



**ENERGY AND EXERGY ANALYSIS OF A HIGH-
TEMPERATURE PEM FUEL CELL INTEGRATED
INTO A SOLAR-BASED HYDROGEN
PRODUCTION SYSTEM**

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PhD THESIS
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FUEL CELL INTEGRATED INTO A SOLAR-BASED HYDROGEN
PRODUCTION SYSTEM**

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September 2022**

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ABSTRACT

PhD Thesis

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Karabük University

Institute of Graduate Programs

The Department of Mechanical Engineering

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The performance of a high-temperature PEM fuel cell (HT-PEMFC) is highly affected by various operational and design parameters. Therefore, in this thesis, a comprehensive performance evaluation of an HT-PEMFC employing a phosphoric acid (PA) doped polybenzimidazole (PBI) membrane was performed with energy and exergy analyses, and the results were discussed. In order to determine the performance characteristics under different operational conditions, the HT-PEMFC was electrochemically modelled on both a cell and stack basis. Thermodynamic analyses were then applied to each model. Two effective methods, the 0-dimensional (0-D) & isothermal model and the 1-dimensional (1-D) & semi-empirical model, were used to obtain the electrochemical performance results at the cell level. In the 0-D & isothermal model, the polarization curve results were compared with two experimental studies conducted on 423 K and 433 K. Different statistical methods were applied to

test and validate the proposed model. In addition, the effects of operating temperature, pressure, relative humidity, and membrane thickness on the cell performance were investigated, and the variation of energy/exergy efficiency, entropy production density, and exergy destruction rate was discussed. In the 1-D & semi-empirical model, the polarization curve results were compared with four experimental studies performed at different operating temperatures from 393 K to 453 K at 20 K intervals. The regression models were derived for each temperature to prove how well the proposed model agrees with these experimental studies. Thus, the effects of leak current density and doping level on cell performance were investigated, and energy, exergy, and ecological analyses were performed. Finally, apart from the cell-based models, the HT-PEMFC was also modelled in the stack-level based on the 1-D and semi-empirical model. In this study, the integration of an HT-PEMFC stack into a hybrid system consisting of a grid-connected solar power plant (SPP) and a PEM electrolyser (PEME) stack to produce hydrogen was investigated to meet the energy demand of a residential area. Thus, the integration of HT-PEMFC into the proposed hybrid system was proven feasible, and the performance variation on a stacked basis with other system components was analysed monthly.

Key Words : High-temperature PEM fuel cell, HT-PEMFC, 0-D, 1-D model, electrochemical analysis, energy, exergy, ecological analysis, solar-based hydrogen production, integrated system, performance assessment.

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ÖZET

Doktora Tezi

GÜNEŞ ENERJİLİ BİR HİDROJEN ÜRETİM SİSTEMİNE ENTEGRE EDİLMİŞ YÜKSEK SICAKLIKLI PEM YAKIT HÜCRESİNİN ENERJİ VE EKSERJİ ANALİZİ

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Yüksek sıcaklıkta çalışan bir PEM yakıt hücresinin (YS-PEMYH) performansı, çeşitli operasyonel ve tasarım parametrelerinden oldukça etkilenmektedir. Bu nedenle, bu tezde, fosforik asit (FA) katkılı polibenzimidazol (PBI) membran kullanılan bir YS- PEMYH'nin kapsamlı bir performans değerlendirmesi, enerji ve ekserji analizleri ile yapılmış ve sonuçlar tartışılmıştır. Farklı çalışma koşulları altında performans özelliklerini belirlemek için YS-PEMYH hem hücre hem de yığın bazında elektrokimyasal olarak modellenmiştir. Daha sonra her bir modele termodinamik analizler uygulanmıştır. Hücre bazında elektrokimyasal performans sonuçlarını elde etmek için 0 boyutlu (0-B) ve izotermal model ve 1 boyutlu (1-B) ve yarı ampirik model olmak üzere iki etkili yöntem kullanılmıştır. 0-D & izotermal modelde, polarizasyon eğrisi sonuçları 423 K ve 433 K'de yapılan iki deneysel çalışma ile karşılaştırılmıştır. Önerilen modeli test etmek ve doğrulamak için farklı istatistiksel

yöntemler uygulanmıştır. Bunun yanı sıra, çalışma sıcaklığı, basınç, bağıl nem ve membran kalınlığının hücre performansı üzerindeki etkileri araştırılmış ve enerji/ekserji verimi, entropi üretim yoğunluğu ve ekserji yıkım oranının değişimi tartışılmıştır. 1-B ve yarı ampirik modelde ise, polarizasyon eğrisi sonuçları, 20 K aralıklarla 393 K ile 453 K arasındaki farklı çalışma sıcaklıklarında gerçekleştirilen dört deneysel çalışma ile karşılaştırılmıştır. Önerilen modelin bu deneysel çalışmalarla ne kadar iyi uyduğunu kanıtlamak için her sıcaklık için regresyon modelleri türetilmiştir. Böylece, kaçak akım yoğunluğu ve katkılama seviyesinin hücre performansı üzerindeki etkileri araştırılmış ve enerji, ekserji ve ekolojik analizler gerçekleştirilmiştir. Son olarak, hücre bazlı modellerin yanı sıra, YS-PEMYH, 1-B ve yarı ampirik modele dayalı olarak yığın seviyesinde de modellenmiştir. Bu çalışmada, bir yerleşim alanının enerji talebini karşılamak için YS-PEMYH yığınının şebekeye bağlı bir güneş enerjisi santrali (GES) ve hidrojen üretmek için bir PEM elektrolizör (PEME) yığınının oluşan hibrit bir sisteme entegrasyonu incelenmiştir. Böylece, YS-PEMYH'nin önerilen hibrit sisteme entegrasyonunun uygulanabilir olduğu kanıtlanmış ve diğer sistem bileşenleri ile yığın bazında performans değişimi aylara göre analiz edilmiştir.

Anahtar Kelimeler: Yüksek sıcaklıklı PEM yakıt hücresi, YS-PEMYH, 0-B, 1-B model, elektrokimyasal analiz, enerji, ekserji, ekolojik analiz, güneş tabanlı hidrojen üretimi, entegre sistem, performans değerlendirmesi.

