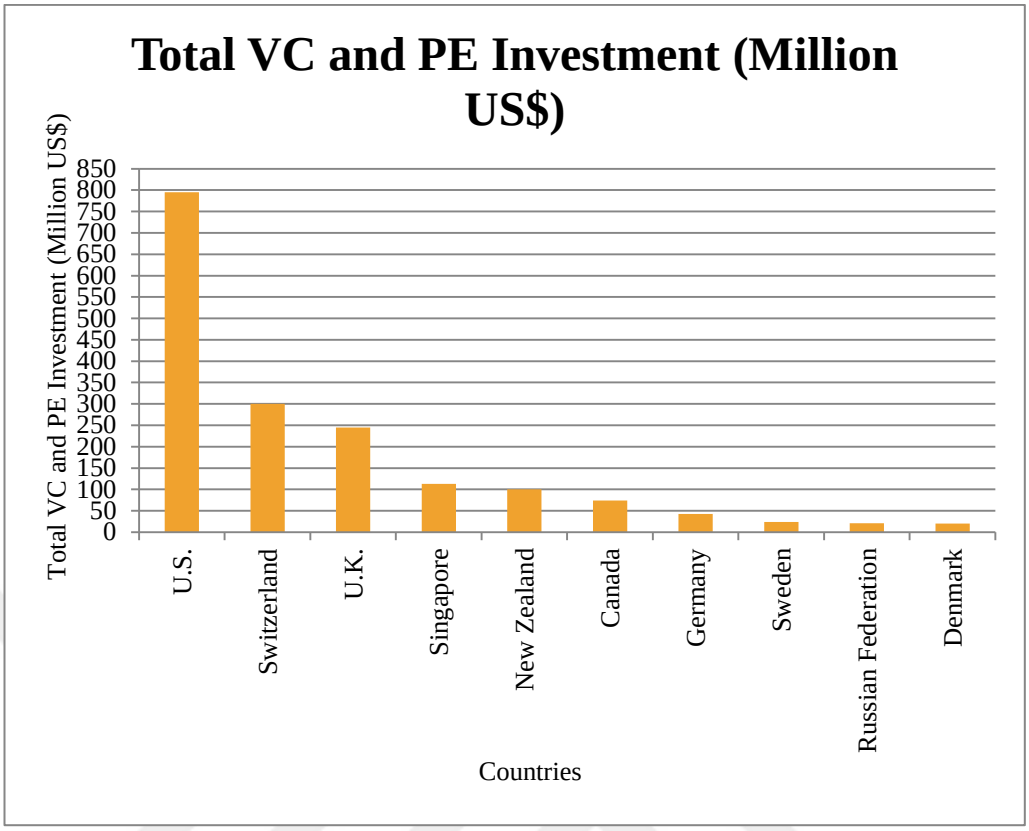

Figure 6.18 The relationship between the countries and their investment with all VC and PE values in terms of $ million US [149]

Beside investments, many fuel cell and hydrogen companies and manufacturers try to grow their money in order to compensate their Research and Development (R&D) studies, capital expenditures, and/or commercialization performances by determining prices of stock shares and making them affordable price. As a result of these endeavours, the money which is greater than $58 million was obtained in the year of 2015 as it can be observed in Table 6.15. Table 6.15 gives capacity and equity investment activities. In addition to Table 6.15, Toyota has also provided significant improvements for the fuel cell market. For example, Toyota designed a novel security,"Model AA" shares which present 7.1 million shares in July so as to enhance $4 billion for future technologies like FCEVs. Furthermore, Toyota expects that the company will make sale which reaches to 150 million Model AA shares [149].

Table 6.15 Capital and equity investment activity of outstanding companies for fuel cells [149]

Company	Net Proceeds	Number of Shares
Ballard Power Systems (Canada)	$13.6 million	9,343,750
	$5 million	3,322,479
Electro Power Systems (Italy)	€14.2 million ($15.2 million)	1,941,177
Hydrogenics (Canada)	$17.8 million	2,448,385
ITM Power (U.K.)	£4.856 million ($7.131 million)	J.C.B 12,853,127
		Valebond Consultants 3,333,333
NEL ASA (Norway)	NOK 67.5million ($8.2 million)	30,000,000
	NOK 69.3 million ($8.9 million)	51,301,852
	NOK 30 million ($3.8million)	148,148,148
	NOK 13 million ($1.7million)	10,000,000

Government has also paid attention to fuel cell or other industry market. The federal governments contribute to make investments for fuel cell and hydrogen technologies at USA universities and private sector or industry provides excellent opportunies for this technology [149].

Many states put into practice various policies so as to improve and distribute fuel cells and hydrogen fueling stations. In addition to these policies, state institutions improve their investments to the fuel cell companies or manufacturers and researchers. These effective states include California, Connecticut and New York [149].

2015 becomes a milestone year for Department of Energy (DOE) because of Energy Policy Act of 2005 (EPAct). This policy is an important federal law which was signed by former President George W. Bush on August 8, 2005 [154]. The main purpose of EPAct is to provide commercialization and demonstration of hydrogen usage for transportation applications such as FCEVs. This expression is related to Title VIII of the EPAct. According to this law, FCEVs can be presented by automakers to the consumer market. DOE achieved its purpose which is based on transportation or automotive applications. Hyundai, Honda and Toyota have become prominent companies or automakers which showed success in fuel cell market with the help of FCEVs [149].

President Obama sustained and fortified remarkable purposes for renewable energies and energy storage devices. These main purposes are to improve the rate of both electrical energy and thermal energy which are produced at federal facilities, provide the usage of energy storage devices which generate no emissions [149].

U.S. Congress took a decision which is based on tax extension up to $8000 so as to buy FCEVs. This tax extension finished at the end of 2014. In the year of 2015, Congress approached positively to the investment of $97 million for the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Office. As well as this investment, this congress made also investment to the Office of Fossil Energy regarding SOFC-related performances [149].

Table 6.16 and Figure 6.19 show three outstanding projects which were executed by America's important investors. Table 6.16 indicates that DOE's ARPA-E (Advanced Research Projects Agency-Energy) established a new funding which is known as OPEN2015. This funding provides investment of $125 million. In addition to this, OPEN2015 contributes also to make energy research and improve projects from America's best innovators for novel technologies in both stationary and transportation applications. Table 6.16 presents significant projects which were occurred in DOE's National Energy Technology Laboratory (NETL) [149].

Table 6.16 Outstanding projects of America's important investors [149]

Recipient	Amount	Details
Dioxide Materials, Inc.(Boca Raton, Florida)	$2 million	This company is going to improve alkaline water electrolyzer in order to use it in developed power to gas system which provides energy storage in hydrogen bonds.
Pajarito Powder, LLC (Albuquerque, New Mexico)	$2.79 million	This company is also going to improve a reversible hydrogen electrode which contributes to decrease cost of fuel cells and hydrogen generation.
Proton Energy Systems (Wallingford, Connecticut)	$2.5 million	This company aims at improvement of a hydrogen-iron flow battery which is able to produce hydrogen so as to use fuel cell vehicles as fuel source and provides energy storage on the electric grid.
TOTAL FUNDING	$7.29 million	

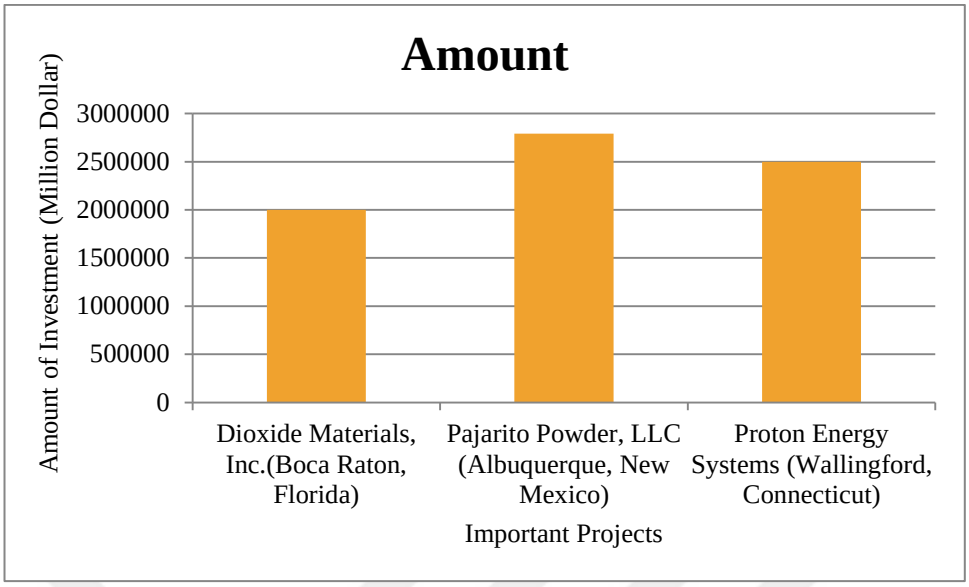

Figure 6.19 The investment amount of three outstanding companies in America [149]

6.2.2 Market Analysis of Supercapacitors

The improvements in the transportation, industrial, energy and consumer electronics have gradually enhanced. At this point, supercapacitors offer promising opportunities for these applications. COVID-19 had a great impact on the supercapacitor market. According to the report which was published in July 2020, it was expected that the supercapacitor market would decrease in 2020 because of global economic decline or stagnation which was caused by COVID-19. By depending on this report, it was indicated that the supercapacitor market will develop in 2021. Furthermore, it was forecasted in this report that the supercapacitor market will reach $3.5 billion until 2025. At the same time, CAGR (Compound Annual Growth Rate) will also from 19% to 21%, from 2020 to 2025 [155]. CAGR can be defined as annual average rate of revenue or investment which improves between two or more given years [156].

The main purpose of the usage of CAGR is to calculate and designate the personal assets, investment values or other things which may increase or decrease in value within a certain time [157].

As it is stated above, basic determinants for supercapacitor market are expressed as developing fabrication of electric vehicles, enhancement in portable or consumer

electronics, and excellent properties of supercapacitors like large energy density, high lifetime, and power stabilization. These properties offer better opportunities than traditional energy storage devices [155].

Transportation application occupies a great place in the supercapacitor market. The main purpose of usage of supercapacitors in this applications or electric vehicles is to provide improvement of vehicle performance, contribute to increase lifetime, improve power stabilization and decrease dependence on fuel. By depending on this report, it was indicated that hybrid supercapacitors can display the largest growth over the estimated period owing to their larger energy density than double layer capacitors. Important countries like China, Japan, and South Africa presented the greatest growth over the estimated oeriod by virtue of enhancing need for supercapacitors in automotive, wind, solar, and consumer electronic industries or portable applications [155].

According to report which was written by Avinash Savekar and partners, the size of the global supercapacitor market was calculated as $3.27 billion in 2019 and they estimate that the supercapacitor market is equal to $16.95 billion until 2027. With this market value, CAGR will also exhibit an increase of 23.3% [158].

As it was mentioned in the part of advantages and disadvantages of supercapacitors, they are environment – friendliness. One of their most outstanding advantages is low emissions. In other words, they can give rise to least environmental pollution such as emissions of greenhouse gases. Therefore, the used materials have played significant roles in supercapacitors. In order to decrease environmental pollution, they can use biodegradable carbon [158].

By depending on this report, the basic factor which controls the supercapacitor market contains more usage of supercapacitors in automotive industries. Additionally, supercapacitors provide also excellent advantages or benefits for automotive industries like large power density, quick charging time, and high shelf time. As well as automotive industry, renewable energy mechanisms have occupied a great place in supercapacitor market. Therefore, in the light of thoughts of the writers of this report, it was foreseen that supercapacitor market will increase. Enhancement

of gasoline or petroleum prices in the whole world have become a great factor for the improvement of the supercapacitor market. Many investigators and entrepreneurs have invested their money in energy storage devices because of this negative situation. But, the improvement of supercapacitor market is prevented due to expensive materials and less familiarness of supercapacitors. In addition to this, long working life time of supercapacitors enables them their usage in renewable energy sources like solar and wind energy systems. Increasing in need for microsupercapacitors provides development of beneficial opportunies in order to improve both supercapacitor industry and supercapacitor market in the near future. Figure 6.20 gives the relationship between 2019 and 2027 in terms of supercapacitor market by looking at types of supercapacitors. According to Figure 6.20, it can be seen that the supercapacitor market will significantly develop in the year 2027 when it is compared with in 2019. Moreover, it is expected that the pseudocapacitors will show better development than other types of supercapacitors which are known as double layer and hybrid supercapacitors in terms of supercapacitor market. Figure 6.20 was analyzed by depending on product type [158].



Figure 6.20 Supercapacitor market by depending on product type [158]

Figure 6.20 was illustrated according to the product type such as pseudocapacitors, double layer capacitor and hybrid supercapacitors. By evaluating module type, the

supercapacitor market can also be classified into lower than 10 Volts, between 10 Volts to 25 Volts modules, between 25 Volts to 50 Volts modules, between 50 Volts to 100 Volts modules and higher than 100 Volts modules. According to results which were obtained in many reports, modules which range from 10 Volts to 25 Volts, presented the largest market share in the year of 2019. At the same time, many reports estimate that the modules which are higher than 10 Volts will improve at the largest CAGR from the year of 2020 to 2027 [158].

Figure 6.21 represents the supercapacitor market in terms of applications. According to this figure, supercapacitor market was analyzed and evaluated by depending on applications and classified into automotive, energy, industrial, consumer electronics, and aerospace defense applications between 2019 and 2027. As it can be shown in the Figure 6.21, it is expected that the automotive applications or industries have become leader position in the supercapacitor market [158].

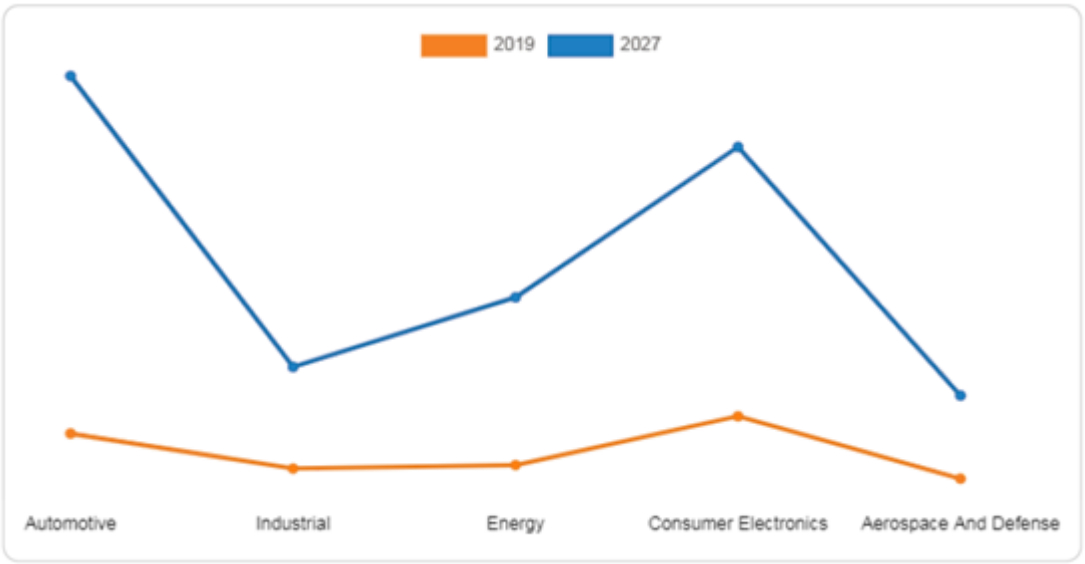

Figure 6.21 Supercapacitor market by depending on applications [158]

Figure 6.22 exhibits the classification of supercapacitor market by depending on region or location. According to this figure, it is expected that the supercapacitor market will develop across North America (U.S., Canada, and Mexico), Europe (The United Kingdom, Germany, France, Italy and rest of Europe), Asia-Pacific (China,

Japan, India, South Korea, and rest of Asia-Pacific), and AMEA (Latin America, the Middle East, and Africa). As it can be seen in Figure 6.22, Turkey does not play an important role on the supercapacitor market. According to the obtained results, Asia-Pacific gains a great importance in 2019 in the supercapacitor market because of improvement of automotive applications and industries as well as enhancement electronic applications and sector in China. Additionally, India has provided outstanding contributions to the supercapacitor market in recent times. On the other hand, North America became the second highest share in the supercapacitor market when it is analyzed from the viewpoint of revenue. According to writers of this report, it is forecasted that the supercapacitor market will grow in next years due to increasing of the need for supercapacitors in automotive applications and industries [158].



Figure 6.22 Supercapacitor market by depending on region [158]

There are also significant factors which have a great effect on the supercapacitor market. These factors consist of enhancement of demand for supercapacitors in many applications (especially automotive applications), outstanding government regulations. The another important factor is that renewable energy systems or mechanisms have benefitted from supercapacitors very much. On the other hand, expensive materials and less familiarness of supercapacitors have hindered the

improvement of the supercapacitor market. Additionally, increasing of need for microsupercapacitors provides improvement of supercapacitor market in the near future [158].

For supercapacitor market, $2272 million was allocated in 2018. According to many researchers, it is estimated that the supercapacitor market will improve with a CAGR of 35.4% from 2018 to 2023. Supercapacitor market can also be classified into material type and supercapacitors which utilize polymeric films possess the largest market share. As well as polymeric films, the price of these supercapacitors which benefit from polyarchylonitrile is $33 million in 2017. Additionally, the price of the polymeric films supercapacitors is $108 million in 2017. Between 2018 and 2023, CAGR will become at the level of 39.7% and 36.1%. North America has also played a great role on the supercapacitors and possess the largest market share in 2017. The price of value of the supercapacitors is $943 million in 2017 in North America. From the viewpoint of the researchers, it is estimated that the supercapacitor market will improve with a CAGR of 33.8% between 2018 and 2023 in North America [159].

Some significant companies control and manage the supercapacitor market. These companies are Murata Manufacturing Co. Ltd., Maxwell Technologies Inc., Nesscap Co. Ltd., Nippon Chemi-Con Corporation, Panasonic Corporation (Japan) and more than 10 other important companies [159].

Innovation has become one of the most important necessities in the energy storage devices. It contributes to improve life time of the supercapacitors in storage technology [160]. Persistence Market Research is one of the leading institutions or organizations which provides combination of market analysis and studies so as to conduce to corporations because of economic and monetary problems [161]. One of the most outstanding components for excellent market analysis and evaluation is good and regular data collection and management [160].

Between 2020 and 2024, the supercapacitor market will be balanced to increase by $949.51 million with a CAGR of 19%. Market management plays also a key role on cost of supercapacitors and other energy storage devices. It is provided by their enduring and safe attributes. Furthermore, supercapacitors can also replace with

rechargeable batteries in electric vehicles and adoption rate should be improved for both affordable supercapacitor cost or price and good market management [162].

The supercapacitor market can be classified into application, geography or region as it can be seen in the above figures. Appearance of several technologies and improvement of research and development investments are going to give rise to be obtained considerable demand in the market [162].

Researchers and investigators offer remarkable and elaborate information for supercapacitor market with the help of study and research, analysis and combination of data from various references by evaluating significant factors. The leading supercapacitor companies project a program in order to both provide excellent opportunities for customers and set their higher supercapacitor's market position. There are also outstanding supercapacitor companies which are known as Cornell Dubilier, Electonics Inc., Eaton Corp. Plc., KEMET Corp., LS MTRON Ltd., Maxwell Technologies Inc, NICHICIN Corp, Nippon Chemi-Con Corp., Panasonic Corp., Systematic Power Manufacturing LLC, and Tecate Group. The market analysis or report provides an insight and gives ideas to the consumers for general financial situations of supercapacitor and other energy storage devices [162].