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SYMBOLS AND ABBREVIATIONS INDEX

SYMBOLS

A	: active electrode area (cm^2 , m^2)
A_0	: pre-exponential coefficient for the doping level
B_0	: pre-exponential coefficient for the humidity
b_{act}	: activation energy
CO	: carbon monoxide
CO_2	: carbon dioxide
C_p	: specific heat (J/mol.K)
E	: voltage (V)
E_0	: ideal standard potential (V)
F	: faraday constant (C/mol)
H_2	: hydrogen
H_2O	: water
j	: current density (A/cm^2 , A/m^2)
j_0	: exchange current density (A/cm^2 , A/m^2)
MW	: molecular weight of species (g/mol)
n_e	: number of electrons
O_2	: oxygen
P	: pressure (Pa, bar)
P_{fc}	: power output (W)
Pt	: platinum
P^*	: power density (W/cm^2 , W/m^2)
R	: universal gas constant (J/mol.K)
R_l	: internal resistance (Ω)
Ru	: ruthenium
S	: standard deviation
S^2	: variance

t	: membrane thickness (mm)
T	: temperature (K)
U	: net output voltage (V)
Δg	: molar Gibbs free energy (J/mol)
ΔG	: total Gibbs free energy of formation (J/mol)
Δh	: molar enthalpy variation (J/mol)
ΔH	: total molar enthalpy variation (J/mol)
Δs	: molar entropy variation (J/mol.K)
ΔS	: total molar entropy variation (J/mol)
$\dot{E}_x$	: exergy rate (W)
$\dot{E}_{x_D}$	: exergy destruction rate (W)
$-\Delta \dot{H}$	: total energy released per unit time (W)
$\dot{m}$	: mass of the species (g/s)
$\dot{n}$	: mass flow rate of the species (mol/s)

SUB INDICES

0	: ideal or standard state
act	: activation
chm	: chemical
con	: concentration
eff	: efficiency
fc	: fuel cell
in	: input
irr	: irreversible
ke	: kinetic
$leak$	: leak current
mem	: membrane
ohm	: ohmic
out	: output
pe	: potential
phy	: physical
ref	: reference

<i>rev</i>	: reversible
<i>th</i>	: thermal

GREEK LETTERS

η	: energy efficiency
ψ	: exergy efficiency
δ	: entropy production rate (W/K)
δ^*	: entropy production density (W/cm ² K)
λ	: stoichiometric ratio of species
ε	: volume fraction of phosphoric acid
X	: doping level
α, β	: charge transfer coefficient
κ, σ	: proton conductivity of the membrane (S/m)
Ω	: resistance (ohm)

ABBREVIATIONS

0-D	: Zero-dimensional
1-D	: One-dimensional
2-D	: Two-dimensional
3-D	: Three-dimensional
AFC	: Alkaline Fuel Cell
BP	: Bipolar Plate
CC	: Current Collector
CCM	: Catalyst Coated Membrane
CL	: Catalyst Layer
DL	: Doping Level
DMFC	: Direct Methanol Fuel Cell
ECOP	: Ecological Coefficient of Performance
EOF	: Ecological Function
EP	: End Plate
FBIAS	: Mean Fractional Bias

FERR	: Absolute Mean Fractional Error
GDE	: Gas Diffusion Electrode
GDL	: Gas Diffusion Layer
GDM	: Gas Diffusion Medium
HOR	: Hydrogen Oxidation Reaction
HT-PEMFC	: High-temperature PEMFC
ICE	: Internal Combustion Engine
IP	: Improvement Potential
LT-PEMFC	: Low-temperature PEMFC
MAE	: Mean Absolute Error
MCFC	: Molten Carbonate Fuel Cell
MEA	: Membrane Electrode Assembly
MFE	: Mean Fractional Error
MPL	: Microporous Layer
MPS	: Macro Porous Substrate
MSE	: Mean Square Error
NMB	: Normalized Mean Bias
NME	: Normalized Mean Error
ORR	: Oxygen Reduction Reaction
PA	: Phosphoric Acid
PAFC	: Phosphoric Acid Fuel Cell
PBI	: Polybenzimidazole
PEI	: Polyethyleneimine
PEMFC	: Proton-exchange Membrane Fuel Cell
PFCA	: Perfluoro-cycloalkene
PFSA	: Perfluoro-Sulfonic Acid
PFSI	: Perfluoro-sulfonyl imide
PSA	: Polystyrene Sulfonic Acid
PTFE	: Polytetrafluoroethylene
RFC	: Regenerative Fuel Cell
RH	: Relative Humidity
RMSE	: Root Mean Square Error
SEM	: Standard Error of Mean

SG	: Sealing Gasket
SLPM	: Standard Liter Per Minute
SOFC	: Solid Oxide Fuel Cell
SPEEK	: Sulfonated Poly (Ether Ether Ketone)
SPS	: Sulfonated Polystyrene
TPB	: Triple Phase Boundary



CHAPTER 1

INTRODUCTION

1.1. GLOBAL ENERGY CONCERNS

Energy has always been a crucial prerequisite for human beings to continue their lives and sustainable development. From nutrition to shelter, education to health, transportation to defence, science to technology, and production to consumption, all life's necessities require great energy need for our age in the ever-changing and developing world conditions. This need continues to rise gradually due to the growing world population, a relatively rising standard of living, and industrialisation depending on technological developments every year. Along with increasing global energy demand, the total primary energy consumption has beaten the record of all time in the historical process, reaching over 174000 terawatt-hours (TWh) in 2019 [1], as depicted in Figure 1.1. This situation led to the excessive use of conventional energy sources, such as crude oil, coal, and natural gas. As seen from the figure, these sources have met most of the world's energy demand because of their availability and convenient use; hence, they have remained the dominant fuel in power generation at a global level. Due to the dramatic impact of the COVID-19 pandemic on the energy market, primary energy consumption decreased by 4.5% in 2020, which was recorded as the fastest decline since the Second World War, 1945. The reduction in energy consumption was mostly driven by oil, which accounted for about three-quarters of the net fall, while natural gas and coal consumption also witnessed large drops [2], as presented in Figure 1.2. Although the global energy demand has dramatically decreased during the pandemic, the consumption and emissions returned to the pre-pandemic levels in 2021, inverting the transient decline in 2020 caused by the pandemic. Furthermore, compared to 2020, the demand for primary energy climbed by 5.8% in 2021, surpassing even 2019 levels by 1.3% [3]. This situation has demonstrated that even if the world confronts an important test such as a pandemic, countries will always need

a high level of energy consumption both to improve their current economic conditions and for sustainable development. Therefore, this indicates that the share of fossil fuels, including coal and gas, in electricity generation will continue to be high for a very long time, as illustrated in Figure 1.3.

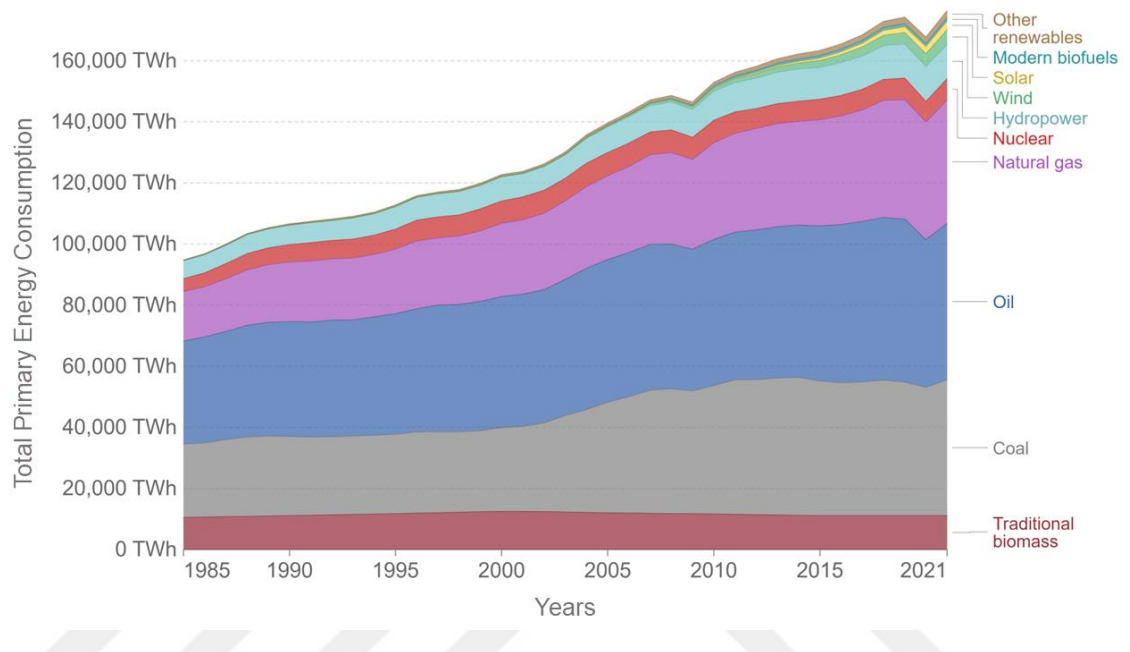


Figure 1.1. The global primary energy consumption from past to today [1].

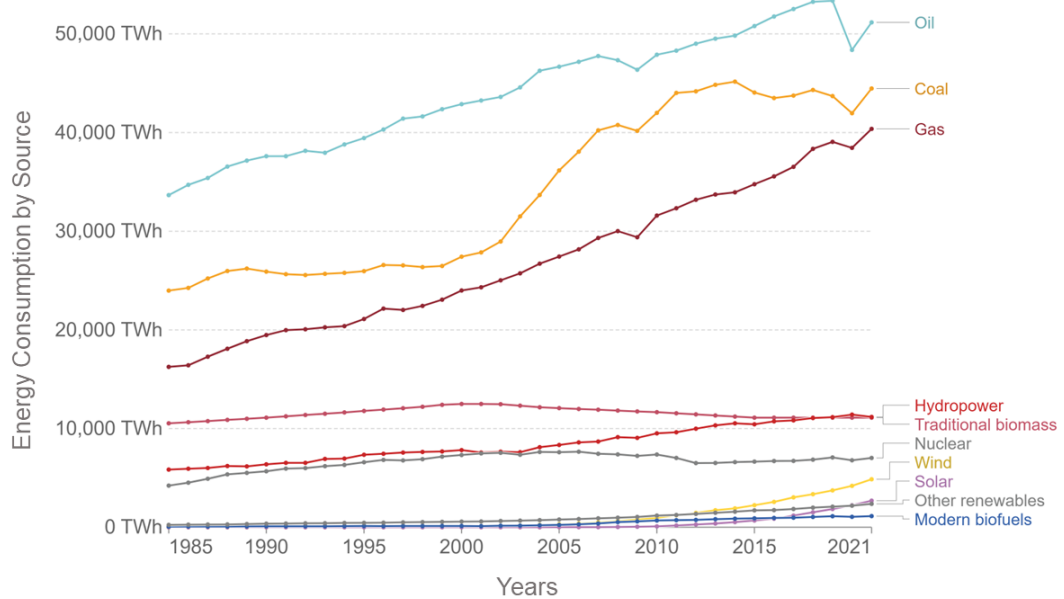


Figure 1.2. The share of primary energy consumption by source [1].

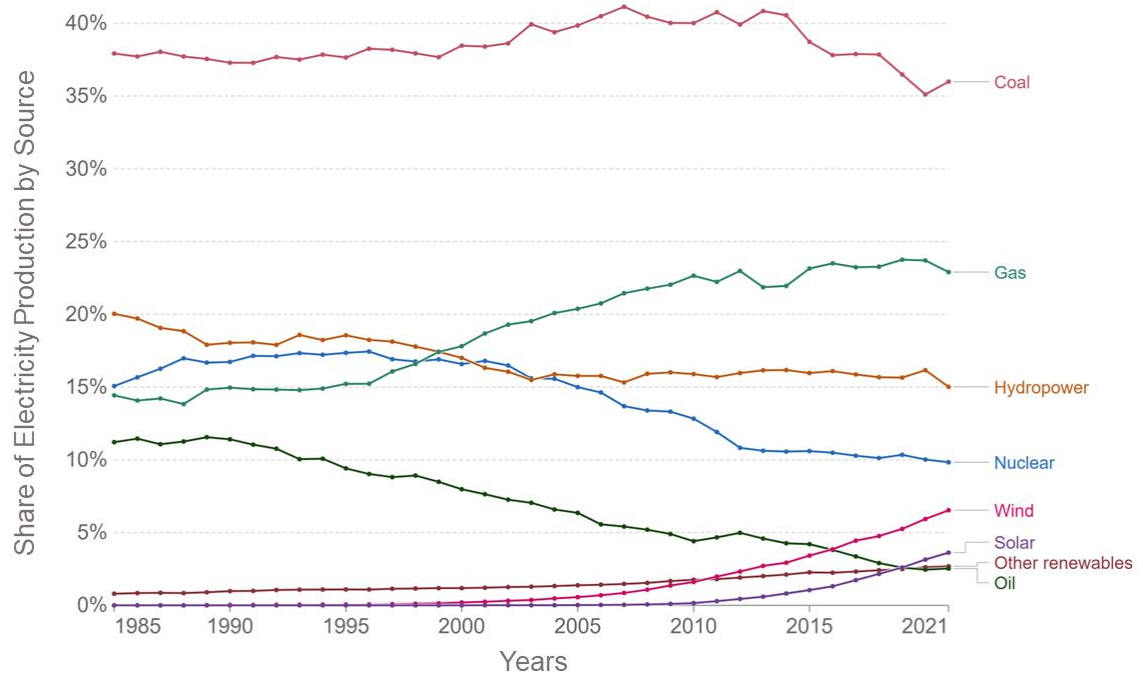


Figure 1.3. The share of electricity production by source [1].

The excessive utilization of fossil fuels to meet required energy needs brings considerable risk. Two significant predicaments began to emerge in general. Firstly, although large reserves have been discovered recently, fossil fuels will be rapidly exhausted in the foreseeable future, making them insufficient to meet future energy demands. According to BP's Statistical Review of World Energy Report published in 2016, roughly 50 years of oil and natural gas reserves are left, whereas coal reserves are much larger, projected to likely last more than one century depending on the additional undiscovered resources [4]. This situation may create a deficit in meeting global energy demand and threaten the world's energy security. Secondly, these fuels and end-use products have several adverse effects on the environment, mainly air and water pollution, due to their combustion, causing humanity to be significantly affected by this situation. The release of various toxic gases such as CO_x , SO_x , NO_x , CH_4 , and so on into the atmosphere by fuel combustion causes the greenhouse effect, ozone layer depletion, and acid rain. This situation leads to global warming and climate change, e.g., the melting of polar and high-altitude glaciers; depending on this situation, the possibility of some countries being submerged by rising sea levels, experiencing hurricanes, floods, or extreme droughts due to sudden temperature

changes, and finally, the extinction of plant, animal, and bacterial species [5]. Therefore, most countries have committed to phasing these sources out of their electricity mix, making zero-carbon pledges that are not legally binding but publicly available. As a result, they have begun to discover an alternative pathway for providing a clean, secure, and affordable energy supply.