The supercapacitor market can gradually be developed by benefitting from improvements and enhancement of needs from applications like wireless internet, mobile phones, communication, transportation in a certain time. These applications need long power supply and supercapacitors can implement this necessity. The supercapacitor market has also been grown by big changes in storing mechanisms as well as an improvement in market department like renewable energy mechanisms, smart grids and hybrid electric vehicles (HEVs). Enhancement of investments in renewable energy systems controls also supercapacitor market in order to reduce environmental disasters and global warming [163].

Tesla carried out very important research and studies for supercapacitors. Therefore, it bought Maxwell Technologies for $200 million for their supercapacitor Technologies or systems in an effort to utilize them in electric vehicles. Supercapacitors are able to make charge and discharge processess of lithium batteries

which have played a vital role on industry development. As it was mentioned in other chapters, supercapacitors show differences from conventional capacitors which do not make energy storage and display low power density. Supercapacitors solve this drawback by virtue of their larger energy storage capacity. As a result of this situation, supercapacitors have higher dominant effect than conventional supercapacitors on the market [163].

The used materials in the supercapacitor like graphene and carbon nanotubes (CNTs) contribute to improve and control the supercapacitor market due to their conductivites and capacitances. Moreover, CNTs and graphene can also be combined and this combination provides that the supercapacitors acquire excellent properties like low-weight, large mechanical durability and strong elastic structure. These properties contribute to enhance their performance and efficiency in many applications like portable and transport applications. In other words, as long as large energy density supercapacitors are produced, the supercapacitor market will continue to develop [163].

Transportation applications use supercapacitors in developed countries like China, Japan, France for increasing of needs in electric vehicles. Supercapacitors have been more preferable and useful than conventional electric car batteries owing to their fast charging time and excellent temperature stability and their flexibility. This situation becomes one of the most determining factors on supercapacitor market [163].

Health sector takes part in the first position between other sectors with the emergence of the COVID-19 epidemic and its rapid spread throughout world. Because this sector needs continuously power source which is known as uninterrupted power supply (UPS). In other words, it provides secondary power source. This situation contributes to increase the market of both supercapacitor and other energy storage devices [163].

Smart grids possess also a great importance for supercapacitor market. Because their main purpose is to manage electricity generation and transmission. Therefore, all countries must attach importance to the utilization of smart grids in an attempt to

provide sustainable and continuous power source and improve the market of energy storage devices [163].

Many prominent companies own a great significance on supercapacitor market. They control and manage this market. These main companies contain Maxwell Technologies, Korchip Corporation, Panasonic Corporation, Niching Corporation, Elna Ltd, Kemet Co., Vishay Intertechnology, Skeleton Technologies, and Loxus Inc. These companies must also concentrate and set sight on acquirements, company coalitions in an effort to create reliable improvement of the supercapacitor market [163].

Between 2017 and 2022, researchers and investors estimate that the supercapacitors market will develop with approximatelly 16% of CAGR because of large need from supercapacitors from end-users in India. End-users benefit from supercapacitors in their own devices like laptops, mobile phones, televisions (TVs), GPS devices etc [163].

Improvements of supercapacitors, market of electric vehicles and supercapacitor's efficiencies and performances create an excellent opportunity and solution for increasing of their usage in renewable energy systems and mechanisms such as solar and wind power application in India in the forthcoming five years [164].

There are also outstanding companies which fulfill their studies about supercapacitor market in India. They involve AVX Corporation, Cap-XX ltd, Eaton Corporation PLC, Elna Co. Ltd., LS Mtron Ltd., Maxwell Technologies Inc., Nippon Chemicon Corporation which have played important roles on the supercapacitor market [164].

Supercapacitors have been one of the most newly-emerging technology in India and the world. In spite of this situation, they are used in many applications. Table 6.17 and Figure 6.23 give the relationship between revenue and years in terms of global supercapacitor market between 2014 and 2025. As it can be clearly seen in Figure 6.23, it could be observed that an 30% increasing of CAGR was observed in the global supercapacitor market. Figure 6.23 was obtained by depending on data of IDTechEx report. According to Figure 6.23, researchers estimate that the

supercapacitor market will come to US$ 8.3 billion in 2025. Automotive and consumer electronics applications dominate the supercapacitor market because people prefer these applications in their daily lives. Supercapacitors present also excellent properties like their regenerative braking system and their easy placeable devices for various applications. Countries like in Europe, Asia and USA in which renewable energy systems are improved, supercapacitors can also be easily applied to these systems and this situation contributes significantly to develop the supercapacitor market [165].

Table 6.17 The relationship between revenue and years in terms of global supercapacitor market [165]

Years	Revenue (US$ billion)
2014	0,46
2015	0,61
2016	0,79
2017	1,02
2018	1,32
2019	1,72
2020	2,24
2021	2,92
2022	3,79
2023	4,93
2024	6,41
2025	8,33

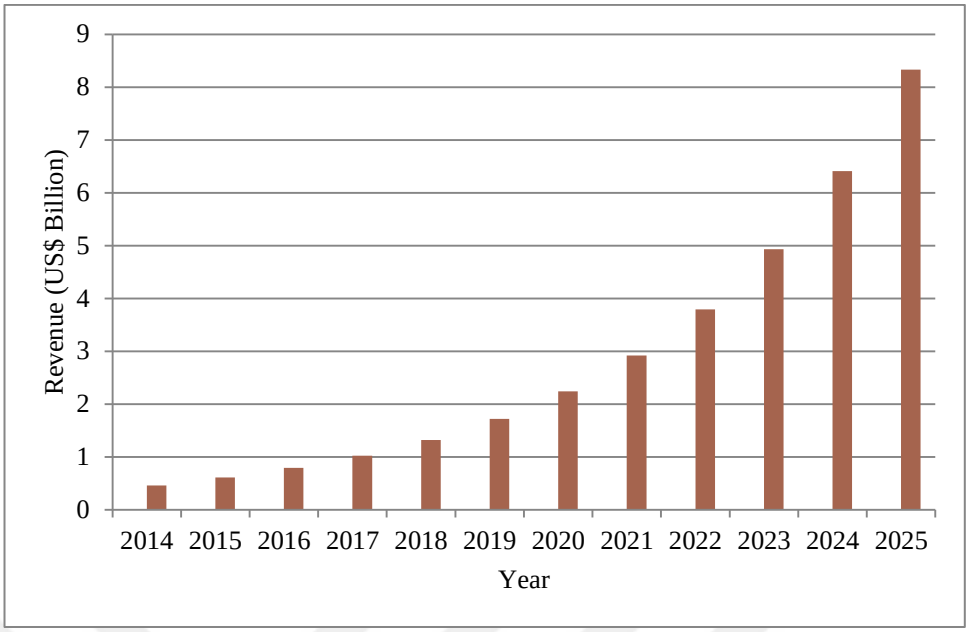

Figure 6.23 The illustration of the relationship between the revenue and years in global supercapacitor market [165]

Table 6.18 shows overall market for supercapacitors in India by 2020. Table 6.18 was arranged with the help of Supercapacitor Market Landspace Study which was written by Electronic Industries Association of India (ELCINA). By depending on this study, the supercapacitor market opportunity will reach 1.3 billion units in the light of total addressable market (million units). Table 6.19 represents the whole revenue opportunity for supercapacitors in India in both pessimistic and optimistic situation. According to Table 6.19, it can be observed that the revenue in the pessimistic situation for supercapacitors is equal to ₹ (Indian ruple) 13.203 billion. This value stands for the minimum revenue. ₹ 39.606 billion is equal to the revenue in the optimistic situation which is known as maximum value [165].

Table 6.18 Overall market for supercapacitors in India by 2020 in terms of million units [165]

Application	Total Addressable market	Pessimistic forecast market penetration	Optimistic forecast for market penetration
Automotive	720	72	216
Electric Vehicle	150	15	60
Railway	20	1,98	5,94
Wind Energy	0,56	0,11	0,17
Solar Energy	0,1	0,04	0,08
Solar Lighting	18	3,6	7,2
Consumer Electronics	372	18,6	37,2

Table 6.19 Whole revenue opportunity in India in both pessimistic and optimistic situation in terms of ₹ billion [165]

Application	Revenue in pessimistic situation	Revenue in optimistic situation
Defence	0,00259	0,00518
Other application sectors	13,2	39,6
Total	13,203	39,606

India has not yet made much of a commercial venture for supercapacitors. Because their usage has not been very widespread in India. Many manufacturers and corporations are operating for their productions. As it was known, India has become one of the highest population density, environmental and air pollution as well as their contributions to the global warming in the world. Therefore, Indian government has engaged and interested in energy sector like the usage of renewable energy sources and energy storage devices. India has also kept face with supercapacitor market and Indian companies or manufacturers have managed to balance and stabilize the Indian market by using supercapacitors in many applications [165].

Tata motors are one of the leading automotive companies in India and have important ideas and considerations regarding the usage of supercapacitors in automobiles. There was also a remarkable project which was executed within National Electric Mobility Mission Plan (NEMMA) 2020 in India. This project is based on the utilization of supercapacitors in Electric Vehicles (EVs) and provides also improvement of both supercapacitor and automotive market in India [165].

Railways have also become one of the most preferable transportation alternatives in the world and India has one of the world's largest rail systems, inclusive of metro trains which started to expand in city centers. Supercapacitors have also been used in railways trains and they provided reliable, safe qualifications like good power quality and energy conservation. Thus, supercapacitors had a great effect on Indian railways.

Both power receperation and dynamic brake energy storage can also be major applications. According to the researchers, it is estimated that demand could come to nearly 10 million units of many supercapacitor modules in the forthcoming three years [165].

Wind energy applications have also used supercapacitors in wind turbine pitch control as it can be seen in the Figure 6.24 [166].

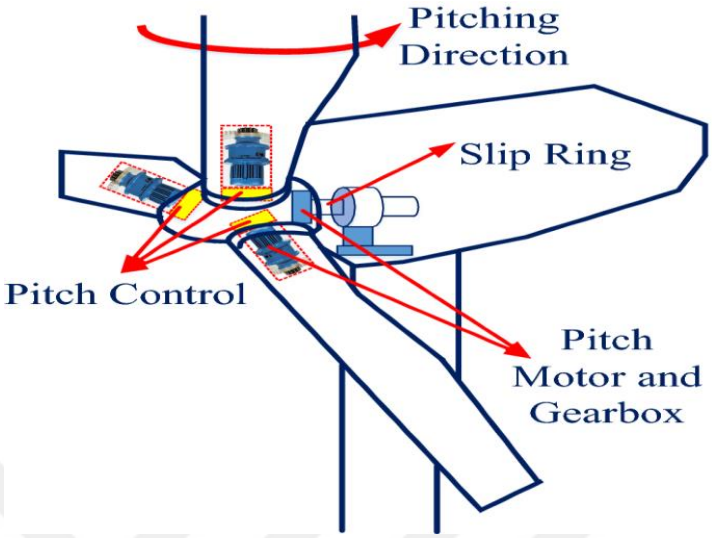

Figure 6.24 The usage of supercapacitors in pitch control of wind turbines [166]

Suzlon is one of the most outstanding and prominent wind energy companies in India and fabricates wind turbines. The main purpose of this company is to benefit from supercapacitors inside their wind turbines so as to improve the efficiency and performance of their wind turbines. This purpose will provide increasing of supercapacitor's usage in wind turbines both in India and all over the world. According to data of many reports, the amount of wind energy of India is equal to 1 GW and 5 GW. The wind turbines which include supercapacitor-based electrical pitch control can offer the most excellent solution. In the whole world, higher than 14000 wind turbines utilize supercapacitors. Supercapacitors will be penetrated into the supercapacitors by 30%. In order to fulfill this process, approximately 0.17 million units of supercapacitors will be used [165].

Solar energy systems such as PV panels can also make use of supercapacitors in India. India carried out important solar missions such as Jawaharlal Nehru National Solar Mission (JNNSM) in 2010. With the help of this mission, India has tarted to penetrate supercapacitors into PV panels or other solar energy devices in India. It is estimated that when the supercapacitors are penetrated by 40% inside the PV panels or solar energy applications, requirements will reach to 416000 units in solar energy

sector. These are also important programmes which are known as SHS (Solar Home Systems) and MNRE (Ministry of New and Renewable Energy)'s solar lanterns. These programmes or projects have been supported by government. Additionally, researchers in these programmes considered that there is additional requirement for supercapacitors which is equal to 10 million units [165].

Table 6.20 exhibits the relationship between exporters and their exported values in different years. By analyzing and evaluating Table 6.20, it was clearly seen that the greatest exported value was equal to 29298660 US Dollar Thousand in the world in 2014. In Table 6.20, Japan is generally located in the first order in given years and achieved 5049500 US Dollar thousand of exported value in 2017 from supercapacitors. World Trade Organization provides outstanding contributions to be created this table. As reported by Table 6.20, China showed important improvements and increasing in 2013, 2014 and 2015. Both in 2016 and 2017, it was observed in Table 6.20 that it reduced their exported values as compared to other three years. Although Turkey's exportation of supercapacitors is less than other countries, important steps have been taken in this regard. An enhancement of Turkey's exported value could be observed from 2013 to 2014. However, these values had been diminished after the year of 2014. 2014 is the year of the largest exported value for supercapacitors in Turkey [167].

Table 6.20 Exported supercapacitor values of outstanding countries in different years in terms of US Dollar Thousand [167]

Exporters	In 2013	In 2014	In 2015	In 2016	In 2017
World	27503327	29298660	28372931	23701557	26871875
Japan	4309204	4337963	4282491	4450228	5049500
Hong Kong	3804340	4039058	4144711	4193455	4463191
China	7528448	7613479	7725947	4023716	4227411
USA	1603231	1584505	1465448	1425951	1674375
Taipei, Chinese	1158869	1043312	950547	1313112	1493132
Singapore	1313497	1140536	918896	985947	1354127
Korea	1141117	1116926	1091348	990086	1277975
Germany	1043974	1104928	1035119	1095397	1306463
Turkey	4341	6203	5336	3824	3695

Figure 6.25 and Figure 6.26 show the illustration of exported supercapacitor values of both world and Turkey and these values were given in Table 6.20.

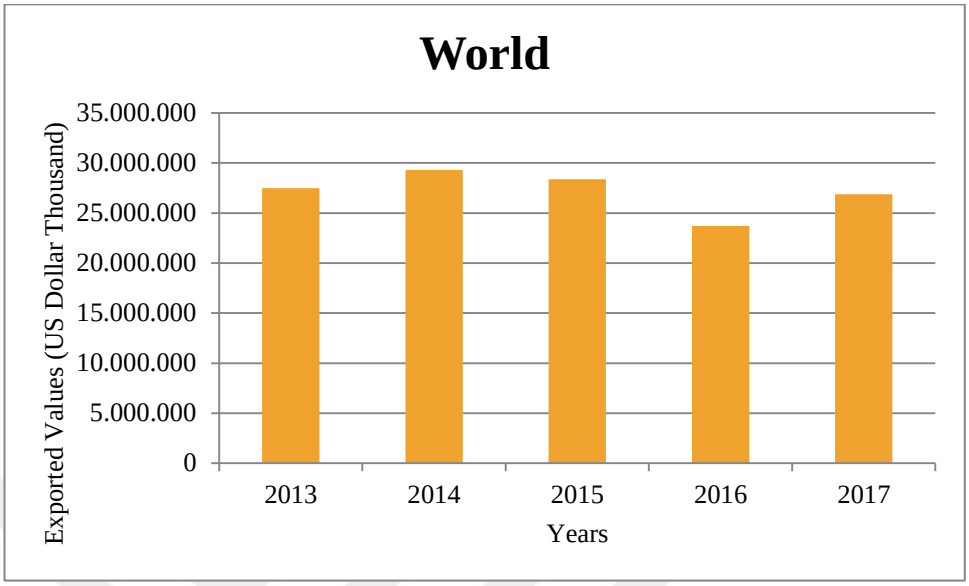

Figure 6.25 The exported supercapacitor values of the world [167]

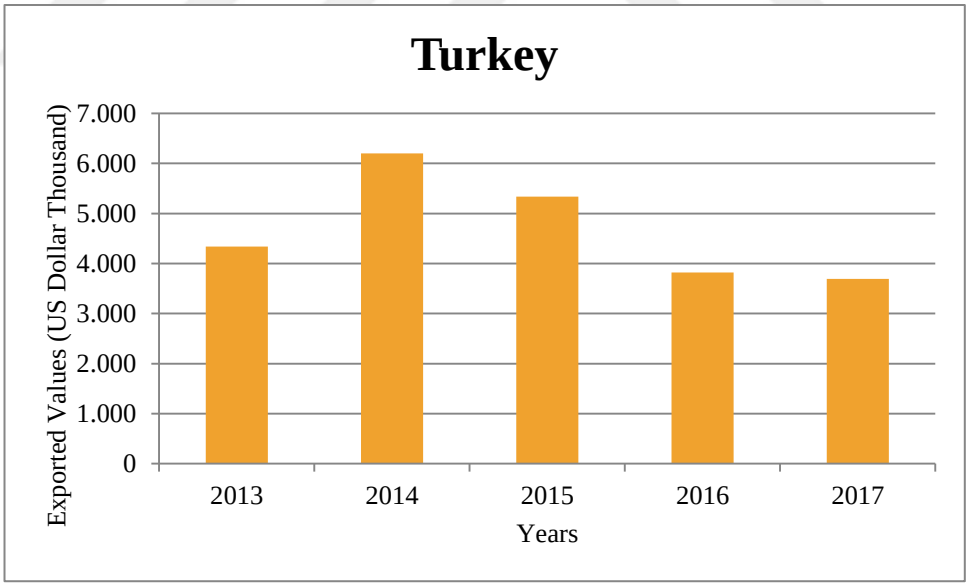

Figure 6.26 The exported supercapacitor values of Turkey [167]

As it was mentioned in the previous chapters, supercapacitors display various benefits and advantages like large power performances, long life cycle, large power rating charge and discharge. Due to their supplying demand, they can be used in a lot

of applications and sectors. This situation has played an important role on the their import values. Table 6.21 gives the relationship between significant importers and their imported values in different years. According to Table 6.21, the year with the highest imported value is 2014. This value is equal to 30508982 US Dollar in the world. In Table 6.21, China was located the first order in terms of its imported values in given years. When Table 6.20 and 6.21 was compared with each other, it can be stated that there is a slight inverse proportion between imported and exported values. For example, China was placed in the third position in Table 6.20. But, China presented the most highest imported value which was equal to 11457339 US Dollar thousand in Table 6.21 in 2014. Hong Kong is ranked in the second position in 2014 in terms of imported value for supercapacitors as it can be observed in the following table. When these tables were carefully analyzed and evaluated, Hong Kong and China have attached importance to importation and exportation of supercapacitors and played important roles on the supercapacitor market [167].

Table 6.21 Imported supercapacitor values of world and several countries in different years [167]

Importer	In 2013	In 2014	In 2015	In 2016	In 2017
World	29.161.255	30.508.952	28.228.988	26.031.052	28.677.015
China	11.204.182	11.457.339	10.213.918	8.030.120	8.684.355
Hong Kong, China	4.358.161	4.606.865	4.902.836	4.636.508	4.887.291
Germany	1.522.564	1.575.765	1.433.669	1.567.593	1.848.880
USA	1.387.523	2.206.636	1.711.399	1.306.769	1.417.994
Mexico	1.137.064	1.210.824	1.127.946	1.144.464	1.217.453
Taipei, Chinese	884.461	814.862	750.771	1.073.448	1.184.076
Korea, Republic of	1.068.626	934.334	925.042	912.025	1.060.618
Singapore	1.058.572	984.371	876.709	948.639	1.155.631
Malaysia	548.18	577.418	559.928	651.686	722.958

Figure 6.27 and 6.28 display the illustrations of the imported values of the world and China in years which were given in the Table 6.21.