Fuel cell technology is one of the most promising candidates to eliminate the above-mentioned environmental effects of the industrial age, promoting the decarbonization of the sector while satisfying energy demands. As clean energy-converting devices, fuel cells are ideal power sources that directly and continuously convert the chemical energy of the fuel into electrical energy without the need for a combustion process. Thanks to the direct conversion process of the internal energy, they are more efficient than traditional power supplies, including internal combustion engines (ICEs) and gas turbines. In comparison, fuel cells can produce electricity with an efficiency of up to 60% (and even higher with cogeneration), whereas the efficiency of classic combustion-based technologies remains only between 33-35% [6]. In addition, fuel cells present fuel flexibility in operation due to the capability of operation with clean (e.g., hydrogen, biogas, and methanol) and conventional fuels including natural gas, propane, and diesel, as given in Figure 1.4. However, the price of fuel, availability, energy content, environmental effects, and ease of storage and transportation should be considered selection criteria. In the case of using fossil-based fuels, carbon dioxide emissions (CO_2) are still lower than those from combustion-based power generators. In the case that pure hydrogen is fed as the fuel, the only by-products will be water and heat, helping to decrease critical climate change since there are no CO_2 emissions or air pollutants [7]. Moreover, fuel cells are compact and flexible in size and generate clean power ranging from less than a fraction of a watt to several megawatts for a wide range of applications, including transportation, stationary, backup, and portable, as indicated in Figure 1.5.

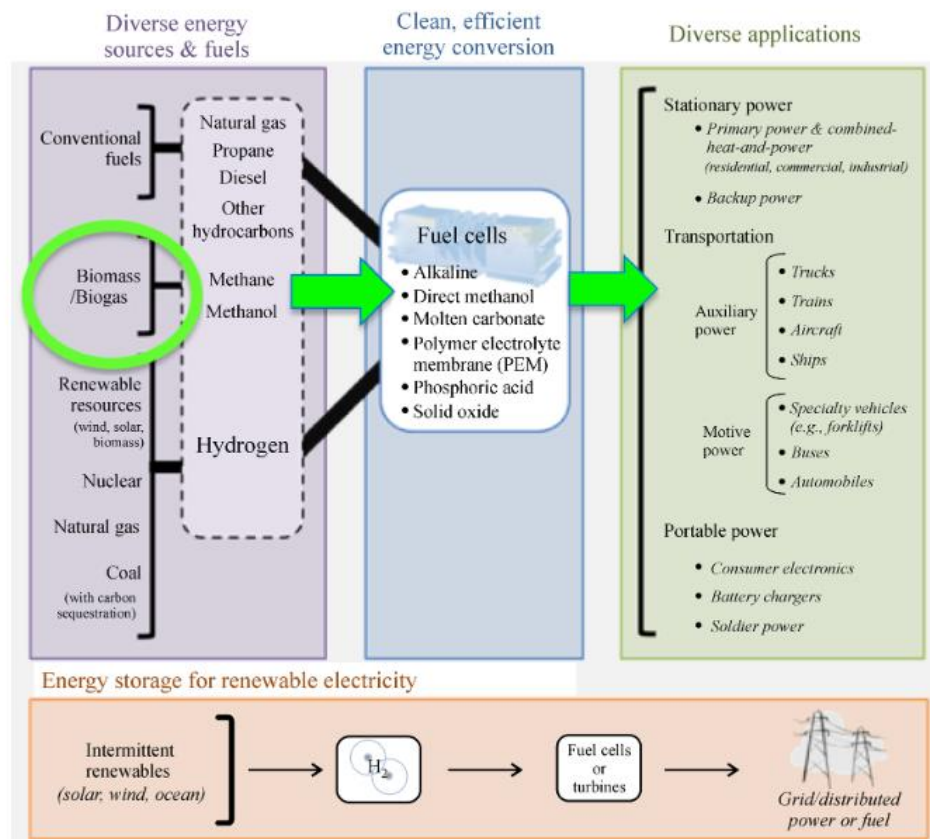


Figure 1.4. Fuel cells applications and diverse fuels [8].

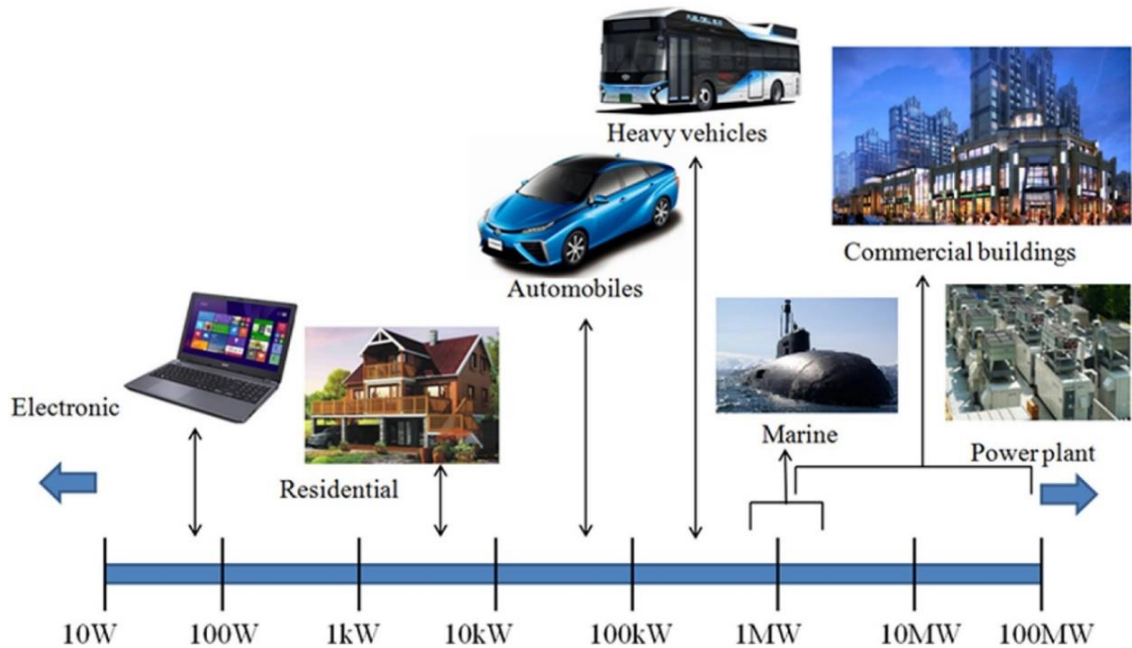


Figure 1.5. The power ranges of fuel cells for different applications [6].

1.2. HISTORY OF FUEL CELLS

Fuel cells, despite their modern characteristics, have been well-known for more than two centuries. The origins of the fuel cell can be traced back to the early 19th century, when a British scientist, Humphry Davy, initially introduced the fuel cell concept in 1801. Long after, in 1838, the German-Swiss scientist, Christian Friedrich Schönbein, published ground-breaking research in *The Philosophical Magazine* outlining the interaction between hydrogen and oxygen electrochemically. These pioneering accomplishments inspired William Grove, a chemist and patent lawyer, to construct the first fuel cell prototype in 1842. He performed a series of experiments with what he termed a gas voltaic battery—nowadays frequently known as the Grove battery. In these experiments, platinum electrodes were located in two tiny, upturned containers filled with hydrogen and oxygen. Both were submerged in an electrolyte solution of diluted sulphuric acid [9]. Thus, it was proved that an electrochemical reaction between hydrogen and oxygen over a platinum catalyst could generate an electric current.

The phrase, fuel cell, actually began to be utilized by Charles Langer and Ludwig Mond, who tried to construct a fuel cell by utilizing air and industrial coal gas in 1889. For more than a half-century, the progress of the ICE pressed fuel cell technology out of the concentration. Broad exploration was continued during the 1930s when Francis Bacon, a British engineering professor, effectively returned to the fuel cell concept through a design by Langer and Mond. In 1932, Bacon fostered a prototype alkaline fuel cell (AFC) by introducing nickel gauze electrodes and utilizing liquid potassium hydroxide as the electrolyte, which replaced sulfuric acid (H_2SO_4) [10]. During the following three decades, he developed the design and finally introduced the first practical and operational AFC in 1959, capable of producing 5 kW of electricity. In the same year, Harry Karl Ihrig, working for Allis-Chalmers, used a modified 15 kW Bacon cell for an agricultural tractor. Allis-Chalmers later built different fuel cell-powered vehicles, including a forklift, a golf cart, and a submersible, in partnership with the US Air Force. Simultaneously, General Electric employees Willard Thomas Grubb and Lee Niedrach extensively worked on an alternate fuel cell technology and discovered proton-exchange membrane fuel cells (PEMFCs). These PEMFCs were

also utilized on the first human-crewed spacecraft by NASA as part of the Gemini project in 1960. In contrast, AFCs designed by Bacon were employed in the Apollo program and later space missions such as Apollo-Soyuz, Skylab, and the Space Shuttle [11].

Along with considerable improvements in the mid 1960ies, due to the need for a more robust cation exchange membrane material, DuPont cultivated the first membrane layer based on polytetrafluoroethylene and perfluoro vinyl ether, recognized by the tradename Nafion®. In 1966, General Motors used fuel cell technology in ground transport, creating the Electrovan, a concept automobile powered by hydrogen fuel cells [12]. Thereupon, fuel cells started to be employed in a wide range of applications, e.g., from submarines to stationary applications for different locations, from small vehicles to big commercial cars, as demonstrated in Figure 1.6.

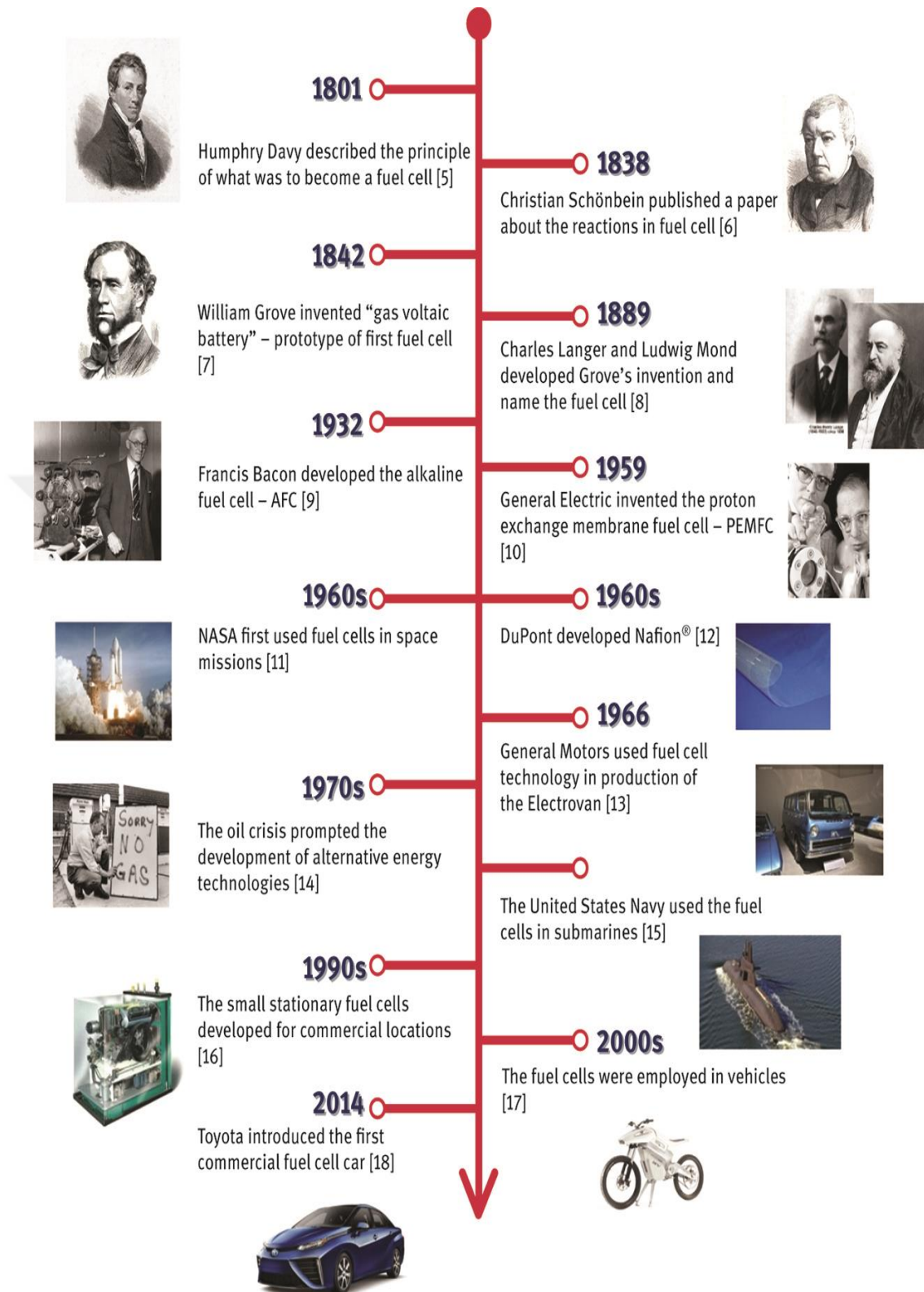


Figure 1.6. The historical development of fuel cells [12].

1.3. BASIC PRINCIPLES AND FUNDAMENTALS

Fuel cells are next-generation power supplies that convert reactants (e.g., hydrogen or a hydrogen-rich gas mixture at the anode and air or pure oxygen at the cathode) into electricity, heat, and water in the presence of a catalyst, thereby converting chemical energy directly and continuously into electrical energy. In its simplest form, the fuel cell consists of three adjacent components: an anode (negatively charged electrode), a cathode (positively charged electrode), and a membrane as an ion-conducting electrolyte in the form of a solid sandwiched between electrodes [6]. Both electrodes are generally comprised of a gas diffusion layer (GDL) with a thin catalyst layer (CL) coating at the electrode-electrolyte interfaces where the reactions take place [13].