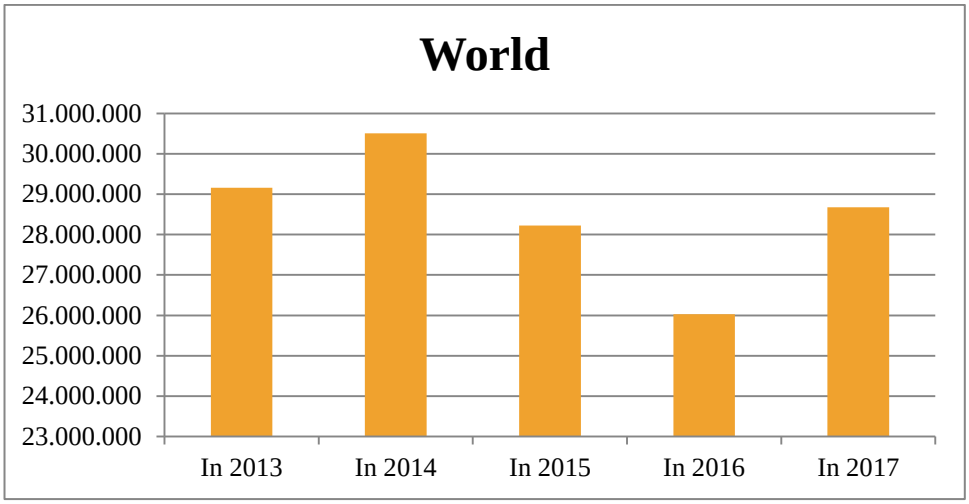

Figure 6.27 Illustration of imported supercapacitor values of world in different years [167]

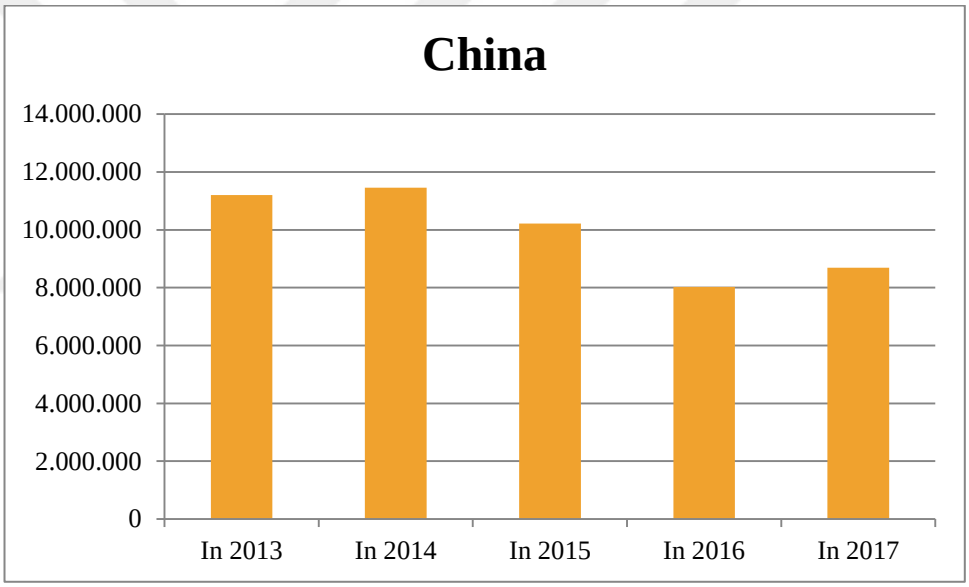

Figure 6.28 Illustration of imported supercapacitor values of China in different years [167]

6.3 Overview of Energy Storage Background In The World and Turkey

6.3.1 Overview of Fuel Cell Background In The World and Turkey

One of the most important purposes of Turkey is to reduce dependence on foreign energy sector which is based on the fossil fuel consumption and to pass low-carbon

economy. In order to overcome this problem, Turkey have attached importance to renewable energy sources and technology for a long time. Hydrogen technology has become the most important part of renewable energy technologies [168].

A report which was called “National Hydrogen Strategy of Turkey for priority areas” was written by SHURA company with the help of Bilkent University Energy Policy Research Center. According to results of this report, Turkey displays 1.6 million tons of green hydrogen potential. All of this green hydrogen is generated from renewable energy sources. This situation gives rise to be used hydrogen in many sectors which include production, transportation, natural gas. These sectors benefit from fossil fuels very much. As reported by the report’s writers, it is estimated that this amount of hydrogen can meet 5% of the annual energy demand. So as to occur this prediction, an investment of at least 45 billion dollars is required [168].

According to this report, the main purpose of both SHURA company and Bilkent University Energy Policy Research Center is to contribute to form Turkey’s green national hydrogen strategy. Investment of 45 billion dollars includes 36 GW renewable energy sources and 12 GW electrolysis installed power in order to obtain 1.6 million tons of green hydrogen [168].

Hydrogen has played important role on the production of substances like ammonia, methanol, heat production in many sectors such as petrochemistry and cement industries, steel fabrication by means of arc furnaces in Turkey’s production industry. To transition to the hydrogen economy requires serious research and development activities. Hydrogen production is a significant area for Turkey. However, the main problem is the production costs which must be decreased. As long as the capacity factors are below 50%, the cost of the hydrogen production is very high. Additionally, processing and transportation of hydrogen has also created problem. Distributed or centralized production can make significant differences [168].

Taxies in France, trains in Germany and metrobuses in Turkey meet their energy demands with the help of hydrogen and hydrogen-based fuel sources [168].

One of the most important points is that the electrolysis technology must be required for the production of hydrogen. Turkey has not dominated this technology. Therefore, researchers and scientists must find a solution for this negative situation [168].

70 – 100 million tons of hydrogen are globally obtained. To use green hydrogen for decarbonization of industrial production will be enough for the future of hydrogen. If investments are not made for the production technologies, many companies or researchers cannot pave the way for hydrogen [168].

Turkey should attached importance to hydrogen technology. Hydrogen can be used in gasification of lignites, pyrolysis of natural gas, and the hydrolysis of metals such as boron and aluminum which must be researched and studied as well as electrolysis of water in hydrogen production. Thanks to this mentioning technology, it provides outstanding benefits and contributions for both abundant boron reservoirs and hydrogen production in portable systems when desired [168].

Several countries are making plans about how they can have a share in the international hydrogen market after domestic consumption. These countries include Morocco, Tunusia which possess abundant and rich renewable energy sources. In addition to this, Europe will provide 1.23 trillion Euro financial support to the hydrogen technology. By drawing inspiration from these countries, Turkey must make plans about hydrogen or fuel cells market since Turkey occupies an important location in terms of renewable energy sources in the world [168].

Hydrogen is also one of the most abundant elements in the world. Therefore, when and how hydrogen will be used is an important topic. Many companies and researchers call attention to hydrogen and Europe needs seriously green hydrogen. Apart from this demand, Turkey has a great potential in terms of renewable energy sources and systems as it was mentioned. By benefitting from these sources and systems, Turkey can play significant role on hydrogen production and exportation this produced hydrogen into other countries. Renewable energy sources and systems can generate hydrogen with the help of the electrolysis and Turkey has great ability for the occurrence of this situation [168].

Germany and other developed industrial countries have carried out significant studies about decarbonization. So as to reduce the amount of carbon level, Germany needs green hydrogen. But, they do not have a high capacity or sufficient amount of hydrogen. Therefore, these countries can significantly import liquified hydrogen from South Africa. As well as this importation, many companies and scientists think that hydrogen pipelines can also be constructed between Germany and Norway or other hydrogen produced countries. By considering all these conditions, Turkey should be the best alternative because of having considerable renewable energy resources and hydrogen potential for exportation [168].

Turkey has become one of the most promising countries for hydrogen production. However, hydrogen technologies, hydrogen transportation or distribution and hydrogen storage methods need also to be improved in Turkey. Hydrogen will be one of the most excellent energy vectors around the world in the next 10 – 15 years. Both private and state sector must provide good contributions to hydrogen technologies about funding. Companies or constitutions which made studies on hydrogen technologies, need collaborate in order to develop hydrogen technology. Hydrogen is also complement for excellent decarbonization [168].

Turkey needs hydrogen strategy as soon as possible. In this framework, targets for hydrogen need to be determined. Furthermore, sectoral priorization must be carried out for hydrogen. In this situation, the exportation can also be evaluated as an alternative. Cost has been one of the most serious issues which most people have brought into the forefront. These costs should be evaluated with infrastructure costs. Because hydrogen is a technology which needs excellent infrastructure. In addition to this, a scientific organization should also be established in order to conduct studies on hydrogen technology [168].

International Energy Agency (IEA) has presented many reports which are related to hydrogen technology and its future improvements. According to these reports, clean hydrogen benefits from remarkable and unexpected acceleration of political and business performances. As well as this, studies and applications of these studies have increasingly continued. As it was mentioned before, hydrogen is one of the most outstanding and excellent elements for energy because the main roperty of hydrogen

is its energy carrier. Therefore, researchers and scientists must seize the opportunity in effort to create viable environment and improve energy secure of the countries [169].

The generation of hydrogen is generally carried out by applying processes to various substances like natural gas, biomass and water. Nowadays, the hydrogen is basically generated by making use of natural gas and this situation constitutes approximately three quarters of the yearly global hydrogen generation of nearly 70 million tonnes. In addition to this, hydrogen can also be obtained from oil, fossil fuels and electrolysis of water. These processes create expensive costs which are affected by financial and technological elements. Because gas and other technological instruments have become one of the most determining factors for cost of hydrogen generation. Hydrogen can easily be produced in the Middle East, Russia, and North America due to their low-costs for their low gas prices. Japan, China and Korea has significantly made gas importation from several countries and this situation provides enhancement of the gas prices and naturally costs of hydrogen generation [169].

Fuel cell electric vehicles (FCEVs) have also been improved at the market because of thier excellent development in China, Japan and Korea. World needs yearly 70 Mt (Metric tonne) of pure hydrogen and most of it is generated by processing of oil and using chemical reactions. Researchers and scientists have also aimed at the low carbon hydrogen generation because a significant amount of carbon dioxide is produced while natural gas or other fuels are processed during hydrogen production [170].

Table 6.22 and Figure 6.29 display the usage of fuel cell electric vehicles (FCEVs) in the world and several countries and FCEVs targets of these countries in several years. As it can be observed in the Figure 6.29 and Table 6.22, Fuel Cell Electric Vehicles (FCEVs) is increasing over the years in the world and several countries [170].

Table 6.22 The number of FCEVs in the world and several countries and their targets in several years [170]

World and Countries	The number of FCEVs
Japan in 2017	2300
Japan in 2018	2926
Japan in 2019	3633
Japan target in 2025	200000
Japan target in 2030	811200
Netherlands in 2017	34
Netherlands in 2018	48
Netherlands in 2019	241
Netherlands target in 2025	18000
Netherlands target in 2030	300000
Worldwide in 2017	7186
Worldwide in 2018	12952
Worldwide in 2019	23354
France target in 2028	52000
France target in 2023	5200
China in 2018	1791
China in 2019	6180
The USA in 2017	3531
The USA in 2018	5899
The USA in 2019	8039

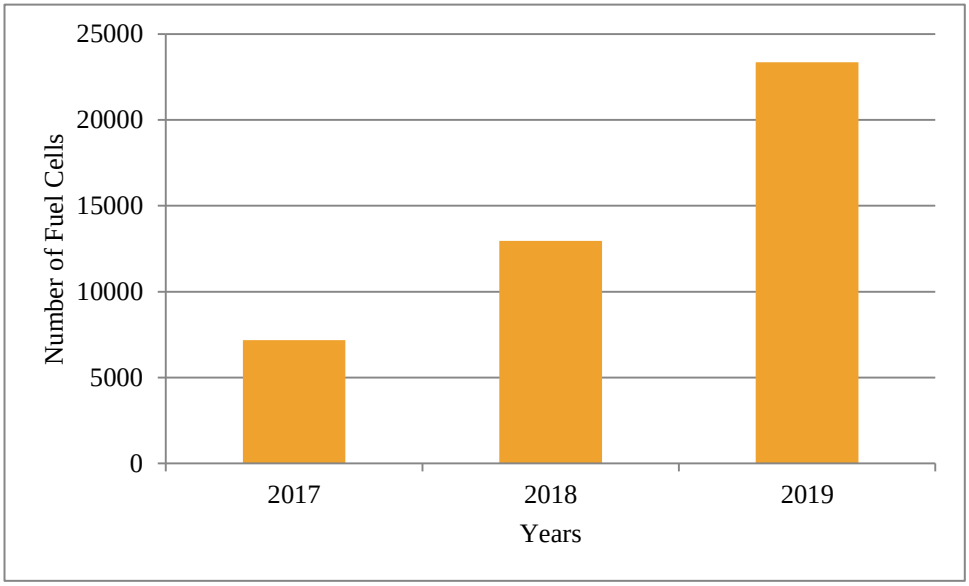

Figure 6.29 The illustration of the number of FCEVs in the worldwide [170]

Both hydrogen generation and hydrogen technologies showed remarkable improvements in 2019 which was also a good year for electrolysis efficiency. Table 6.23 and Figure 6.30 exhibit the low-carbon hydrogen generation between 2010 and 2030 with the values with the announced and SDS (Sustainable Development Scenario) [170].

Table 6.23 The relationship between Metric tonne (Mt)/year in different years [170]

Years	Metric tonne (Mt)/year
2010	0.04
2011	0.04
2012	0.05
2013	0.23
2014	0.23
2015	0.36
2016	0.37
2017	0.37
2018	0.37
2019	0.36
2020	0,46
2021	0,55
2022	0.86
2023	1.45
2030 target	7.92

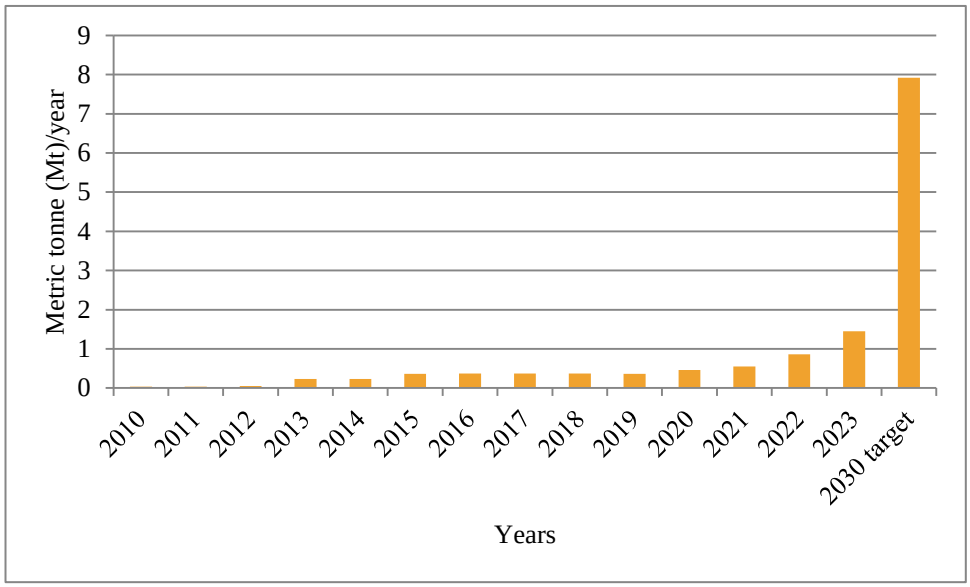

Figure 6.30 The relationship between the amount of Metric tone (Mt)/year and different years [170]

Low-carbon hydrogen generation is provided by means of the electrolysis. There are two main low-carbon hydrogen generation ways which are known as Coupling Conventional Technologies with CCUS (Carbon Capture and Utilization or Storage) and water electrolysis [170].

Several companies and institutions are working on the combination of conventional technologies with CCUS in order to produce low-carbon hydrogen. In 2019, 350000 tonnes of low-carbon hydrogen were produced by using this process. In addition to this, in 2020 higher than 20 new projects was disclosed in neighbouring countries to North Sea [170].

The USA carried out important sales of FCEV. For example, the number of FCEV sales in the USA was equal to 2300 in 2018 and 2100 in 2019. According to this statement, a decreasing was observed in 2019 in terms of number of FCEV sales. But, the USA has become one of the most outstanding countries for FCEV sales. After the USA, China, Korea and Japan have been the leading countries regarding FCEV sales [170].

The main purpose of Asian countries was to close their differences with the USA from the point of FCEV sales. For example, Japan made 700 FCEV sales in 2019 and this value is higher than the FCEV sales in 2018 (600 FCEV) [170].

So as to utilize the FCEVs, the hydrogen refuelling stations have been built. 470 hydrogen refuelling stations were put into service in 2019. This value is equal to 20% higher than the value in 2018. Table 6.24 and Figure 6.31 present the number of hydrogen refuelling stations in several countries [170].

Table 6.24 The number of hydrogen refuelling stations of countries [170]

Countries	The number of hydrogen refuelling stations
Japan	113
Germany	81
USA	64
China	61

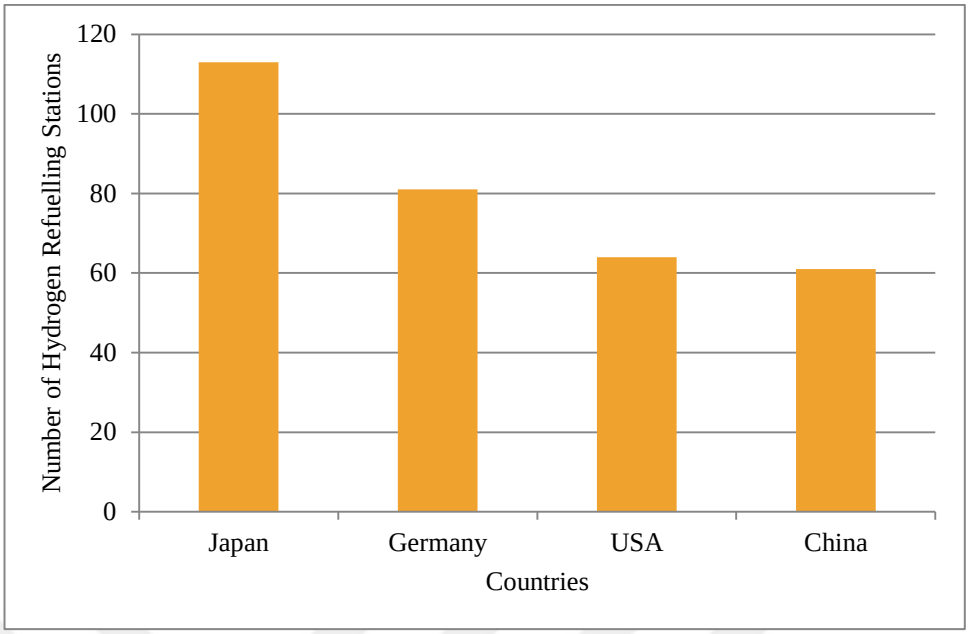

Figure 6.31 The illustration of the number of hydrogen refuelling stations of countries [169]

Alstom has been one of the most outstanding companies in railway technologies and the main purpose of this company is to fabricate rail vehicles [171]. Germany put into service two fuel cell rail trains with the association of Alstom in 2018. Furthermore, 14 fuel cell trains will also be used in 2021 in Germany. Both the Netherlands and the United Kingdom have drawn their attention to Alstom fuel cell trains. China started to use these trains in 2019 [170].