Fuel cells operate according to the principle of electrolytic charge exchange between anode and cathode plates [14]. All known types of fuel cells, in general, consume hydrogen and oxygen. The pure hydrogen or hydrogen-rich gases from conventional sources are continuously supplied to the anode, whereas oxygen from the air is fed to the cathode. The hydrogen molecules react with a catalyst on the anode side, splitting into positively charged ions (H^+) and negatively charged electrons (e^-) [12]. Thus, these electrons are being liberated by the reaction known as the hydrogen oxidation reaction (HOR). The electrolyte membrane prevents hydrogen and oxygen from direct contact, acting as an insulator for electrons and enabling only positive ions to migrate from the anode to the cathode side. The electrons, by nature, desire to recombine beyond the membrane layer to form a steady system. Therefore, released electrons are forced to flow through an external circuit to reach the cathode side, whereas H^+ ions advance through the electrolyte that encourages the ionic movement. When they reach the cathode, these ions encounter oxygen molecules and produce water. This operation is known as the oxygen reduction reaction (ORR) [15]. The flow of electrons generates an electric current and completes the cycle. Thus, water, heat, and electrical energy are obtained as products, as demonstrated in Figure 1.7.

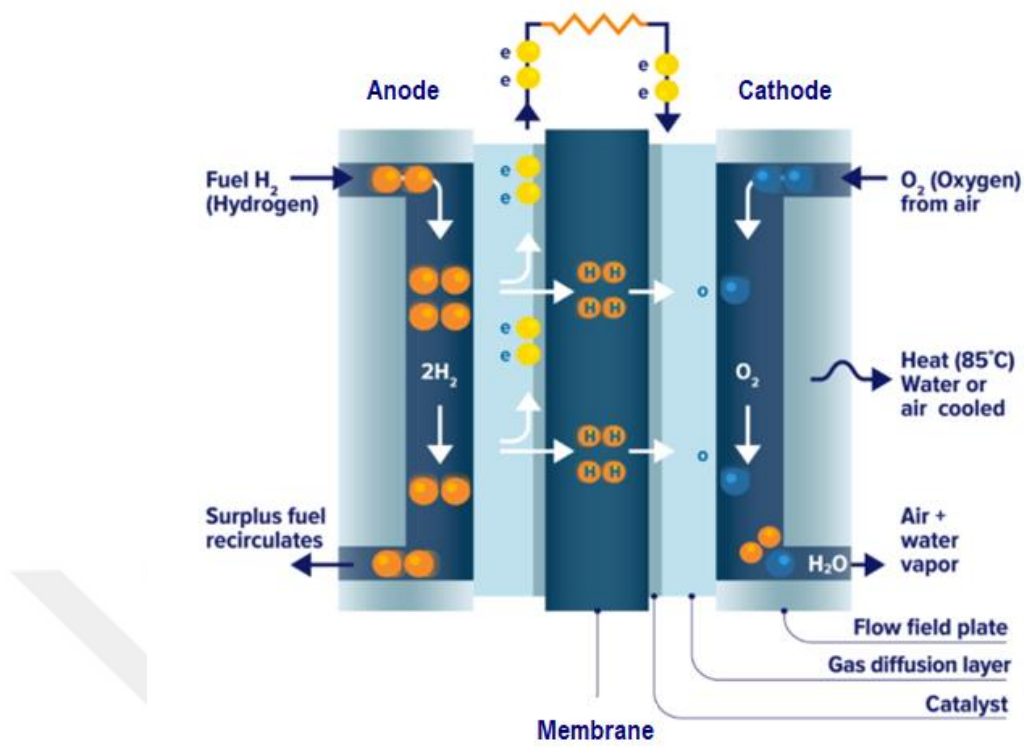
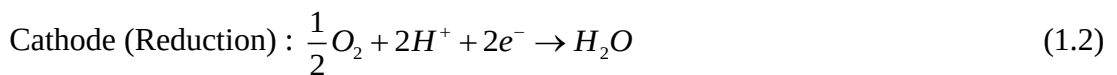


Figure 1.7. The structure of a typical hydrogen/oxygen fuel cell [16].

Electrochemical reactions happening simultaneously in a typical hydrogen/oxygen fuel cell can be expressed as follows [15]:



In order to sustain continuous isothermal operation for optimal power generation, by-products (heat and water) must be continuously eliminated. Consequently, water and temperature management are critical components in fuel cells' effective design and operation [10].

1.4. CLASSIFICATION OF FUEL CELLS

Fuel cells are typically categorised based on the type of electrochemical material (e.g., electrolyte) they employ. The properties of this material govern the ideal operating temperature as well as the fuel type utilised to produce energy. According to their electrolytes, six types of fuel cells are actively being developed given as [17]:

- Alkaline fuel cell (AFC)
- Direct methanol fuel cell (DMFC)
- Molten carbonate fuel cell (MCFC)
- Phosphoric acid fuel cell (PAFC)
- Proton-exchange membrane fuel cell (PEMFC)
- Solid oxide fuel cell (SOFC)

In the list mentioned above, DMFC is the only exception since the fuel methanol is utilised for classification rather than the electrolyte. In addition, the regenerative fuel cells (RFCs) are also subject to another category due to the mode of operation. The comparison of these fuel cells including electrochemical reactions and distinguishing characteristics is outlined in Table 1.1. Each type has its own unique set of advantages and disadvantages. The fundamental distinctions between these kinds are determined by the electrolyte and catalyst employed, the charge carrier, the need for an external reformer, operating temperature, primary cell components, and water and heat management [18]. Apart from these fuel cells, there are also less popular types, including air depolarized cells, alkali metal halogen cells, biochemical fuel cells, inorganic redox cells, RFCs, and sodium amalgam cells. However, these fuel cells are still under research and may be employed for special applications in the future [19]. All types of fuel cells, including those at the commercial (C) and research stage (R), are presented in Figure 1.8. Among these fuel cell types, PEMFCs have received the greatest interest due to their pollution-free operation, rapid start-up, simplicity, and viability. Therefore, the next chapter is devoted to the basics of PEMFC technology.

Table 1.1. The comparison of major fuel cell types [17].

Types of fuel cells			
		AFC	DMFC
Chemical Reactions	Anode	$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$	$CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^-$
	Cathode	$O_2 + 4H_2O + 4e^- \rightarrow 4OH^-$	$6H^+ + 6e^- + 3/2O_2 \rightarrow 2H_2O + CO_2$
	Overall	$2H_2 + O_2 \rightarrow 2H_2O$	$CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2$
Charge carrier		OH^-	H^+
Operating temperature (°C)		23-70 °C	>60 °C
Electrolyte		KOH	Polymer membrane
Fuel		H ₂	Methanol
Electrical efficiency		60-70%	20-30%
Power range		10 W-200 kW	100 mW-1 kW
Advantages		• High efficiency • Cheaper • Highly active • Simple heat management • Fast kinetics	• High power density • Low operating temperature • Zero CO₂ emission • Tolerant to CO poisoning
Disadvantages		• Expensive • Intolerant to CO₂ • Highly pure O₂ required • Corrosion	• Expensive • Poisoning by-products • Low efficiency • Toxic due to methanol
Applications		• Aerospace • Submarines • Aircrafts	• Automobile • Small portable devices
		MCFC	PAFC
Chemical Reactions	Anode	$2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e^-$	$2H_2 \rightarrow 4H^+ + 4e^-$
	Cathode	$O_2 + CO_2 + 4e^- \rightarrow 2CO_3^{2-}$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
	Overall	$2H_2 + O_2 \rightarrow 2H_2O$	$2H_2 + O_2 \rightarrow 2H_2O$
Charge carrier		CO_3^{2-}	H^+
Operating temperature (°C)		550-700 °C	180 °C
Electrolyte		Molten carbonate	H ₃ PO ₄
Fuel		H ₂ /CO/CH	Phosphoric acid
Electrical efficiency		55%	55%
Power range		< 1 kW-1 MW	50 kW-1 MW
Advantages		• High efficiency • Direct fossil fuel • Variety of fuel • Cheaper • Highly active	• Commercial • Resistant to impure H₂ • Highly stable • Low vapor pressure

Table 1.1. Continued.

Disadvantages		• High temperature • Low power density • Corrosion • Cathode dissolution	• Low power density • Corrosion • Low ionic conductivity • Resistant to CO
Applications		• Large, distributed generation • Electrical energy storage	• Distributed generation
		PEMFC	SOFC
Chemical Reactions	Anode	$2H_2 \rightarrow 4H^+ + 4e^-$	$2O^{2-} + 2H_2 \rightarrow 2H_2O + 4e^-$
	Cathode	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$O_2 + 4e^- \rightarrow 2O^{2-}$
	Overall	$2H_2 + O_2 \rightarrow 2H_2O$	$2H_2 + O_2 \rightarrow 2H_2O$
Charge carrier		H^+	O^{2-}
Operating temperature (°C)		< 80 °C (LT-PEMFC) 120-200 °C (HT-PEMFC)	700-1000 °C
Electrolyte		Polymer membrane	Ceramics
Fuel		H ₂	H ₂ /CO/CH
Electrical efficiency		50-70%	60-65%
Power range		1 W-500 kW	5 kW-3 MW
Advantages		• High power density • Operating low temperature • Broad power range • Easy scale up	• High efficiency • Direct fossil fuel • Variety of fuel • Cheaper • Highly active
Disadvantages		• Expensive • Highly pure H₂ required	• High temperature • Low power density • Corrosion • Cathode dissolution
Applications		• Automobile • Portable devices	• Utility electrical energy storage • Aircraft • Automobiles

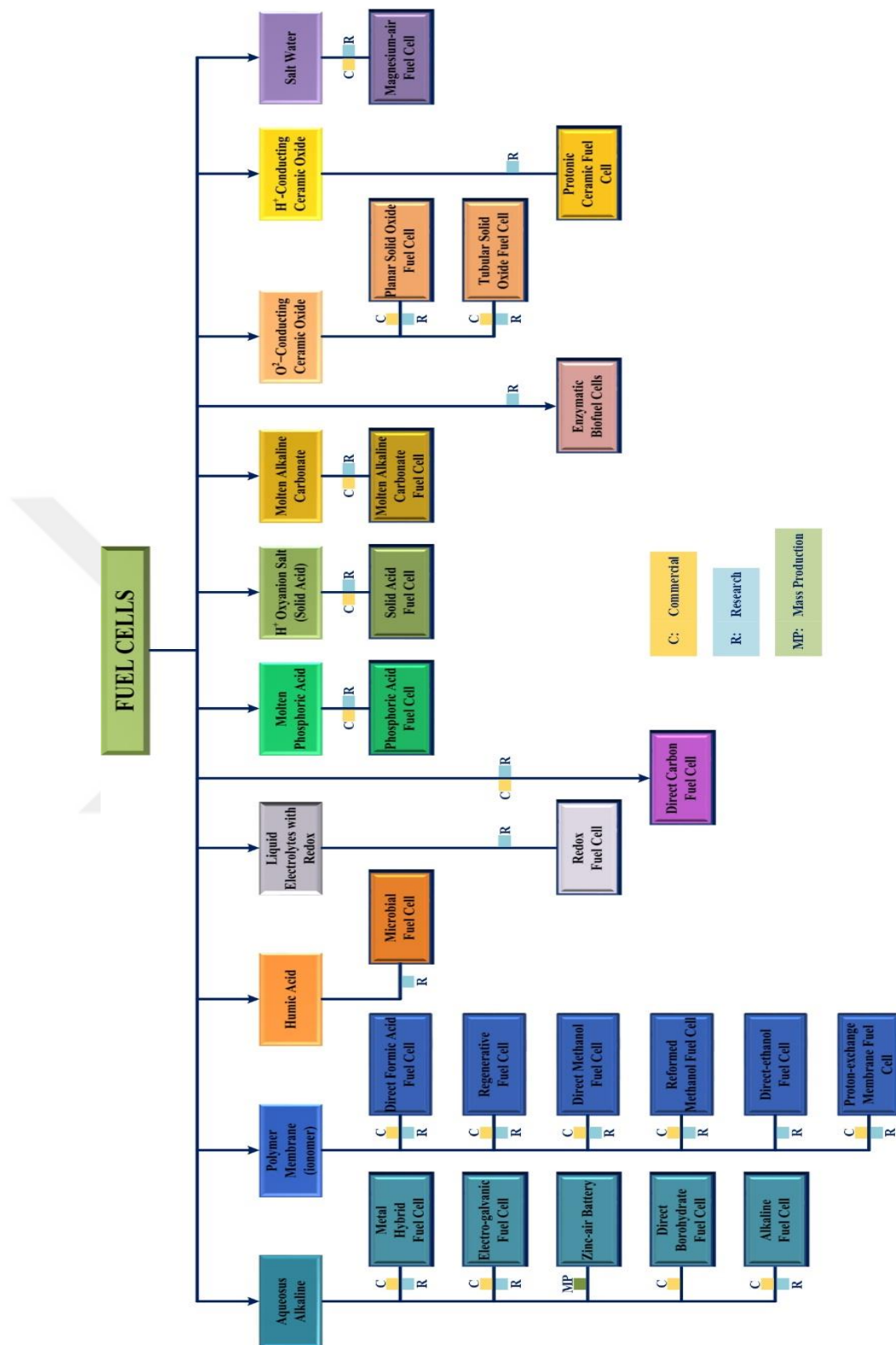


Figure 1.8. The general classification of fuel cells.