Several important developments took place in the world for hydrogen technology. The USA, the European Commission and Japan made an agreement on hydrogen Technologies. Additionally, in 2019 Hydrogen Initiative was also started at the 10th Clean Energy Ministerial (CEM10). This initiative was held in Vancouver, Canada. The main purpose of this initiative is to attach importance to and improve the fuel cell and hydrogen Technologies. Canada, the USA, the Netherlands, Japan and European Commission participated in this initiative and made leadership in this initiative. As well as this, Hydrogen Joint undertaking and the European Fuel Cells put the Hydrogen Roadmap for Europe in order to make decarbonization of gases during the hydrogen production. Apart from these targets, Korea made also important strides for fuel cell technology. In January 2019, they determined its own Hydrogen

Economy Roadmap. Thanks to this roadmap, Korea generated FCEVs which have passenger capacity of 6.2 million and improved the usage of 40000 fuel cell buses, 30000 fuel cell trucks by 2040. Netherlands made a publication of a Climate Agreement which is related to hydrogen generation and various environmental problems. According to this agreement, 500 MW generation of hydrogen will be obtained by benefitting from electrolysis by 2025. In addition to this, 15000 FCEVs and 3000 hydrogen-based trucks were put into service [170].

35 international establishments and countries took part in Second Hydrogen Ministrial Meeting in 2019 and their main purpose is to enhance studies and the usage of hydrogen. According to this meeting, 10 million FCEVs will be brought into service within ten years and this meeting aims at the improvement of hydrogen technology [170].

6.3.2 Overview of Supercapacitor Background In The World and Turkey

Japan, USA and China have fulfilled important and outstanding studies about hybrid vehicles. Good improvements have been observed for a long time. As it was mentioned in the previous chapters, supercapacitors or other energy storage devices have been utilized for an auxiliary power supply. Electrical Double Layer Capacitors (EDLCs) have been used in elevators, health applications, and heavy duty equipments because of their sustainable discharge of power source. Pseudocapacitors have been preferred in personal devices such as laptops, wireless tools. As a result, researchers estimated that the supercapacitor market will be increased in consumer electronics applications by pseudocapacitors [163].

North America has been placed in the first position in supercapacitor market. According to the researchers, North America will continue to become dominant on supercapacitor market and technology. By means of the usage of renewable energy systems and high technologies like electric vehicles in the USA and Canada, the improvement of the energy market will be provided. The supercapacitor market is on the onset or newly-emerging market. It is estimated that the supercapacitor market will exponentially increase in the Acia Pacific area. The enhancement quantity of business investments in Asia-Pacific location can lead to ameliorate industry. By

depending on this expression, the existence of fabrication consumer electronics and automotive companies in China, Japan and South Korea has contributed to make progress the usage of supercapacitors in Asia-Pacific location [163].

Table 6.25 and Figure 6.32 put emphasis on the supercapacitor industry in the world and give the number of patent of leading 10 companies. As it can be clearly seen in Table 6.25 and Figure 6.32, Matsushita Electric Ind. Co. Ltd. has become by far one of the most developed companies owing to its large number of patents (837). Samsung Electro Mech has also paid attention to the supercapacitor market and is located in the second order in the leading supercapacitor industry [167].

Table 6.25 The supercapacitor industry in the world [167]

Companies	Number of Patent
MATSUSHITA ELECTRIC IND CO LTD	837
SAMSUNG ELECTRO MECH	478
NEC CORP	362
ASAHI GLASS CO LTD	355
TDK GROUP	332
NIPPON CHEMICON	302
HONDA MOTOR CO LTD	272
MURATA MANUFACTURING CO	260
OCEANS KING LIGHTING SCIENCE	245
ELNA CO LTD	240

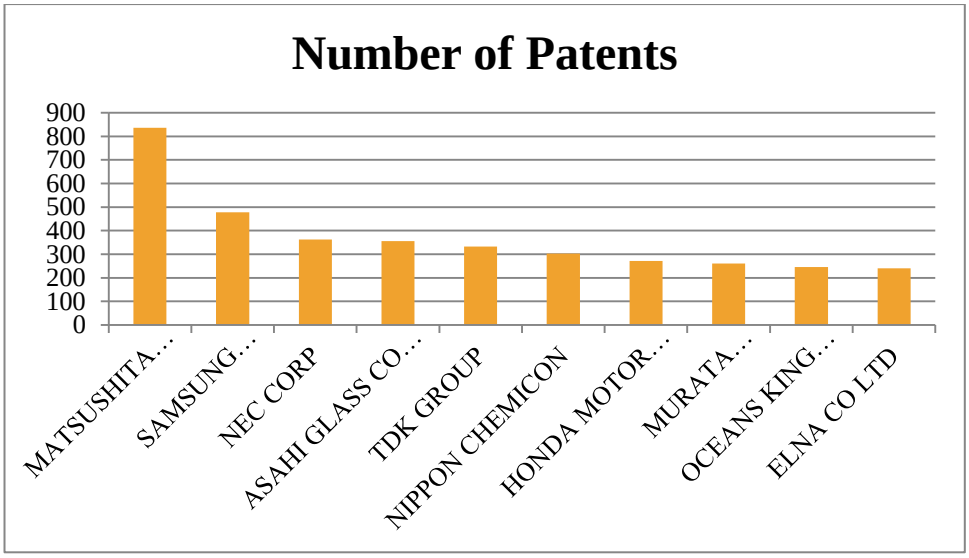

Figure 6.32 The graph of the number of patents of 10 companies in supercapacitor industry [167]

Table 6.26 and Figure 6.33 indicate that some universities possess a significant number of patents. All of these universities are in China which has made efforts for improvement of supercapacitor industry and market [167].

Table 6.26 Number of patents of important universities [167]

Universities	Number of Patents
TSINGHUA UNIVERSITY	129
ZHEJIANG UNIVERSITY	126
TIANJIN UNIVERSITY	100
JILIN UNIVERSITY	100
CENTRAL SOUTH UNIVERSITY	96
SOUTHEAST UNIVERSITY	92
SHANGAI JIAOTONG UNIVERSITY	83

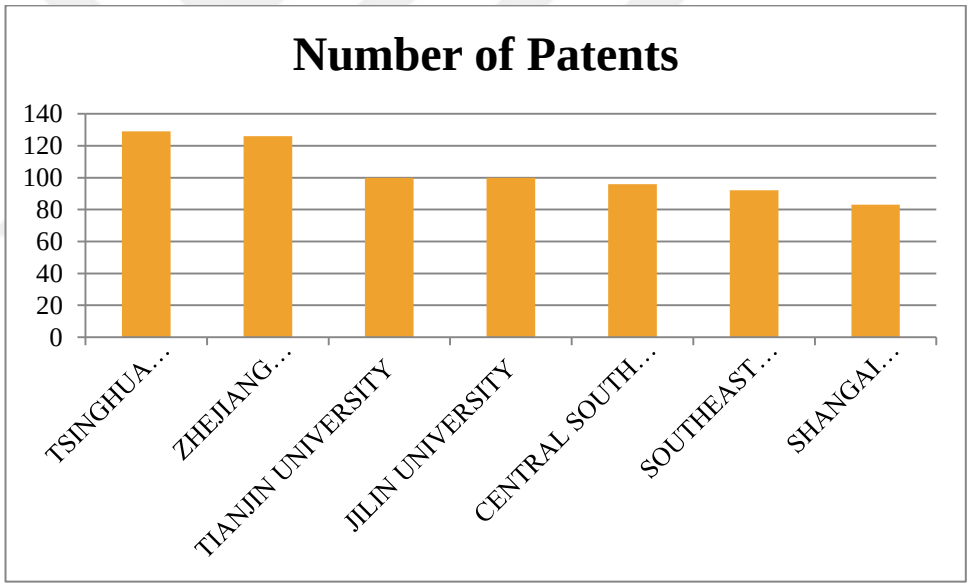

Figure 6.33 Illustration of Table 6.26[167]

Table 6.27 and Figure 6.34 represent the number of patents of 9 countries by depending on their markets. According to Table 6.27 and Figure 6.34, Japan has become one of the most leading countries in the world in terms of patents. The number of patents in Japan is equal to 2868. Matsushita Electric Ind. Co. Ltd. is one of the most outstanding companies in Japan and contributes to develop the supercapacitor market. In addition to this, this company has also the greatest share in

the supercapacitor market of Japan. These companies continue also to remain their studies regarding supercapacitor technology and fabrication [167].

Table 6.27 Number of supercapacitor patents of countries [167]

Countries	Number of Patents
JAPAN	2868
USA	2470
KOREA	2262
CHINA	1059
GERMANY	821
FRANCE	378
RUSSIA	164
GREAT BRITAIN	112
CANADA	108

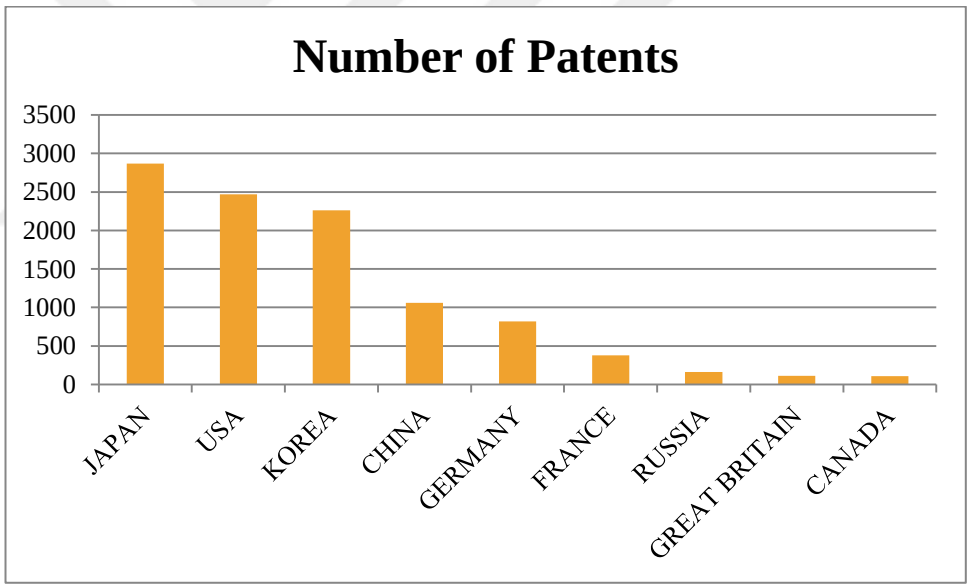

Figure 6.34 Graph of Table 6.27 [167]

Table 6.28 and Figure 6.35 shows 10 important investors and their supercapacitor patents. As it can be clearly seen in Table 6.28 and Figure 6.35, Zhou Mingjie carried out important investments for the supercapacitors and possesses 228 patterns. Thus, she is ranked in the first place in terms of the supercapacitor patents. Apart from this, she has aldo 70% share of Ocean's King Lighting which has become one of the best suppliers in China. Wang Yaobing occupied the second place of Table 6.28 and is a

member of Chinese Academy of Science which has been one of the most outstanding institutions in China [167]. The main purpose of this institution is to discover and improve their technology and natural sciencies for both China and the world [172].

Table 6.28 The number of patents of supercapacitor investors [167]

Investors	Patents
ZHOU MINGJIE	228
WANG YAOBING	227
HIRATSUKA KAZUYA	207
MORIMOTO TAKESHI	155
YOSHIDA AKIHIKO	152
RUAN DIANBO	145
WANG YONG	117
FU GUANSHENG	113
NISHINO ATSUSHI	110
GUAN CHENGSHAN	101

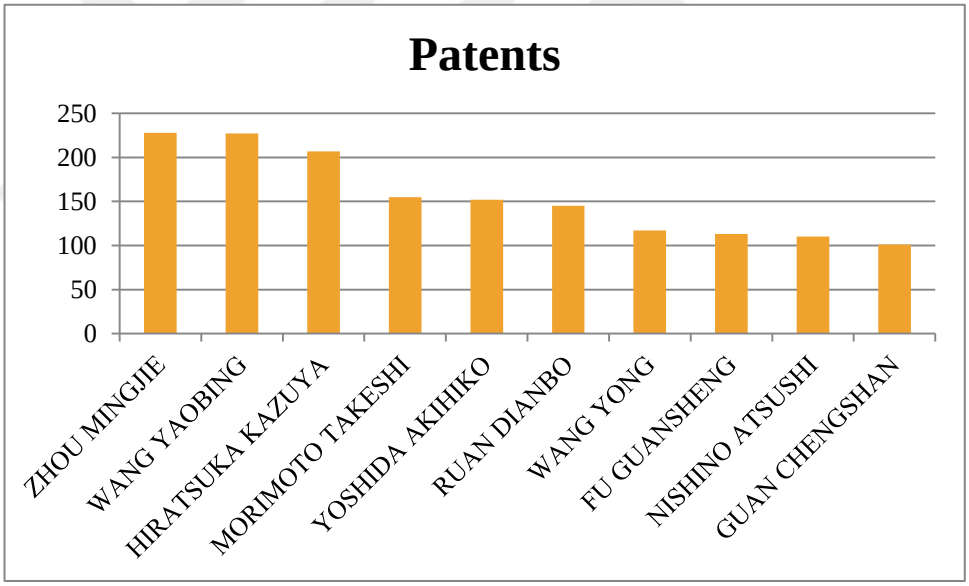

Figure 6.35 The relationship between investors and their patents [167]

Table 6.29 and Figure 6.36 presents the most eminent cited applicants or candidates which possess a great effect on supercapacitors. They were prepared on the basis of their supercapacitor patents. According to Figure 6.36, Matsushita Electric Ind. Co. Ltd. involves 942 cited applicants. At the same time, Toyota Motor Corporation owns also 341 cited applicants and was ranked in the second order. The most striking

point in Figure 6.36 is that Zhejiang University occupie seventh place in Table 6.29. This means that this university has undertaken initiatives and studies for supercapacitors [167].

Table 6.29 The quantities of patents of the highest cited applicants [167]

The Highest Cited Applicants	Number of Patents
MATSUSHITA ELECTRIC IND CO LTD	942
TOYOTA MOTOR CORP	341
SANYO ELECTRIC CORP	301
SONY CORP	262
NEC CORP	252
TDK CORP	243
ZHEJIANG UNIVERSITY	229
MITSUBISHI ELECTRIC CORP	212
HITACHI LTD	206
TOSHIBA CORP	206

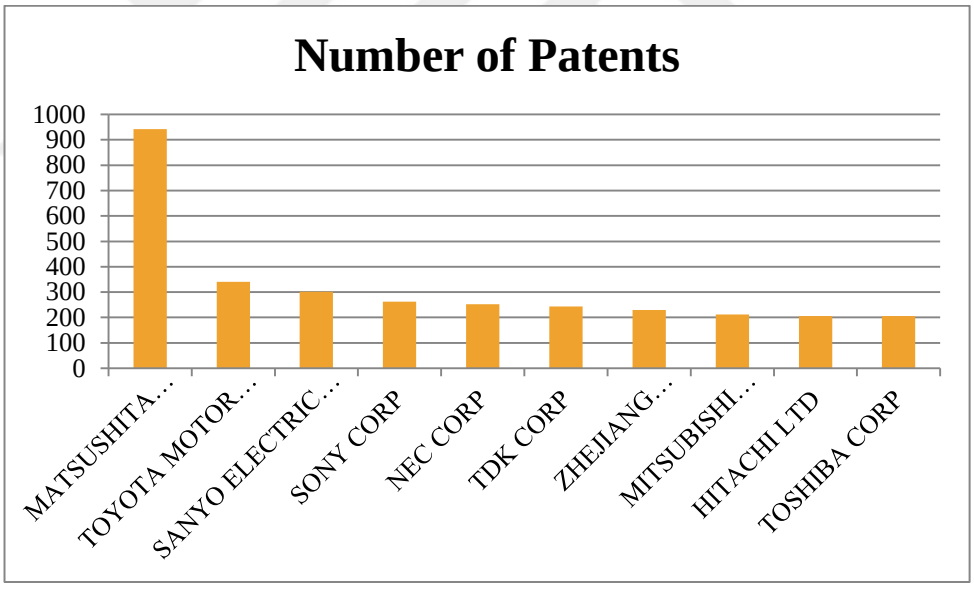

Figure 6.36 The relationship between the highest cited applicants and number of patents [167]

Table 6.30 and Figure 6.37 represent the number of patents of the leading companies which have played vital roles on the supercapacitor market and technology. They were created by analyzing various data in 2018. According to Figure 6.37, Samsung Electro-Mechanics made 23 patents publications in 2018 and it takes place in the first

order. On the other hand, Nanotek Instruments Inc has taken important responsibilities for the development of supercapacitors and published 19 patents in 2018. It was ranked in the second order after Samsung. As it can be clearly seen in Figure 6.37, Samsung showed a remarkable increasing in the supercapacitor technology in terms of patent publication [167].

Table 6.30 Number of patent publications of outstanding institutions and companies [167]

Institutions or Companies	Number of Patent Publications
SAMSUNG ELECTRO MECH	23
NANOTEK INSTRUMENTS INC	19
MURATA MANUFACTURING CO	17
SEMICONDUCTOR ENERGY LAB	16
CENTRE NAT RECH SCIENT	14
CALIFORNIA UNIVERSITY	14
BLUE SOLUTIONS	13
CRRC ZHUZHOU LOCOMOTIVE CO LTD	13
STATE GRID CORP CHINA	13
TAIYO YUREN KK	13

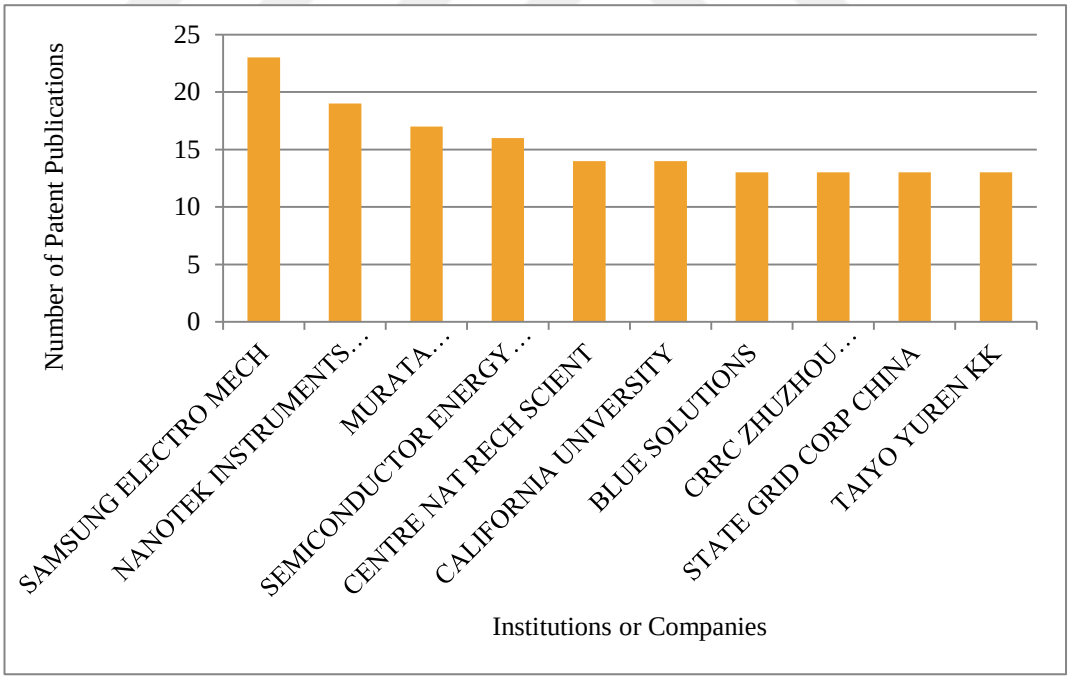

Figure 6.37 The relationship between institutions and companies and their number of patent publications [167]

In addition to this, as Figure 6.36 can be analyzed and evaluated, Matsushita Electric Ind. Co. Ltd. possesses the largest cited applicants as compared to other companies or institutions [167].

Turkey has also taken part in significant studies and investigations of supercapacitors. Some scientists have 3 applications for supercapacitor technology in Turkey. Furthermore, Nokia Technologies has improved 2 applications. One of the most prominent inventors in Turkey with his 4 patents is Husnu Emrah Unalan at METU [167].

As it was mentioned in the chapter of supercapacitor market, Turkey made also important exportations in several years and 2014 was a lucrative year for Turkey in terms of exported values (6203 US Dollar Thousand). When the table of exported values of outstanding countries in different years in terms of US Dollar Thousand is analyzed and evaluated, 2017 is one of the years with the lowest supercapacitor exportation (3695 US Dollar Thousand) [167].

6.3.3 Overview of Batteries Background In The World and Turkey

Since December 2019, there have been 115 billion lithium ion battery Megafactories in the world. Additionally, one of the most outstanding battery producers provided a great 564 GWh of contribution in 2019 and this value will reach to 2068.3 GWh worldwide. The Figure 6.38 represents the yearly lithium-ion battery requirement in the world. According to Figure 6.38, passengers EVs constitute a large part of the demand. Europe have played important roles on batteries and possessed 348 GWh in 2018. One of the most important purposes of China is to provide addition of 564 GWh by 2028 [173].

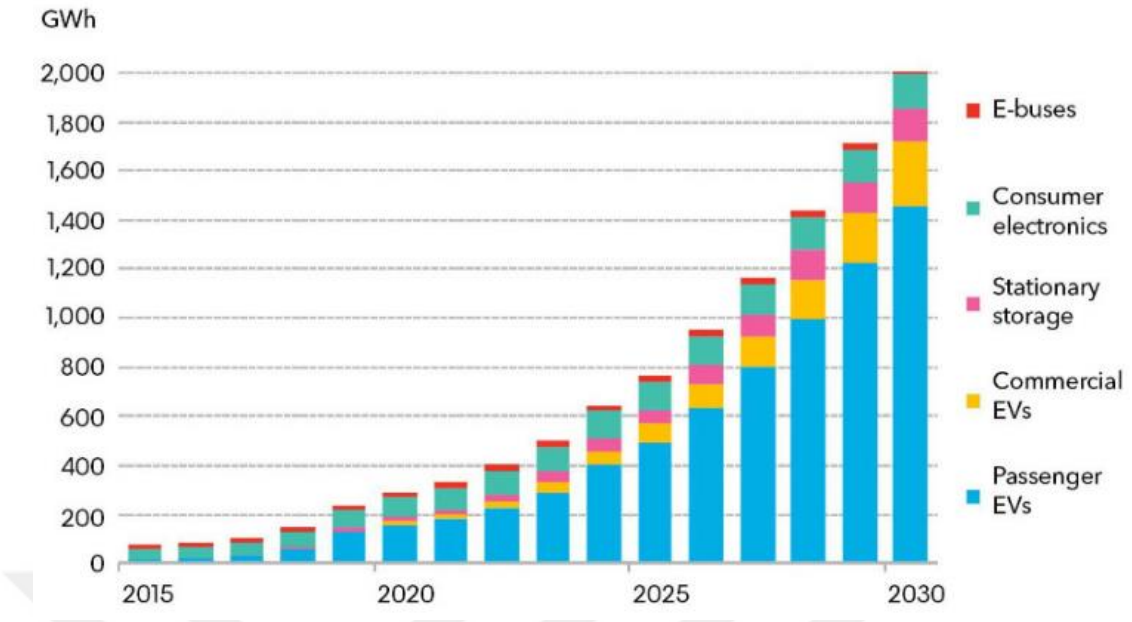

Figure 6.38 Yearly lithium – ion battery requirement for the several applications [173]

Lithium-ion battery requirement has increased from a generation basis of 19 GWh in 2010 to a generation of 160 GWh in 2019 [173].

LG Chem has become one of the most prominent companies which work on both battery and chemical industry [174]. LG Chem presented excellent lithium-ion batteries which have higher than 50 GWh of generation capacity. The main purpose of this company is to improve its capacity to at least 170 GWh in 2024 for lithium batteries. Contemporary Amperex Technology indicated that its lithium battery generation capacity is higher than 40 GWh. According to calculations and evaluations of this company, its battery generation capacity can reach 137 GWh in 2022. Contemporary Amperex Technology is establishing a 146 GWh battery plant and this establishment process will be brought into completion in 2022. Panasonic has also carried out important studies of batteries and designed approximately 35 GWh of batteries which will increase their generation to 54 GWh [173].

According to Table 6.31 and Figure 6.39, LG Chem, CATL and Panasonic have been leading companies in the battery market share. Remarkable differences could be observed between these companies and other three companies [175].

Table 6.31 The relationship between the companies and their battery market [175]

Companies	Battery market share of these companies
LG Chem	26,50%
CATL	25,80%
Panasonic	20,60%
SDI	6,80%
BYD	6,20%
Others	14,10%

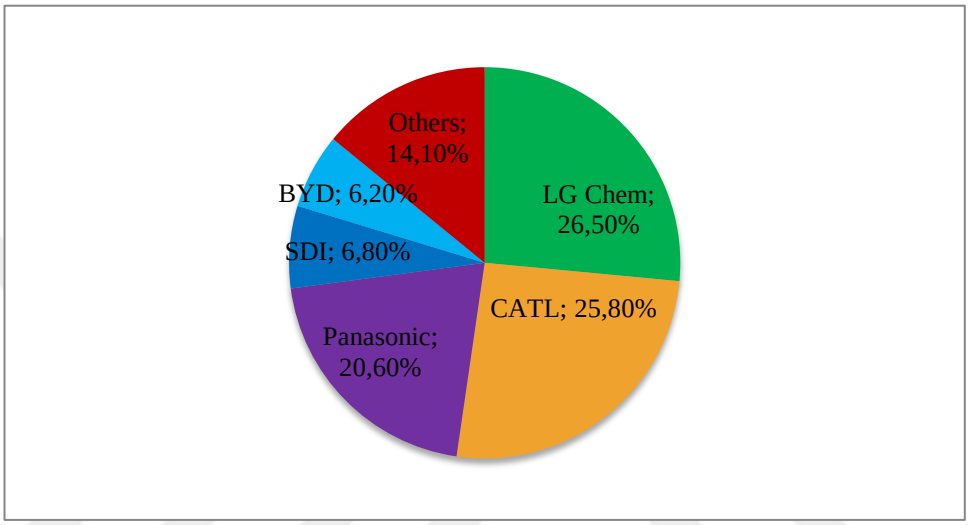

Figure 6.39 The illustration of the relationship between the companies and their battery market [175]

By depending on Table 6.32, LG Chem played important role on the batteries and produced 15.9 GWh between January and August 2020 [175].

Table 6.32 The amount of energy of the outstanding battery companies [175]

Company	Gigawatt-hours (GWh)
LG Chem	15,9
CATL	15,5
Panasonic	12,4
SDI	4,1
BYD	3,7
SKI	2,7
AESC	2,2
Guoxuan	1,2
PEVE	1,2
CALB	1,2

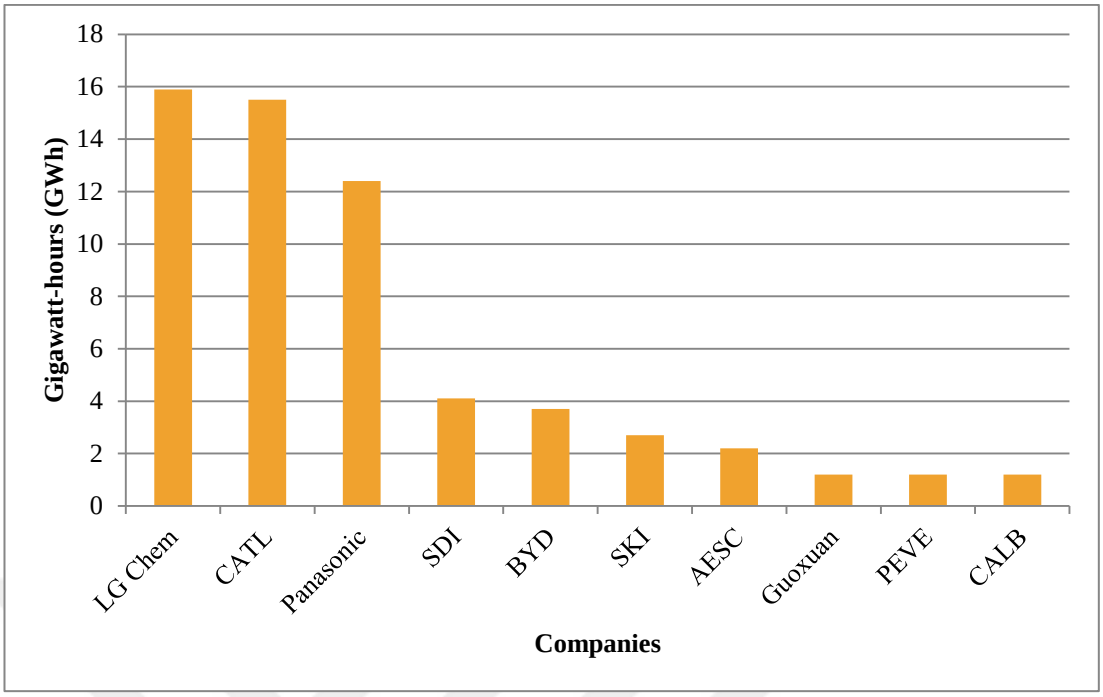

Figure 6.40 The relationship between outstanding battery companies and their amount of energy [175]

Meanwhile, there are higher than 100 Turkish car battery producers in Turkey. However, a great majority of these companies involves the small producers or companies. There are three main battery producers such as Mutlu Battery, Inci Battery and Yigit Battery in Turkey when battery sales were analyzed and evaluated. They can be regarded as three main leading battery manufacturers by depending on their battery sales according to many reports [176].

Mutlu Battery has played a key role on the car battery production and fabricates yearly approximately 6 million units. This battery has been used in 70 of every 100 car which are generated in Turkey [176].

Inci Aku or Battery has also a great effect on the battery production in Turkey. This company started to colloborate with CEAC in 1993. CEAC has become one of the most eminent companies which carried out important studies about batteries. By means of this colloboration, Inci Battery entered globally the battery market and production. CEAC was bought by Exide which made excellent car battery productions. Thus, Inci Battery got into the world market. Developed technology has

also enabled it to keep up with many innovations. Nowadays, Inci Battery made exportation which is equal to 67% of the company's production [176].

Yigit Battery has obtained yearly 7000000 batteries by using high technology and carried out exportations of batteries to over 90 countries which are found in 5 continents. These continents are Europe, Asia, America, Middle East and Africa [176].

CHAPTER 7

DISCUSSION AND CONCLUSION

This thesis study consists of seven parts. Firstly, it was mentioned general information about significance of energy, energy crisis in the world, fuel cells and supercapacitors that are described as the definition of these energy storage devices. In the second chapter, types, advantages and disadvantages of fuel cells and supercapacitos are given in detail. The third chapter emphasizes their working principles and mechanisms. The fourth chapter includes information about the used materials in fuel cells and supercapacitors with their significant properties. In the fifth chapter, applications benefitted from these energy storage devices are given. Sixth chapter presents the comparisons of several properties like electrical conductivity, specific surface area of fuel cells and supercapacitors, market analysis of them and general overview of the supercapacitor, fuel cells and batteries in the world and Turkey. In the seventh chapter, the obtained results have been discussed. Briefly, the main purpose of this study is to give information about fuel cells, supercapacitors as well as analysing their energy storage performances with materials used in them.

As it can be seen in the Table 2.1, fuel cells benefit from the hydrogen-based fuel sources like natural gas, biogas, coal gas and oxygen. According to Table 2.1, fuel cells which displays excellent electrical efficiency and operating temperature is Solid Oxide Fuel Cells (SOFCs). Alkaline Fuel Cells can also be generally used in space applications like Apollo and Gemini program. The most significant factors which greatly affect the fuel cell performance are pressure, humidification and temperature. Furthermore, there are also outstanding several used materials for each fuel cell. For example, AFCs usually make use of Pt/Co alloys, Pt/C as their electrode materials. The main reason of usage of these materials is that Platinum offers superb activity for Oxygen reduction due to its excellent exchange current density. Tafel plot, Figure 2.1 has become one of the most prominent plots which determines the electrochemical kinetics of the materials for Alkaline fuel cells. The most promising

material of PEMFC is Nafion membrane which exhibits its larger acidity and its good conductivity. In order to excellent membranes, some important methods or techniques have been utilized such as plasma polymerization or radiation grafting. Among these techniques, the most useful method is plasma polymerisation which contributes to create thin exchange films. Ohmic resistances can also be reduced and drying of the membrane is prevented with the help of this method which provides creation of stable, cross-linked and uniform thin films.

The membranes of the fuel cells have significantly utilized water due to its high conductivity and water content must also be managed. Because, reactions which take place in the cathode of the fuel cells produce water and the control of the water content has become one of the most important issues.

The most preferable membranes for DMFC is phosphoric acid doped polybenzimidaole (PBI) membranes owing to their superior protonic conductivity and low gas permeability. One of the most important problems for DMFCs is the methanol cross-over effect because they make use of methanol as fuel source. In order to achieve this problem, methanol tolerant cathode must be fabricated. This type of cathode may not prevent methanol diffusion very well but it provides that fuel cells possess an durable structure against methanol diffusion or cross-over.

Phosphoric acid fuel cells (PAFCs) provide outstanding contributions like low electrolyte votality at operating temperatures, high thermal, chemical and electrochemical stability. They can also easily be constructed. Corrosion has been one of the most serious problems for PAFCs and diluted acid have been used so as to avoid this problem. It also contributes to increase the conductivity of the electrolyte. Tungsten carbide has also been preferred in PAFCs. The main reason of usage of this material is that it has long life time and presents outstanding resistance and stability structure. When CO was produced in the fuel cell in this case, this material does not harm the fuel cell.

MCFC usually benefit from methanol, hydrogen or carbonaceous fuels. Due to the utilization of these fuel sources, CO_2 is also obtained as it can be clearly seen in the (2.15) reaction. So, material for MCFCs must carefully be selected. One of the most

remarkable points about MCFCs is that CO_3^{2-} (Carbonate molecules) are produced as a result of fedding of CO_2 into the cathode side of the MCFCs. SOFCs may not encounter any issues which are based on water management, flooding of catalyst layer etc. The basic reason of this is that they include two-phase gas-solid system.

EDLCs possess better position than conventional capacitors in terms of energy density and greater advantage than batteries from the point of power density. There are also different mechanisms between types of supercapacitors. The system of EDLCs is pertinent to the adsorption and desorption of electrolyte ions on the interface which takes place in between the electrode and electrolyte when charge-discharge processes carried out without presence of the charge transfer reaction. But, the mechanism of the pseudocapacitors depends on the charge storage by means of Faradaic redox reactions. In EDLCs, absorption/desorption of ions and storing electric charges between two conductive plates occur with the help of the electric field. EDLCs benefit from materials like CNTs, graphene, activated carbon and pseudocapacitors make use of materials like TMOs, conducting polymers. RuO_2 has become one of the most prominent TMOs and presents higher theoretical capacitance (1450 Fg^{-1}) than that of carbon-based materials (>100 Fg^{-1}). When the Table 3.6 is carefully analyzed, supercapacitor offers greater specific power, quicker charge time, excellent coulombic efficiency and higher cycle life than battery. As it can be seen in the Table 3.5, EDLC and pseudocapacitance display similar characteristics with each other like charge time, cost per kWh, operating temperature, self discharge per month. EDLC has higher cycle life and cell voltage than pseudocapacitance. The mechanism of the fuel cell is generally based on the fuel source as it can be understood from the Table 3.1. Hydrogen is an important energy carrier and as long as hydrogen is fed into the fuel cell, fuel cell produces electricity. One of the most outstanding points is hydrogen storage. As it was explained in the Table 3.1, hydrogen storage is classified into two methods which are known as physical-based and material-based. In physical based method, hydrogen can be stored in tanks or other containers under certain pressure and conditions. In material-based method, hydrogen is absorbed on the substance's surface under certain pressure-temperature conditions. In addition to this, materials must show several important properties like great hydrogen fraction, good interaction of material with thydrogen, structure or

morphology of the material in this type of method. The utilized materials for hydrogen adsorption are generally Activated Carbon (AC), Zeolites, Metal-organic adsorbents and carbon nanomaterials. When Zeolites and other hydrogen storage systems are compared with each other, Zeolites display smaller storage capacity (10 cm^3/g) than that of other types of hydrogen storage systems. To overcome this problem, metal organic frameworks have been used as adsorbent material. As well as these hydrogen storage methods, Hydrogen cryo-adsorption on Activated Carbon has become more preferable and useful method owing to their lower power consumption than LH_2 and low-cost. Many researchers and scientists have also paid attention to carbon nanomaterials for hydrogen adsorption due to their excellent interaction with hydrogen like graphite nanofibers, fullerenes and nanotubes. Complex Hydrides which are also known as Alanates, can also be used for hydrogen storage because of its high hydrogen fraction. The main reason of the utilization of interstitial hydrides is that they can provide quicker a large amounts of hydrogen adsorption and desorption than other hydrogen storage methods. This method can also be preferred by virtue of their broader range of hydride stability, more excellent sorption kinetics and their their generation of a greater variety of hydrides than other hydrogen storage methods. According to the Table 3.4, hydrogen gas, liquid hydrogen and water include more hydrogen content than other interstitial hydrides like MgH_2, $LaNi_5H_6$. However, hydrogen densities of these interstitial hydrides show differences by depending on their mass and volume.

Water electrolysis has become one of the most known hydrogen production methods. Therefore, hydrogen which is generated from the electrolysis can be used in the fuel cell as a fuel source.

Several important factors which have played key roles on the hydrogen storage capacity or performance, include sample weight, degree of purity, and Pressure (P)-Temperature (T) conditions.

The main difference between working principles of fuel cells and supercapacitors is that fuel cells and supercapacitors are based on the electrochemical reactions and electrical field, respectively.

Graphene has been one of the most preferable candidates for fuel cells owing to its great charge mobility, superb thermal conductivity, good adsorption of visible light, high specific surface area and excellent mechanical strength. One of the most important points is that it displays higher electron mobility and electrical conductivity than other used materials in fuel cells and this situation provides its more usage.

Perovskites have also been preferred because of their high absorption coefficient, excellent conductivity, charge ordering, colossal magnetoresistance etc. When Table 4.3 is carefully analyzed, perovskites have a great effect on the improvement of the electrical and gas diffusion properties of fuel cells. Table 4.4 indicates that Perovskites types materials have offered better properties than other types of materials like conductivity, performance and operating temperature.

One of the most remarkable materials is Ni/YSZ. The main purpose of this combination is that Ni gives rise to degrade anode. YSZ acts as an inhibitor against this degradation. In addition to this, the electrical conductivity of Ni/YSZ cermet is related to the nickel content in this composite material. When this cermet includes more nickel content, this material displays excellent electrical conductivity. According to the Table 4.5, Nickel possesses larger thermal expansion coefficient (TEC) than YSZ. This situation indicates that size of Nickel can show a change when the temperature starts to increase or decrease. Table 4.6 explains that Sr has a great effect on improvement of the electrical conductivity of Lanthanum Manganite.

SnO_2 can also combine with metal (M). This combination aims at decrease the electrical resistivity, increasing in the electrical conductivity and improvement of the activity and stability of SnO_2. Pt can also be used in SnO_2 nanowires in order to provide improvement of electrical contact which occurs between SnO_2 nanowires and carbon fibers.

Tungsten Oxide has also been preferred and used by virtue of its perfect proton transfer. Furthermore, it can also provide more excellent thermal stable structure to the fuel cell under electrochemical oxidation conditions. This material can also be

combined with Platinum (Pt) so as to abstain from the Carbon Monoxide (CO) poisoning which is very important issue for DMFC.

The materials which are going to be used in supercapacitors, must exhibit several outstanding properties to get more efficiency from them. These properties contain ionic size and type, the ion and solvent concentration. Activated Carbon, Carbon Nanotubes, CPs and TMOs have been the most preferable and useful materials for supercapacitors. For example, Activated Carbon has been utilized by virtue of their great surface area and perfect electrical characteristics. When Table 4.14 has been carefully analyzed, it can be observed that Activated Carbon presented different specific capacitances in different electrolyte solutions. By depending on this table, the specific capacitance value of Activated Carbon in aqueous electrolytes have been greater than that of in organic electrolytes. Another promising material for supercapacitors is CNTs which display excellent electrical conductivity, good pore structure and excellent mechanical and thermal stability. Conducting Polymers show better electrical conductivity and larger capacitance than carbon-based electrode materials. Wang and partners carried out a study about the types of Conducting Polymers like Polyaniline (PANI), Polypyrrede(PPy) and obtained that the graphene oxide (GO)-doped PANI (531 $F.g^{-1}$) is greater than that of PANI (216 F/g).

According to the performances and properties of used materials in both fuel cells and supercapacitors, these energy storage devices provide important benefits for future power generation plants and many aplications. Additionally, they present cleaner, more sustainable and reliable power generation source. Important and outstanding materials are used in fuel cells and supercapacitors in order to increase their performance as well as being low-cost, providing more usage in future applications. These used materials provide excellent electronic conductivity and contribute to increase their durability.

Electrolytes must hinder leakage and improve the capacitance. Therefore, aqueous electrolytes make use of different gels. As a result of this combination, a perfect stable electrolytic system is created with excellent cycling stability, rate capability, and large specific capacitance. As it can shown in the Figure 4.12, gate capacitance of the ionic liquids has been lower than that of organic electrolytes. Many kinds of

organic electrolytes which can operate at between 0 and 2.7 V, have also been available. These voltage values provide the improvement of the energy density of the supercapacitor.

Graphene can also be combined with Conducting Polymers. The main reason of this is that CPs display low stability during their long cycling exposure and graphene has prevented this negative situation. By depending on the Figure 4.13, it can be observed that a rectangular area which leads to change in oxidation states of PANI with two peaks. As it can be seen in the second plot of the Figure 4.13, the IR drop of CCG is smaller than the PANI-NF. Figure 4.14 made a comparison between G-PPyNF1 and G-PPyNF2. According to this figure, G-PPyNF1 exhibits higher conductivity than G-PPyNF2 because of its high graphene ratio and rectangular CV shape. Graphene can also benefit from organic molecules so as to improve its modification for electrode materials and increase performance of electrode materials. Metal-oxide based supercapacitive electrodes contribute to improve the capacitance of supercapacitors. Each of metal oxides materials presents larger energy density than carbon-basis materlals with EDLC. However, Metal Oxide-basis substances display sometimes low conductivity and slow ion transfer and this situation causes some problems that are related to cycle stability. When hybrid nanostructures that are obtained with combination of metal oxide and conducting material like graphene are used, electrical conductivity, morphological stability, and capacitance will improve. Ragone plot can be used to compare several energy storage devices like supercapacitors, fuel cell from the point of energy and power density. In accordance with the Figure 4.15, supercapacitors which are called as electrochemical capacitors, possess also greater power density and faster power delivery than batteries. In addition to this, they exhibit larger energy density than conventional electrostatic capacitors. In Figure 4.16, several materials were compared with each other in terms of annually development. According to this figure, carbon materials have become one of the most excellent, useful and outstanding electrode materials for supercapacitors by virtue of their large surface areas that store charges by benefitting from the physical adsorption of ions on the substance surface.

Fuel cells and supercapacitors have also been utilized in many applications such as military, portable, space, transportation etc. The main purpose of the usage of these devices is that energy sources have rapidly been consumed. These energy storage devices are inevitable for human beings and also known as environmentally friendly.

As Table 6.1 and Figure 6.1 are carefully analyzed and evaluated, the electrical conductivity of graphene is significantly higher than other used materials in fuel cell because of its structure. This situation indicates that graphene has become one of the most preferable materials in fuel cells. Electrical conductivity has been very important property for both fuel cells and supercapacitors for the electron transportation. Thermal conductivity is based on temperature, the porosity structure of the material, humidification, physical and metallurgical properties of the material. If the thermal conductivity of the material is low, this material displays insulating structure. Thermal conductivity is directly proportional to the movement or transportation of the electrons or ions and the increasing of the thermal conductivity contributes to the improvement of the kinetic energy of electrons. So, electrons can easily move inside both fuel cells and supercapacitors. According to Table 6.2 and Figure 6.2, Graphene exhibits larger thermal conductivity than other materials and this situation provides that the conduction and transmission of electrons are faster. In Table 6.3, it was observed that the thermal expansion coefficient (TEC) of the graphene is negative. The main reason of this situation is that it can originate from the bond energy width which depends on the change of the temperature. This width explains the locations of thermal vibrations of particle and is directly proportional to the temperature. If the width increases with the increasing of the temperature, the thermal expansion coefficient (TEC) can also be positive. For graphene, thermal expansion coefficient of graphene is negative due to its anharmonic effect at large temperatures. Anharmonic effect can be defined as the deviation of a system. As long as the temperature of the material increases, bond energy width of the materials will also increase and this situation contributes also to improve the TEC of the materials. According to Figure 6.3 and Table 6.3, Nickel has the leading position in terms of TEC and when Nickel combined with YSZ, it provides enhancement of TEC of YSZ from $11.0*10^{-6}$ to $12.48*10^{-6}$ because Nickel presents excellent electrical and thermal conductivity.

Specific surface area is one of the most important factors for the performance of the energy storage devices. As long as the specific surface area of the materials enhances, the adsorption of more electrons and other particles is carried out. Table 6.4 and Figure 6.4 depict that graphene shows significantly greater specific surface area than other used materials in fuel cells. Thanks to more adsorption of the electrons or particles which help their conduction or transmission, the performance of the energy storage devices can improve. Specific surface area of the material is significantly based on the structure and the porous morphology of it. As a result of these tables and figures, graphene presents excellent properties such as high specific surface area, great electrical and thermal conductivity except of TEC.

According to Table 6.5 and Figure 6.5, it can be easily observed that several used materials in supercapacitors display different specific capacitances. The specific capacitances of Carbon-based materials like Activated Carbon, Carbon Nanotubes are very close to each other. Amorphous Ruthenium Oxide has the highest specific capacitance between these materials. Capacitances are basically related to the number of ions which are collected at the interface which is located between the electrode and the electrolyte. The increasing of the temperature provides the movement of ions and electrons toward electrodes via pores. This movement contributes to increase specific capacitance and performance of supercapacitors. In other words, specific capacitance can be determined by temperature and specific surface area. Specific capacitance has a significant effect on both energy and power density as the relationship between specific capacitance and temperature helps the movement of electrons and ions.

When Table 6.6 and Figure 6.6 are carefully analyzed and evaluated, CNTs have the largest thermal conductivity among the used materials in supercapacitors. The electrolyte is one of the most significant components in the supercapacitor and can specify the performance of the supercapacitor. Because a perfect electrolyte gives a broad voltage window, great electrochemical stability, good ionic concentration and conductivity. Energy density can significantly be affected by voltage breakdown of the electrolyte. Additionally, power density depends on the electrolyte conductivity. As it can be understood from this statement, both energy and power density have

played key roles on the supercapacitor performance. Thermal conductivity has a great effect on the supercapacitor performance owing to the dependence of the power and energy density on the conductivity. Activated carbon has also the greatest specific surface area between the used materials in supercapacitors. In Table 6.7 and Figure 6.7, the working principle of the supercapacitors is based on the adsorption of ions and the improvement of specific surface area provides fulfillment of this adsorption. According to Table 6.8 and Figure 6.8, CNTs and Ruthenium Oxide (RuO_2) display the largest electrical conductivities between the used materials in supercapacitors. Electrical conductivity is one of the most important factors for the conduction or transmission of the ions. Fossil fuels have been used for a long time and give rise to several environmental problems like global warming, air pollution. Therefore, fuel cells offer excellent opportunities in order to prevent these drawbacks.

Figure 6.9 indicates that fuel cells are the most preferred and used energy storage devices in stationary power applications as compared to two other applications in terms of number of fuel cells. According to Figure 6.10, fuel cells provide high amount of power for the transportation application in terms of Megawatts (MWs) in 2016. Figure 6.11 gives important information about fuel cells and states that many Asian countries contribute to distribute the fuel cells to the world. After Asian countries, North America has played a vital role on the distribution of fuel cells. Table 6.9, Figure 6.12 and Figure 6.13 present the values of the gross revenue and cost of revenue for the fuel cell market. According to these figures, FuelCell Energy Company exhibits a stable stance in both gross revenue and cost of revenue of the fuel cells in given years. Figure 6.16 has become one of the most informative figures about fuel cell shipments and indicates that fuel cell companies had shown outstanding improvements during six years in North America. Table 6.13 shows that three leading companies can also dominate the fuel cell market. As it can be observed in Table 6.14, the USA has attached importance to the fuel cell investments. The result which can be inferred from Table 6.14 is that the USA has drawn attention to the environmental disasters and made great efforts to reduce them. After USA, the European countries prevail also the fuel cell market and show outstanding improvement. As the companies were compared with each other in

Figure 6.17, CreditSuisse made higher investments to the fuel cells than other companies and has become one of the most prominent companies. In addition to this, US invested an important part of its budget to the fuel cells as compared to other countries in Table 6.18. With the help of these investments, environmental problems will reduce and a cleaner environment will be created. These expectations are the most basic purposes of these investments. Figure 6.21 indicates that the supercapacitor market continues to develop over the years. According to this table, automotive applications were one of the most determining factors on supercapacitor market in 2019.

COVID-19 created a serious problem for the world and has negatively affected the financial and economic conditions of many industries and sectors. Many people cannot attend many activities during this period and they spend usually their time at home. Furthermore, many countries cancelled them. As a result of this negative situation, they pay a large amount of bills such as electric. So as to decrease this amount of bill, they can benefit from these energy storage devices.

As Figure 6.22 is analyzed, Turkey does not have a great effect on the supercapacitor market as compared to other countries. Several North-American, European, Asia-Pacific and Middle East countries have been placed near the top. When Table 6.17 and Figure 6.23 are carefully evaluated, it can be observed that a revenue of 30% more than the previous year has been made each year in given years. It is estimated that the revenue of US$ 8.33 billion was globally obtained in 2025 from the supercapacitor market.

Many countries have carried out a number of importations and exportations between them. According to the exported supercapacitor values which were given in Table 6.20, 2014 was one of the most outstanding years in terms of supercapacitor market for the world in given years. Turkey has also made good attempts to export supercapacitors and displayed lower exported values than other countries. In Table 6.20, Japan, Hong Kong and China have become the three leading companies in terms of exported values of supercapacitors. On the basis of the imported values of countries in Table 6.21, the world exhibited the largest imported value in 2014. In other words, 2014 has become one of the most important year for both importation

and exportation of supercapacitors. In addition to this, China has also taken place near the top in terms of importation and exportation of supercapacitors. As well as China, Hong Kong imported a number of supercapacitors and is placed in the second position in both exportation and importation of supercapacitors.

Turkey is one of the most dependent countries on energy sources of foreign countries and pay attention to both fuel cells and supercapacitors by virtue of this reason. As a report which was written by SHURA company was analyzed, it is estimated that Turkey presents 1.6 million tons of green hydrogen potential which can be used as fuel sources in fuel cells.

The amount of hydrogen is between 70 and 100 million tons in the world. Europe attached importance to fuel cell technology and will make an investment of 1.23 trillion Euro to the hydrogen technology. Hydrogen can also be obtained from natural gas, biomass and other hydrogen based fuel sources. North America, Russia and Middle East have capacity to make conversion of these fuel sources into hydrogen due to their possession of a significant amount of hydrogen based fuels.

In Table 6.22, the increasing of the number of fuel cell electric vehicles (FCEVs) was observed worldwide. Hydrogen generation has become one of the most important topics for the operation of the fuel cells and many countries continued to carry out remarkable studies about it. Table 6.23 gives the hydrogen generation in different years in terms of Metric tonne (Mt). According to this figure, hydrogen generation is gradually increasing and it is expected that the amount of hydrogen generation will reach to 7.92 Mt/year. In order to start engine of FCEVs, many countries built many hydrogen refuelling stations and Japan has been one of the outstanding countries which has the greatest hydrogen refuelling stations (113) as it can be seen in Table 6.24. With the help of hydrogen refuelling stations and FCEVs, the emission of Carbon dioxide and other detrimental greenhouse gases will decrease.

Some countries have made agreements and studies with each other in an effort to develop the hydrogen technology. One of them is that 35 international establishments came together in an attempt to produce 10 million FCEVs within ten years. Many

universites have continued their studies about fuel cells and possess a number of patents. As the universities were compared with each other in Table 6.26, Tsinghua University has the highest number of patents between these universities. According to Table 6.27, Japan, the USA and Korea have the greatest number of patents. As a comparison was made between the investors in Table 6.28, Zhou Mingjie, Wong Yaobing and Hiratsuka Kazuka have a large number of patents which are close to each other. Toyota Motor Corporation, Sony Corporation and Mitsubishi Electric Corporation own high supercapacitor patents and dominate many sectors. The number of patents has a great effect on the supercapacitor industry and market. The main purpose of the patent is to support invention, innovative and creative ideas. Thus, economical, technical and social improvements are provided by patents which contributes also to find many solutions for technical issues. On the basis of these benefits of patents and in the light of these values in the tables, number of patents has played important roles on the improvement of the country.

Batteries have been one of the most preferable energy storage devices and used nowadays in many sectors and applications. It can be observed in Figure 6.38 that passenger EVs must make use of more lithium-ion batteries and this situation creates serious requirement which is gradually enhancing. There are also important companies which produce batteries and their types. As it can be shown in the Table 6.31 and Figure 6.32, LG Chem, CATL and Panasonic occupied important places and positions in the battery market. The batteries which were fabricated by these companies, have high power capacity. Turkey has also made outstanding initiatives in battery production. Mutlu Battery, Inci Battery and Yigit Battery are the most prominent battery producers in Turkey. These companies have made exportation of batteries to many countries.

As a result of this paper, various properties of the used materials in both fuel cells and supercapacitors play vital role on their performance. In addition to this, scientists and researchers in companies and universities should increase their investments and revenues in energy storage devices to reduce the dependence on exported foreign energy resources and improve their economical and technological situations.

REFERENCES

[1] Kim, B. K., Sy, S., Yu, A., Zhang, J. Electrochemical Supercapacitors for Energy Storage and Conversion. Handbook of Clean Energy Systems, 6, 2775-2800. Retrieved March 20, 2020, https://doi.org/10.1002/9781118991978.hces112. July 16,2015

[2] Khartchenko, N.V., Khartchenko,V.M. *Advanced Energy Systems* (2nd ed.). CRC Press. https://doi.org/10.1201/b14928. 2013

[3] Sönnichsen, N. *Distribution of primary energy supply worldwide in 2018, by source*. January 2, 2021, https://www.statista.com/statistics/270528/global-energy-supply-by-source/. 2021

[4] Andrew, J., Jelley, N. *Principles, Technologies, and Impacts Energy Science* (2nd ed.). United Kingdom :Oxford University Press. 2013

[5] The Earth's climate during the past 1000 years or, Global warming and cooling during the past 1000 years. (n.d.). Retrieved March 20, 2020, from https://planetforlife.com/gwarm/glob1000.html

[6] Yu, A., Davies, A., Chen, Z. Electrochemical Supercapacitors. *Electrochemical Technologies for Energy Storage and Conversion*, (Volume: 2) (317-376). Wiley-VCH Verlag GmbH & Co. 2012

[7] Carrette,L., Friedrich, K.A., Stimming, U. Fuel Cells: Principles, Types, Fuels, and Applications. CHEMPHYSCHEM, *1*, 162-193. Retrieved March 30, 2020, from https://doi.org/10.1002/1439-7641(20001215)1:4<162::AID-CPHC162>3.0.CO;2-Z. 2000

[8] Shah, R.K., Desideri, U., Hsueh, K.L., Vikar, A.V. Research Opportunities And Challenges In Fuel Cell Science And Engineering, *4 th Baltic Heat Transfer Conference*, Retrieved April 5, 2020, from https://inis.iaea.org/search/searchsinglerecord.aspx?recordsFor=SingleRecord&RN=35025335. 2003

[9] Fuel Cells. (n.d.). Retrieved April 5, 2020, from https://users.encs.concordia.ca/~pillay/fuel-cells.html

[10] Singh, R.K., Neergat, M. Oxygen reduction reaction (ORR) on Ir, Rh, and Ru Selenides. European Fuel Cell Forum 2011. 1-10. Retrieved April 15, 2020, from https://www.researchgate.net/publication/275135165_Oxygen_reduction_reaction_ORR_on_Ir_Rh_and_Ru_Selenides. 2011

[11] Millet, P. Hydrogen production by polymer electrolyte membrane water electrolysis. Compendium of Hydrogen Energy, (1st ed.), (255-286). United Kingdom :Woodhead Publishing. Retrieved April 20, 2020, from https://doi.org/10.1016/B978-1-78242-361-4.00009-1. 2015

[12] Giorno, L. Permselectivity in Dense Membranes. Encyclopedia of Membranes. Retrieved May 7, 2020, from https://doi.org/10.1007/978-3-642-40872-4_2245-1. 2016

[13] Drag (physics). (n.d.). Retrieved May 7, 2020, from https://en.wikipedia.org/wiki/Drag_(physics)#:~:text=In%20fluid%20dynamics%2C%20drag%20(sometimes,respect%20to%20a%20surrounding%20fluid.

[14] Panayiotou, G.P., Kalogirou, S.A., Tassou, S.A. PEM Fuel Cells for Energy Production in Solar Hydrogen Systems. Recent Patents on Mechanical Engineering, (*3*), 226-235. doi: 10.2174/2212797611003030226. 2010

[15] Palchoudhury, S., Ramasamy, K., Gupta, R.K., Gupta, A. Flexible Supercapacitors: A Materials Perspective. Frontiers in Materials, 5(83), 1-9. Retrieved May 11, 2020, from https://scihub.wikicn.top/10.3389/fmats.2018.00083. doi: 10.3389/fmats.2018.00083. 2019

[16] Zhou, L., Li, C., Liu, X., Zhu, Y., Wu, Y., Ree, T.V. Metal oxides in supercapacitors. Metal Oxides in Energy Technologies (1st ed.) (169-203). Retrieved May 11, 2020, from https://doi.org/10.1016/B978-0-12-811167-3.00007-9. 2018

[17] El-kady, M., Ihns, M., Li, M., Hwang, J.Y., Mousavi, M.F., Chaney, L., Lech, A.T., Kaner, R.B. Engineering three-dimensional hybrid supercapacitors and microsupercapacitors for high-performance integrated energy storage. CrossMark, 112(14). doi: 10.1073/pnas.1420398112. 2015

[18] Cyclic Voltammetry. (n.d.). Retrieved May 18, 2020, from https://en.wikipedia.org/wiki/Cyclic_voltammetry#:~:text=In%20cyclic%20voltammetry%20(CV)%2C,rate%20(V%2Fs).&text=Hence%2C%20CV%20data%20can%20provide,potentials%20and%20electrochemical%20reaction%20rates.

[19] Giorgi, L., Leccese, F. Fuel Cells: Technologies and Applications. The Open Fuel Cells Journals, 6(1):1-20. doi: 10.2174/1875932720130719001. 2013

[20] 18 Advantages and Disadvantages of Hydrogen Fuel Cells. (n.d.). Retrieved May 18, 2020, from https://futureofworking.com/10-advantages-and-disadvantages-of-hydrogen-fuel-cells/

[21] What is Hydrogen Energy? (n.d.). Retrieved June 18, 2020, from https://www.conserve-energy-future.com/advantages_disadvantages_hydrogenenergy.php

[22] Sapthagiri College of Engineering. Supercapacitors [Presentation]. Singh, N: Author Retrieved June 18, 2020, from https://www.slideshare.net/nikhilkumar75873/supercapacitor-47543411

[23] Gidwani, M., Bhagwani, A., Rohra, N. Supercapacitors: the Near Future of Batteries. International Journal of Engineering Inventions, 4(5), 22-27. 2014

[24] Fuel Cell Basics. (n.d.). Retrieved June 20, 2020, from http://www.fchea.org/fuelcells#:~:text=A%20typical%20fuel%20cell%20works, molecules%20into%20electrons%20and%20protons.

[25] Fuel Cell. (n.d.). Retrieved June 20, 2020, from https://en.wikipedia.org/wiki/Fuel_cell

[26] Supercapacitor. (n.d.). Retrieved June 20, 2020, from https://www.cei.washington.edu/education/science-of-solar/supercapicitor/

[27] The Supercapacitors: its Basic Principles, Classification, and its Electrical Performance. (n.d.). Retrieved June 25, 2020, from https://www.kamcappower.com/the-supercapacitors-classification-and-its-electrical-performance.html

[28] Supercapacitor Working, Applications, Advantages, Disadvantages, and Future. (n.d.). Retrieved June 25, 2020, from https://www.etechnog.com/2019/01/supercapacitor-working-applications-advantages.html

[29] Woodford, C. Supercapacitors. Retrieved June 30, 2020, from https://www.explainthatstuff.com/how-supercapacitors-work.html#:~:text=Porous%20supercapacitor%20plates%20are%20electricity%20sponges!&text=When%20the%20capacitor%20is%20charged,field%20and%20reduce%20its%20strength.

[30] Yartys, V.A, Lototsky, M.V. An Overview Of Hydrogen Storage Methods. Veziroglu, T.N., Zaginaichenko, S.Y., Schur, D.V., Baranowski, B., Shpak, A.P., Skorokhod, V.V., Kale, A. (Ed.). Hydrogen Materials Science and Chemistry of Carbon Nanomaterial, 75-104. doi: 10.1007/1-4020-2669-2_7. Dordrecht: Kluwer Academic Publishers. 2004

[31] Spiegel, C. Polarization Curves. (n.d.). Retrieved June 30, 2020, from https://www.fuelcellstore.com/blog-section/polarization-curves#:~:text=The%20polarization%20curve%20displays%20the,the%20fuel%20cell%20output%20voltage. June 20, 2017

[32] Bouaicha, A., Allagui, H., Aglzim, E., Ruane, A., Mami, A. Description and Development of a Measuring System for the PEM Fuel Cell Polarization Curve. International Journal of Science and Engineering Investigations, 5(54), 120-124. 2016.

[33] Hydrogen Storage. (n.d.). Retrieved June 31, 2020 from https://hydrogeneurope.eu/hydrogen-storage

[34] Hydrogen and Fuel Cells. (n.d.). Retrieved July 2, 2020, from https://present5.com/hydrogen-and-fuel-cells-1-hydrogen-the/

[35] Akiba, E. Solid Hydrogen Storage Materials: Interstitial Hydrides. Sasaki, K., Li, H.-W., Hayashi, A., Yamabe, J., Ogura, T., Lyth, S.M. (Ed.). Hydrogen Energy Engineering, (1st ed.) (191-206). doi: 10.1007/978-4-431-56042-5_14. 2016

[36] Rashid, M.M., Al Mesfer, M.K., Naseem, H., Danish, M. Hydrogen Production by Water Electrolysis: A Review of Alkaline Water Electrolysis, PEM Water Electrolysis and High Temperature Water Electrolysis, International Journal of Engineering and Advanced Technology (IJEAT), 4(3), 80-93. 2015

[37] Dr. Zhang, J., Dr. Cui, Y., Prof. Dr. Shan G., Metal oxide nanomaterials for pseudocapacitors. Material Science, Physics, 1-93. Retrieved July 7, 2020, from https://arxiv.org/ftp/arxiv/papers/1905/1905.01766.pdf. 2019

[38] Javed, K., Ashfaq, H., Singh, R., Hussain, S.M.S., Ustun, T.S. Design and Performance Analysis of a Stand-alone PV System with Hybrid Energy Storage for Rural India, *Electronics*, 8(9), 952, 1-16.doi:10.3390/electronics8090952. August 28, 2019

[39] Ali, M., Repalle, S.C., Wahab, A. Experiment Report of Advanced Power Electronics APE 02 Buck Converter. Otto Von Guericke University Magdeburg Faculty of Electrical Engineering and Information Technology. doi: 10.13140/RG.2.2.34846.33609. 2014

[40] Dubey, R., Guruviah, V. Review of carbon-based electrode materials for supercapacitor energy storage. Ionics, 25, 1419–1445. 2019

[41] Libich, J., Máca, J., Vondrák, J., Čech, O., Sedlaříková, M. Supercapacitors: Properties and applications. *Journal of Energy Storage*. 17, 224-227. Retrieved July 10, 2020, from https://doi.org/10.1016/j.est.2018.03.012. 2018

[42] Yip, G. Copper (II) hydroxide nanorods grown on copper and nickel plated nanofibres for pseudocapacitor electrodes in regenerative braking doi: 10.14288/1.0357460. The University of British Columbia. 2017

[43] Hossain, S., Abdalla, A.M., Suhaili, S.B.H., Kamal, I., Shaikhd, S.P.S., Dawood, M.K., Azad, A.K. Nanostructured graphene materials utilization in fuel cells and batteries. A review. Journal of Energy Storage. https://doi.org/10.1016/j.est.2020.101386. 29 , 1-30. 2020

[44] Graphene: structure and shape. Retrieved July 19, 2020, from https://www.graphene-info.com/graphene-structure-and-shape. December 31, 2018

[45] Sarfraz, A., Raza, A.H., Mirzaeian, M., Abbas, Q., & Raza, R. Electrode Materials for Fuel Cells. Reference Module in Materials Science and Materials Engineering. Amsterdam: Elsevier. doi:10.1016/B978-0-12-803581-8.11742-4. 2020

[46] Kuterbekov, K.A., Bekmyrza, K.Zh., Nikonov, A.V., Aydarbekov, N.K. Characteristics of cathode materials for solid oxide fuel cells with mixed conductivity. IOP Conference Series: Materials Science and Engineering. doi: 10.1088/1757-899X/447/1/012037. 447 (1): 012037. 2018

[47] Taroco, H. A., Santos, J. A. F., Domingues, R. Z. and Matencio, T. Department of Chemistry/Universidade Federal de Minas Gerais Brasil. Ceramic Materials for Solid Oxide Fuel Cells. Advances in Ceramics - Synthesis and Characterization, Processing and Specific Applications. doi: 10.5772/18297. 423-446. Brasil. 2011

[48] Kozuka, H., Ohbayashi, K., Koumoto, K. Electronic Conduction in La-based perovskite-type oxides, Science and Technology of Advanced Materials, 16(2): 026001, doi: 10.1088/1468-6996/16/2/026001. 1-16. 2015

[49] Yttria-stabilized zirconia. (n.d.). Retrieved July 19, 2020, from https://en.wikipedia.org/wiki/Yttria-stabilized_zirconia

[50] Antolini,E., Gonzalez, E.R. Ceramic materials as supports for low-temperature fuel cell catalysts. SOLID STATE IONICS, 180 (9-10), 746-763. https://doi.org/10.1016/j.ssi.2009.03.007. 2009

[51] Tin(IV) oxide. (n.d.). Retrieved July 20, 2020, from https://en.wikipedia.org/wiki/Tin(IV)_oxide

[52] Tungsten(IV) oxide. (n.d.). Retrieved July 22, 2020, from https://en.wikipedia.org/wiki/Tungsten(IV)_oxide

[53] Zirconium dioxide. (n.d.). Retrieved July 25, 2020, from https://en.wikipedia.org/wiki/Zirconium_dioxide

[54] Silicon dioxide. (n.d.). Retrieved July 25, 2020, from https://en.wikipedia.org/wiki/Silicon_dioxide

[55] Iro, Z.S., Subramani, C., Dash, S.S. Short Review A Brief Review on Electrode Materials for Supercapacitor. International Journal of ELECTROCHEMICAL SCIENCE. doi: 10.20964/2016.12.50. 11 (12), 10628 – 10643. 2016

[56] Carbon Nanotube. (n.d.). Retrieved August 15, 2020, from https://en.wikipedia.org/wiki/Carbon_nanotube

[57] Conductive Polymer. (n.d.). Retrieved August 15, 2020, from https://en.wikipedia.org/wiki/Conductive_polymer#/media/File:ConductivePoly.png

[58] Raza, W., Ali, F., Raza, N., Luo, Y., Kim K.H., Yang, J., Kumar, S., Mehmood, A., Kwon E.E. Review Recent advancements in supercapacitor technology. Nano Energy, 52, 441–473. https://doi.org/10.1016/j.nanoen.2018.08.013. 2018

[59] Li, Q., Horn, M., Wang, Y., MacLeod, J., Motta, N., Liu, J. A Review of Supercapacitors Based on Graphene and Redox-Active Organic Materials. Materials, 12(5):703 doi: 10.3390/ma12050703, 1-30. 2019

[60] Gambhir, S., Jalili, R., Officer, D.L., Wallace, G.G. Chemically converted graphene: scalable chemistries to enable processing and fabrication. NPG Asia Materials. doi:10.1038/am.2015.47. 7(6): e186, 1-15. 2015

[61] Wu, Q., Xu, Y., Yao, Z., Liu, A., Shi, G. Supercapacitors based on flexible Graphene/polyaniline nanofiber composite films. ACS Nano, doi: https://doi.org/10.1021/nn1000035, 4(4), 1963-1970. 2010

[62] Introduction to Fuel Cell Applications. (n.d.). Retrieved August 27, 2020, from https://www.fuelcellstore.com/blog-section/intro-fuel-cell-applications

[63] Olabi, A.G., Wilberforce, T., Abdelkareem, M.A. Fuel cell application in the automotive industry and future perspective. Journal Pre-proof, 214. Retrieved August 28, 2020, from https://doi.org/10.1016/j.energy.2020.118955. 2020

[64] World Largest Automobile Encyclopedia. (n.d.). Retrieved August 29, 2020, from https://www.allcarindex.com/concept/germany/mercedes-benz/necar-4/

[65] Apollo Fuel Cell. (n.d.). Retrieved August 29, 2020, from http://ryanseper.com/blog/2018/12/20/apollo-fuel-cell

[66] Brey, J., Munoz, D., Mesa, V., Guerrero, T. Use Of Fuel Cells And Electrolyzers In Space Applications: From Energy Storage To Propulsion/Deorbitation, *ESPC 2016*. 16:17004. Retrieved August 31, 2020, from https://www.researchgate.net/publication/317119586_Use_of_Fuel_Cells_and_Electrolyzers_In_Space_Applications_From_Energy_Storage_To_PropulsionDeorbitation, doi: 10.1051/e3sconf/20171617004. 2017

[67] Fuel Cell Gemini. (n.d.). Retrieved September 11, 2020, from https://airandspace.si.edu/collection-objects/fuel-cell-gemini

[68] NASA exploring space applications of hydrogen and fuel cells. (n.d.). Retrieved September 11, 2020, from https://climate.nasa.gov/news/788/nasa-exploring-space-applications-of-hydrogen-and-fuel-cells/

[69] Bagotsky V.S., Skundin A.M., Volfkovich Y.M. Electrochemical Power Sources: Batteries, Fuel Cells, and Supercapacitors (1st ed.). New Jersey: John Wiley&Sons. doi: 10.1002/9781118942857. 2015

[70] Garche, J., Jörissen, L. Applications of Fuel Cell Technology: Status and Perspectives. The Electrochemical Society Interface. doi: 10.1149/2.F02152IF. 24(2), 39-43. 2015

[71] Kundu, P.P., Dutta, K. Hydrogen fuel cells for portable applications. Compendium of hydrogen energy (1st ed.) 4 (111-131). United Kingdom: Woodhead Publishing (Elsevier). http://dx.doi.org/10.1016/B978-1-78242-364-5.00006-3. 2015

[72] Applications Portable. (n.d.). Retrieved November 12, 2020, from https://fuelcellsworks.com/knowledge/applications/portable/

[73] Supercapacitor. (n.d.). Retrieved November 20, 2020, from https://en.wikipedia.org/wiki/Supercapacitor#Applications

[74] Jiang, S.P. Development of lanthanum strontium manganite perovskite cathode materials of solid oxide fuel cells: a review. Journal of Materials Science, volume 43, 6799–6833. 2008

[75] Material: Thermal silicon oxide. (n.d.). Retrieved March 2, 2021, from http://www.mit.edu/~6.777/matprops/sio2.htm

[76] Hernandez-Ramirez, F., Tarancon, A., Casals, O., Pellicer, E., Rodriguez, J., Romano-Rodriguez, A., Morante, J.R., Barth, S., Mathur, S. Electrical Properties of Individual Tin Oxide Nanowires Contacted to Platinum Electrodes. Physical Review, 76(8), 1-5, doi: 10.1103/PhysRevE.76.085429. 2007

[77] Makarov, V.O., Trontelj, M. Sintering and Electrical Conductivity of Doped $W0_3$. Journal of the European Ceramic Society, 16 (1996), 791-794, doi: https://doi.org/10.1016/0955-2219(95)00204-9. 1995

[78] Grahl-Madsen, L., Larsen, P.H., Bonanos, N., Engell, J., Linderoth, S. Mechanical strength and electrical conductivity of Ni-YSZ cermets fabricated by viscous processing. Journal of Materials Science, 41(4), 1097-1107, doi: 10.1007/s10853-005-3647-3. 2006

[79] Hara, S., & Miyayama, M. Proton conductivity of superacidic sulfated zirconia. Solid State Ionics, 168 (2004), 111-116. Doi: https://doi.org/10.1016/j.ssi.2004.01.030. 2004

[80] Material Properties of Indium Tin Oxide (ITO). (n.d.). Retrieved March 25, 2021, from https://www.msesupplies.com/pages/material-properties-of-indium-tin-oxide-ito#:~:text=Indium%20tin%20oxide%20(ITO)%20is,%2C%20PET%2C%20and%20other%20substrates.

[81] Rahmawati, F., Permadani, I., Syarif, D.G., Soepriyanto, S. Electrical Properties Of Various Composition Of Yttrium Doped Zirconia Prepared From Local Zircon Sand. International Journal of Technology, 5, 328-335, doi: 10.14716/ijtech.v8i5.876. 2017

[82] Wang, H., Xu, Y., Goto, M., Tanaka, Y., Yamazaki, M., Kasahara, A., Tosa, M. Thermal Conductivity Measurement of Tungsten Oxide Nanoscale Thin Films. Materials Transactions, 47(8), 1894-1897, doi: 10.2320/matertrans.47.1894. 2006

[83] Poulier, C., Smith, D.S., Absi, J. Thermal conductivity of pressed powder compacts: tin oxide and alumina. Journal of the European Ceramic Society, 27(2-3), 475-478, doi: https://doi.org/10.1016/j.jeurceramsoc.2006.04.068. 2007

[84] Cho, J., Losego, M.D., Zhang, H.G., Kim, H., Zuo, J., Petrov, I., Cahill, D.G., Braun, P.V. Electrochemically tunable thermal conductivity of lithium cobalt oxide. Nature Communications, 5(4035), doi: 10.1038/ncomms5035. 2014

[85] Zhao, H., Yu, F., Bennett, T.D., Wadley, H.N.G. Morphology and thermal conductivity of yttria-stabilized zirconia coatings. Acta Materialia 54(19), 5195-5207, doi: https://doi.org/10.1016/j.actamat.2006.06.028. 2006

[86] He, Y. Heat capacity, thermal conductivity, and thermal expansion of barium titanate-based ceramics. Thermochimica Acta, 419(1-2), 135-141, doi: https://doi.org/10.1016/j.tca.2004.02.008. 2004

[87] Pillai, C.G.S., George, A.M. Thermal Conductivity of La_2CuO_4, La_2NiO_4, and Nd_2CuO_4 in the Semiconducting and Metallic Phases. International Journal of Thermophysics, 7(5), doi: 10.1007/BF00502380. 1986

[88] Radovic, M., Lara-Curzio, E., Trejo, R.M., Wang, H., Porter, W.D. Thermophysical Properties Of YSZ And Ni-YSZ As A Function Of Temperature And Porosity. Ceramic Engineering and Science Proceedings, 39(4), 79-85, doi: 10.1002/9780470291337.ch8. 2008

[89] Fink, J.K., Leibowitz, L. Thermal conductivity of zirconium. Journal of Nuclear Materials, 226(1-2), 44-50, doi: https://doi.org/10.1016/0022-3115(95)00110-7. 1995

[90]Kamble, B.S., Fulari, V.J., Nimat, R.K. Strontium Doping Concentrations Influence on $La_{1-x}Sr_xMnO_{3-\delta}$ Micro Structural and Electrical Conductivity. Journal of Applied Physics, 8(3), 66-71, 2016.

[91] Bland, J.A. The Thermal Expansion Of Cubic Barium Titanate ($BaTiO_3$) 350 °C To 1050 °C. Canadian Journal of Physics, 37(4), 417-421, doi: https://doi.org/10.1139/p59-046. 1959

[92] Osinkin, D.A., Bronin, D.I., Beresnev, S.M., Bogdanovich, N.M., Zhuravlev, V.D., Vdovin, G.K., Demyanenko, T.A. Thermal expansion, gas permeability, and conductivity of Ni-YSZ anodes produced by different techniques. Journal of Solid State Electrochemistry, 18(1), 149-156, doi: 10.1007/s10008-013-2239-4. 2014

[93] Nikonov, A.V., Kuterbekov, K.A., Bekmyrza, K.Zh, Pavzderin, N.B. A brief review of conductivity and thermal expansion of perovskite-related oxides for SOFC cathode. Eurasian Journal of Physics and Functional Materials, 2(3), 274-292, doi: 10.29317/ejpfm.2018020309. 2018.

[94] Shaina, P.R., George, L., Yadav, V., Jaiswal, M. Estimating the thermal expansion coefficient of graphene: The role of graphene-substrate interactions. Journal of Physics Condensed Matter, 28(8), 1-7, doi: 10.1088/0953-8984/28/8/085301. 2016

[95] Tokunaga, T., Kawamoto, T., Tanaka, K., Nakamura, N., Hayashi, N., Sasaki, K., Kuroda, K., Yamamoto, T. Growth and structure analysis of Tungsten oxide nanorods using Environmental TEM. Nanoscale Research Letters, 7(1):85, 1-7, doi: 10.1186/1556-276X-7-85. 2012

[96] AZoM. Silica - Silicon Dioxide (SiO_2). Retrieved April, 2 2021, from https://www.azom.com/article.aspx?ArticleID=1114. December 13, 2001.

[97] Cheng, E.F., Taylor, N.J., Wolfenstine, J., Sakamoto, J. Elastic properties of lithium cobalt oxide ($LiCoO_2$). Journal of Asian Ceramic Societies, 5(2), 1-5, doi: https://doi.org/10.1016/j.jascer.2017.03.001. 2017

[98] Miyazaki, H., Ushiroda, I., Itomura, D., Hirashita, T., Adachi, N., Ota, T. Thermal expansion of hydroxyapatite between − 100 °C and 50 °C. Materials Science and Engineering, 29(4), 1463-1466, doi: 10.1016/j.msec.2008.12.001. 2009.

[99] Partially Stabilized Zirconia (PSZ) - Highly Durable, Highly Resistant to Acid Corrosion and High Temperatures. (n.d.). Retrieved April 3, 2021, from https://www.taissic.com/eng/page.php?pageid=JCU1IyE=#:~:text=Partially%20Stabilized%20Zirconia%20(PSZ)%20is,products%20than%20standard%20ceramics%20do.

[100] Deng, J., Zhang, L., Hui, L., Jin, X., Ma, B. Indium Tin Oxide Thin-Film Thermocouple Probe Based on Sapphire Microrod. Sensors, 20(5), 1-8, doi: 10.3390/s20051289. 2020

[101] Coefficient of Thermal Expansion Converter. (n.d.). Retrieved April 3, 2021, from https://www.translatorscafe.com/unit-converter/en-US/thermal-expansion/2-1/

[102] Guo, G., Lian, K., Wang, L., Gu, F., Han, D., Wang, Z. High specific surface area $LaMO_3$ (M = Co, Mn) hollow spheres: synthesis, characterization and catalytic properties in methane combustion. RSC Advances, Issue: 102. Retrieved April 5, 2021 from https://pubs.rsc.org/en/content/articlelanding/2014/ra/c4ra10053k#!divAbstract. 2014

[103] American Elements. Strontium Titanate Particles. Retrieved April 7, 2021, from https://www.americanelements.com/strontium-titanate-nanoparticles-12060-59-2

[104] Verwilghen, C., Rio, S., Nzihou, A., Gauthier, D., Flamant, G., Sharrock, P.J. Preparation of High Specific Surface Area Hydroxyapatite for Environmental Applications. Journal of Mterial Sciences, 42(15), 6062-6066, doi: 10.1007/s10853-006-1160-y. 2007

[105] Zhang, J., Liu, F., Cheng, J.P., Zhang, X.B. Binary Nickel–Cobalt Oxides Electrode Materials for High-Performance Supercapacitors: Influence of its Composition and Porous Nature. ACS Applied Materials & Interfaces, 7(32), 1-39, doi: 10.1021/acsami.5b04463. 2015

[106] Arakaki, A.R., Yoshito, W.K., Ussui, V., Lazar, D.R.R. Hydrothermal Treatment of Coprecipitated YSZ Powders. Materials Science Forum, Volume: 660-661, 983 – 988, doi: 10.4028/www.scientific.net/MSF.660-661.983. 2010.

[107] Kim, S.D., Moon, H., Hyun, S.H., Moon, J., Kim, J., Lee, H.W. Ni-YSZ cermet anode fabricated from NiO-YSZ composite powder for high-performance and durability of solid oxide fuel cells. Solid State Ionics, 178(21-22), 1304-1309, doi: 10.1016/j.ssi.2007.06.014. 2007

[108] Wang, N., Yao, M., Zhao, P., Zhang, Q., Hu, W. Highly mesoporous structure nickel cobalt oxides with an ultra-high specific surface area for supercapacitor electrode materials. Journal of Solid State Electrochem, 20(5), 1429-1434, doi: 10.1007/s10008-016-3149-z. 2016

[109] American Elements. Lanthanum Strontium Cobalt Ferrite (LSCF). Retrieved April 9, 2021 from https://www.americanelements.com/lanthanum-strontium-cobalt-ferrite-lscf

[110] Xiong, S., Tang, Y., Ng, H.S., Zhao, X., Jiang, Z., Chen, Z., Ng, K.W., Loo, S.C.J. Specific surface area of titanium dioxide (TiO_2) particles influences cyto- and photo-toxicity. Toxicology, 304, 132-140, doi: 10.1016/j.tox.2012.12.015. 2013

[111] Salas, P., Hernandez, J.G., Lopez-Salinas, E., Schifter, I., Llanos, M.E., Navarrete, J. Sulfated SnO_2-SiO_2 Superacid Catalysts by Sol-Gel Method. Journal of Porous Materials 3(4), 241-245, doi: 10.1007/BF01137913. 1996

[112] Sigma Aldrich. Silica. Retrieved April 10, 2021, from https://www.sigmaaldrich.com/catalog/product/aldrich/718483?lang=en&region=TR

[113] Rachmat, A., Trisunaryant, W., Wijaya, S&K. Synthesis and characterization of sulfated zirconia mesopore and its application on lauric acid esterification. Materials for Renewable and Sustainable Energy, 6:13, 1-9, doi: 10.1007/s40243-017-0097-1. 2017

[114] Ibukun, O., Jeong, H.K. Effects of Aqueous Electrolytes in Supercapacitors. New Physics: Sae Mulli, 69(2), 154-158, doi: 10.3938/NPSM.69.154. 2019

[115] Wang, X., Li, Y., Lou, F., Buan, M.E.M., Sheridan, E., Chen, D. Enhancing capacitance of supercapacitor with both organic electrolyte and ionic liquid electrolyte on a biomass-derived carbon. RSC Advances, 7(38), 23859-23865, doi: 10.1039/C7RA01630A. 2017

[116] Verma, R., Nagendra, H.N., Kasthurirengan, S., Shivaprakash, N.C., Behera, U. Thermal conductivity studies on activated carbon based cryopanel. IOP Conference Series: Materials Science and Engineering, 502(1), 1-5, doi: 10.1088/1757-899X/502/1/012197. 2019

[117] Grundler, M., Derieth, T., Heinzel, A. Polymer compounds with high thermal conductivity. Proceedings Of The Regional Conference Graz 2015 – Polymer Processing Society Pps: Conference Papers, 1779(030015), 1-5, doi: 10.1063/1.4965485. 2016

[118] Thermal Conductivities of some common Liquids - Some fluids and their thermal conductivities (n.d.). Retrieved April 11, 2021 from https://www.engineeringtoolbox.com/thermal-conductivity-liquids-d_1260.html

[119] Yebra, F., Troncoso, J., Romaní, L. Thermal conductivity of ionic liquids under pressure. Fluid Phase Equilibria, 515, 1-9, doi: 10.1016/j.fluid.2020.112573. 2020

[120] Thermal Conductivity of Acetonitrile. (n.d.). Retrieved April 12, 2021, from http://www.ddbst.com/en/EED/PCP/TCN_C3.php

[121] Music, D., Kremer, O., Pernot, G., Schneider, J.M. Designing low thermal conductivity of RuO2 for thermoelectric applications. APPLIED PHYSICS LETTERS, 106(6):063906, 1-4, doi: 10.1063/1.4909513. 2015

[122] Li, A., Zhang, C., Zhang Y.F. Thermal Conductivity of Graphene-Polymer Composites: Mechanisms, Properties, and Applications. Polymers, 9(9), 1-17, doi: 10.3390/polym9090437. 2017

[123] Abad, B., Alda, I., D´ıaz-Chao, P., Kawakami, H., Almarza, A., Amantia, D., Gutierrez, D., Aubouy, L., Mart´ın-Gonzalez, M. Improved power factor of polyaniline nanocomposites with exfoliated graphene nanoplatelets (GNPs). Journal of Materials Chemistry A, 1(35), 10450-10457, doi: 10.1039/C3TA12105D. 2013

[124] Xiang, M., Yang, Z., Chen, J., Zhou, S., Wei, W., Dong, S. Polymeric Thermoelectric Composites by Polypyrrole and Cheap Reduced Graphene Oxide in Towel-Gourd Sponge Fibers. ACS Omega, 5(46), 29955-29962, doi: 10.1021/acsomega.0c04356. 2020

[125] Peigney, A., Laurent, C., Flahaut, E., Bacsa, R.R., Rousset, A. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. Carbon, 39, 507-514, doi: 10.1016/S0008-6223(00)00155-X. 2001

[126] Xu, H., Li, X., Wang, G. Polyaniline nanofibers with a high specific surface area and an improved pore structure for supercapacitors. Journal of Power Sources, 294, 16-21, doi: https://doi.org/10.1016/j.jpowsour.2015.06.053. 2015

[127] Wang, Z., Zhou, M., Chen, H., Jiang, J., Guan, S. Hierarchical activated mesoporous phenolic-resin-based carbons for supercapacitors. Chemistry: An Asian Journal, 9(10), 2789-2797, doi: 10.1002/asia.201402338. 2014

[128] Aouissi, A., Aldhayan, A., Abduh, N.A.Y., Kahtani, A.A. Propylene carbonate synthesis from propylene oxide and CO_2 over Ga-Silicate-1 catalyst. De Gruyter, 9, 440-450, doi: https://doi.org/10.1515/gps-2020-0048. 2020

[129] Zhang, Z., Feng, J., Jiang, Y., Feng, J. Hierarchically porous carbon aerogels with high specific surface area prepared from ionic liquids via salt templating method. Carbon Letters, 28(1), 47-54, doi:10.5714/CL.2018.28.047. 2018

[130] Roberts, A.J., Slade, R.C.T. Effect of specific surface area on capacitance in asymmetric carbon/α-MnO_2 supercapacitors. Electrochimica Acta, 55(25), 7460-7469, doi: 10.1016/j.electacta.2010.01.004. 2010

[131] Ramani, M., Haran, B.S., White, R.E., Popov, B.N. Synthesis and Characterization of Hydrous Ruthenium Oxide-Carbon Supercapacitors. Journal of The Electrochemical Society, 148(4), A374-A380, doi: 10.1149/1.1357172. 2001

[132] Li, Z.F., Zhang, H., Liu, Q., Sun, L., Stanciu, L.A., Xie, J. Fabrication of High-Surface-Area Graphene/Polyaniline Nanocomposites and Their Application in Supercapacitors. Applied Materials & Interfaces, 5(7), 1-25, doi: 10.1021/am4001634. 2013

[133] Zhang, E., Liu, W., Liang, Q., Liu, X., Zhao, Z., Yang, Y. Polypyrrole nanospheres@graphene aerogel with high specific surface area, compressibility, and proper water wettability prepared in dimethylformamide-dependent environment. Polymer, 185:121974, 1-9, doi: 10.1016/j.polymer.2019.121974. 2019

[134] Huang, Y. Thermal and electrical properties of activated carbon fibers**.** *Activated Carbon Fiber and Textiles* (1st ed.) (179-190). Cambridge: Woodhead Publishing. 2016

[135] Wang, Y., Weng, G.J. Electrical Conductivity of Carbon Nanotube- and Graphene-Based Nanocomposites**.** Micromechanics and Nanomechanics of Composite Solids (1st ed.) (123-156). New York: Springer International Publishing. 2018

[136]Le, T.H., Kim, Y., Yoon, H. Electrical and Electrochemical Properties of Conducting Polymers. Polymers, 9(4):150, 1-32, doi: 10.3390/polym9040150. 2017

[137] Ramachandran, R., Wang, F. Electrochemical Capacitor Performance: Influence of Aqueous Electrolytes. *Supercapacitors - Theoretical and Practical Solutions*, (51-68). London: InTechOpen. 2018

[138] Vila, J., Franjo, C., Pico, J.M., Varela, L.M., Cabeza, O. Temperature Behavior of the Electrical Conductivity of Emim-Based Ionic Liquids in Liquid and Solid States. Portugaliae Electrochimica Acta, 25(1), 163-172, doi: 10.4152/pea.200701163

[139] Tshibangu, P.N., Ndwandwe, S.N., Dikio, E.D. Density, Viscosity and Conductivity Study of 1-Butyl-3- Methylimidazolium Bromide. International Journal of Electrochemical Science, 6(6), 2201-2213. 2011

[140] Triggs, P., Levy, F. Electrical Properties of Rutile Type Oxides: Doped TiO_2 and RuO_2. Retrieved April 14, 2021, from https://link.springer.com/chapter/10.1007/978-94-009-6440-2_9. 1984

[141] Kaur, G., Adhikari, R., Cass, P., Bown, M., Gunatillake, P. Electrically conductive polymers and composites for biomedical applications. RSC Advances, 5(47), 1-17, doi: 10.1039/C5RA01851J. 2015

[142] Firdaus, S.M., Anasyida, A.S., Zubir, S.A., Mariatti, M. Graphene/polyaniline nanocomposites: Effect of surfactant and fabrication methods. AIP Conference Proceedings, 2267(1), 020029-1-020029-9, doi: https://doi.org/10.1063/5.0015751. 2020.

[143] Nithya, S., Selvasekarapandian, S., Karthikeyan, S., Pandi, D.V. Effect of propylene carbonate on the ionic conductivity of polyacrylonitrile-based solid

polymer electrolytes. Journal of Applied Polymer Science, 132(14), 1-7, doi: 10.1002/app.41743. 2014

[144] Electrical resistivity and conductivity. (n.d.). Retrieved April 15, 2021 from https://en.wikipedia.org/wiki/Electrical_resistivity_and_conductivity

[145] Curtin, S., Gangi, J. Fuel Cell Technologies Market Report 2016 U.S. Department of Energy, 1-63, Retrieved March 1, 2021, from Office of Energy Efficiency & Renewable Energy Database, October 2017.

[146] Stationary fuel-cell applications. (n.d.). Retrieved, April 17, 2021 from https://en.wikipedia.org/wiki/Stationary_fuel-cell_applications

[147] Hayes, A. Venture Capital. Retrieved March 2, 2021, from https://www.investopedia.com/terms/v/venturecapital.asp#:~:text=Venture%20capital%20(VC)%20is%20a,and%20any%20other%20financial%20institutions. March 16, 2021

[148] Chen, J. Private Equity. Retrieved March 2, 2021, from https://www.investopedia.com/terms/p/privateequity.asp#:~:text=Private%20equity%20is%20an%20alternative,the%20delisting%20of%20public%20equity. April 30, 2020

[149] Curtin, S., Gangi, J. Fuel Cell Technologies Market Report 2015 U.S. Department of Energy, 1-72, Retrieved March 2, 2021, from Office of Energy Efficiency & Renewable Energy Database, 2016.

[150] Home-Use Fuel Cell (ENE-FARM) Appliances (n.d.). Retrieved March 1, 2021, from https://www.j-lpgas.gr.jp/en/appliances/

[151] Credit Suisse (n.d.). Retrieved March 4, 2021, from https://www.credit-suisse.com/about-us/en/our-company/who-we-are.html

[152] Emerald Technology Ventures (n.d.). Retrieved March 5, 2021, from https://emerald-ventures.com/

[153] 350 Investment Partners (n.d.). Retrieved March 7, 2021, from https://www.350ip.co.uk/

[154] Energy Policy Act of 2005 (n.d.). Retrieved March 8, 2021, from https://en.wikipedia.org/wiki/Energy_Policy_Act_of_2005#:~:text=George%20W.%20Bush%20signing%20the,for%20six%20new%20nuclear%20plants. April 25, 2021.

[155] Lucintel. *Supercapacitor Market Report: Trends, Forecast and Competitive Analysis*. Retrieved March 10, 2021, from https://www.lucintel.com/supercapacitor-market.aspx. July 2020.

[156] Compound Annual Growth Rate (CAGR) (n.d.). Retrieved March 15, 2021, from https://www.gartner.com/en/information-technology/glossary/cagr-compound-annual-growth-rate

[157] Wayman, R. *Compound Annual Growth Rate: What You Should Know*. Retrieved March 15, 2021 from https://www.investopedia.com/investing/compound-annual-growth-rate-what-you-should-know/. September 24, 2019

[158] Savekar, A., Tewari, D., Kumar, V. Supercapacitor Market by Product Type (Double-Layer Capacitor, Pseudocapacitors, andHybrid Capacitors), Module Type (Less Than 10 Volts Modules, 10 Volts to 25 VoltsModules, 25 Volts to 50 Volts Modules, 50 Volts to 100 Volts Modules, and Above 100Volts Modules), Material (Activated carbon, Carbide Derived Carbon, Carbon Aerogel, andOthers), and Application (Automotive, Industrial, Energy, Consumer Electronics, andAerospace & Defense): Global Opportunity Analysis and Industry Forecast, 2020–2027. Allied Market Research. 1-335. Retrieved March 17, 2021 from https://www.marketresearch.com/Allied-Market-Research-v4029/Supercapacitor-Product-Type-Double-Layer-13468638/. June 2020.

[159] Supercapacitor Market - Forecast(2021 - 2026). (n.d.). Retrieved March 8, 2021 from https://www.industryarc.com/Report/212/Global-Supercapacitor-Market-analysis-report.html

[160] Supercapacitors Market (Supercapacitors Market: Global In dustry Analysis and Forecast 2016 – 2025). (n.d.). Retrieved March 9, 2021, from https://www.persistencemarketresearch.com/market-research/supercapacitors-market.asp

[161] About Us, Overview. (n.d.). Retrieved March 10, 2021, from https://www.persistencemarketresearch.com/about-us.asp

[162] TechNavio. Global Supercapacitor Market 2020-2024. ID: 5232344. December 2020

[163] Global Market Insights. Supercapacitor Market Size, Industry Analysis Report, Regional Outlook, Application Development Potential, Price Trend, Competitive Market Share & Forecast, 2021 – 2027, Report ID: GMI3732. Retrieved March 11, 2021, from https://www.gminsights.com/industry-analysis/supercapacitor-market. June 2019.

[164] Businesswire (A Berkshare Hathaway Company). India Supercapacitors Market, Competition Forecast & Opportunities, 2022 - Research and Markets. Retrieved March 10, 2021, from https://www.businesswire.com/news/home/20171011005785/en/India-Supercapacitors-Market-Competition-Forecast-Opportunities-2022---Research-and-Markets. October 11, 2017

[165] Electronics B2B All About Electronic Industry. Evaluating the Market Capacity of Supercapacitors. Retrieved March 11, 2021, from

https://www.electronicsb2b.com/eb-specials/industry-report/evaluating-the-market-capacity-of-supercapacitors-2/. February 21, 2019

[166] Kamarzarrin, M., Refan, M.H. Intelligent Sliding Mode Adaptive Controller Design for Wind Turbine Pitch Control System Using PSO-SVM in Presence of Disturbance. Journal of Control, Automation and Electrical Systems, 31, 912-925, doi: https://doi.org/10.1007/s40313-020-00584-x. 2020

[167] Alptekin, F.M., Cakir, M., Celiktas, M.S. Supercapacitor As An Energy Storage Device: Current And Future Prospect. Conference: Solartr 2018, 45-58. 2018.

[168] Saygın, D., Gençer, E., Sanlı, B., Türkiye'nin Hidrojen Stratejisi Online Etkinlik Özet Raporu. SHURA Energy Transition Center and Bilkent University Energy Policy Research Center. Retrieved April 5, 2021, from https://www.shura.org.tr/wp-content/uploads/2021/03/Hidrojen_Online_Etkinlik_Ozet_Raporu.pdf. March 23, 2021

[169] International Energy Agency (IEA). The Future of Hydrogen Seizing today's opportunities. Retrieved April 30, 2021, from https://www.iea.org/reports/the-future-of-hydrogen. June 2019.

[170] Bermudez, J.M., Hasegawa, T. Hydrogen. Retrieved May 2, 2021, from https://www.iea.org/reports/hydrogen. June 2020.

[171] Alstom. Alstom in Germany. Retrieved May 2, 2021, from https://www.alstom.com/alstom-germany. 2021

[172] Chinese Academy of Sciences. (n.d.). Retrieved May 5, 2021, from https://english.cas.cn/about_us/

[173] Wang, B. World Battery Production. Retrieved May 7, 2021, from https://energycentral.com/c/ec/world-battery-production. Feb 5, 2020.

[174] LG Chem About Us. (n.d.). Retrieved May 7, 2021, from https://www.lgchem.com/company/company-information/about

[175] Palandrani, P. Four Companies Leading the Rise of Lithium & Battery Technology. Retrieved May 9, 2021, from https://www.globalxetfs.com/four-companies-leading-the-rise-of-lithium-battery-technology/. December 9, 2020

[176] Best Car Battery Manufacturers in Turkey (Includes Industrial Battery Manufacturers). (n.d.). Retrieved May 9, 2021, from https://gungorkaya.com/en/battery-manufacturers-turkey/

June 2021
ANKARA

Department of Energy Systems Engineering

Umut YAĞCIOĞLU