CHAPTER 2

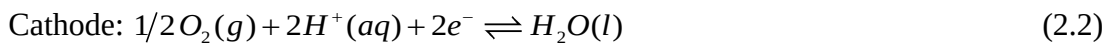
PROTON-EXCHANGE MEMBRANE FUEL CELLS

Proton-exchange or polymer electrolyte membrane fuel cells (PEMFCs) are electrochemical energy converters, transforming the chemical energy stored in the fuel (e.g., hydrogen) accompanied by an oxidant (e.g., oxygen) into electrical energy through chemical reactions [13]. In this type of fuel cell, a solid proton exchange membrane is utilized as an electrolyte, conducting protons while acting as an insulator for electrons. This electrolyte's characteristics greatly depend on operating circumstances, including temperature and pressure. Accordingly, PEMFCs can be divided into two categories according to their operating temperatures: low-temperature PEMFCs (LT-PEMFCs), operating below 100 °C (generally 80 °C), and high-temperature PEMFCs (HT-PEMFCs), operating between 120-200 °C [20]. LT- PEMFCs were initially discovered in 1959 by General Electric for use on the first human-crewed spacecraft of NASA under the scope of Gemini program [21]. The sulfonated polystyrene (SPS) polymer membrane was used in this project; however, the stability of this membrane was not sufficient [22]. Along with considerable improvements in the mid 1960ies, as a result of the need for a more robust cation exchange membrane material, a new polymer (notably Nafion®) was developed by DuPont [21]. Since Nafion® has greater acidity and conductivity and is much more stable than SPS membranes [22], it became a proper option to be employed in both PEMFCs and DMFCs in the 1990s [23]. Thus, a perfluoro-sulfonic acid (PFSA) polymer membrane commercialized as the Nafion® has soon become an industrial standard as being one of the most popular and commonly used electrolytes for LT- PEMFCs [20]. Because of its extremely high ionic conductivity, excellent thermal and mechanical stability, also resilience [24], it is still in use today [21]. These prominent features of this membrane allow LT-PEMFCs to be one of the most

interesting and potentially successful candidates for transportation [25], power generation [26], and portable and immobile operations [27].

2.1. OPERATING PRINCIPLES OF PEMFC

The conversion of chemical energy to electrical energy in a PEMFC occurs through electrochemical half-reactions at its electrodes. Humidified hydrogen and oxygen, either pure or in air form, stream through the anode and cathode compartments, and correspondingly, the oxidation and reduction reactions take place, respectively. During the oxidation half-reaction, hydrogen gas creates H^+ ions, which move through the ionically conducting polymer electrolyte membrane to the cathode, and free electrons, which flow to the cathode through an external circuit. H^+ ions advance through the electrolyte, which encourages ionic movement. During the reduction half-reaction, oxygen from the air that flows into the cathode reacts with these H^+ ions and electrons to generate water. Electrons flowing through the external circuit generate electricity and complete the cycle. Since the electrochemical reactions in the fuel cell happen in an exothermic process, the energy is released as heat. Thus, the water, heat, and electrical energy are obtained at the end as the products. The two electrochemical half-reactions and the overall reaction are summarized as follows [28]:



where (g) denotes to the gaseous state, (aq) refers a substance in the aqueous phase that is dissolved in water, and (l) stands for the liquid state.

Here, it is worth noting that the two-directional arrows in these reactions mentioned above express that these reactions are electrochemically or chemically reversible but not thermodynamically, owing to their restricted reaction rates in both directions [29].

These two half-reactions typically proceed extremely slowly at the LT-PEMFC, operating at a low temperature of approximately 80°C. Therefore, catalysts are applied to both the anode and cathode in order to accelerate each half-reaction.

2.2. MAIN COMPONENTS OF PEMFC

A PEMFC, in its most basic form, is composed of two electrodes (anode and cathode), a polymer membrane as an ion-conducting electrolyte in the form of a solid sandwiched between the electrodes, and flow field plates located on either side of the electrodes, as presented in Figure 2.1 [30]. However, indeed, the PEMFC is a multilayer structure consisting of different fundamental components from the inner surface to the outer, as follows:

- Polymer electrolyte membrane (PEM)
- Catalyst layers (CLs) that support the electrodes (the side facing the membrane)
- Gas diffusion layers (GLs) adjacent to a microporous layer (MPL)
- Sealing gaskets (SGs) surrounding the cell at the outermost
- Bipolar plates (BPs) that supply the fuel and oxidant to the reactive sites on both sides
- Current collectors (CCs)
- End plates (EPs)

The multilayer structural view of the PEMFC is represented in Figure 2.2 [31]. Among these components, the most crucial building block of the fuel cell is the membrane electrode assembly (MEA), which consists of an electrolyte, anode and cathode electrodes, CLs, and GDLs. Another key component is a GDL, generally coated with a carbon-based ink, thereby forming an MPL. Together, they are referred to as the gas diffusion medium (GDM). In addition, in Figure 2.2, anode and cathode electrodes are not displayed separately. This is because these electrodes are typically composed of CLs applied as coatings on the opposite sides of the membrane, and GDM.

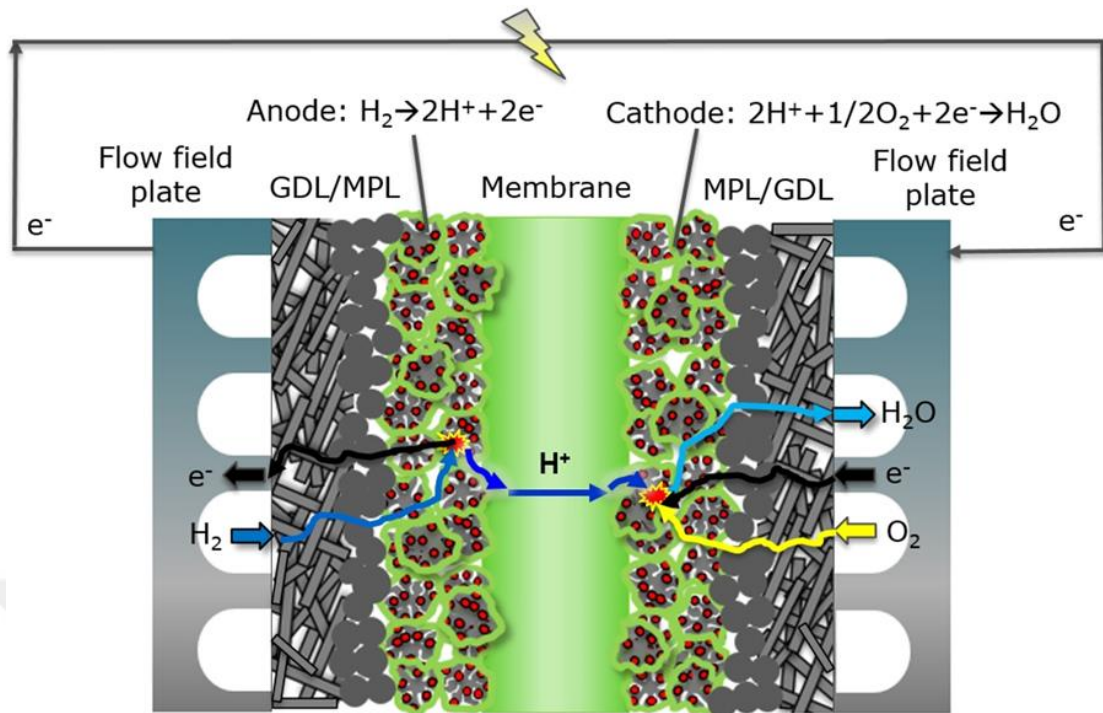


Figure 2.1. The basic schematic view of a PEMFC [30].

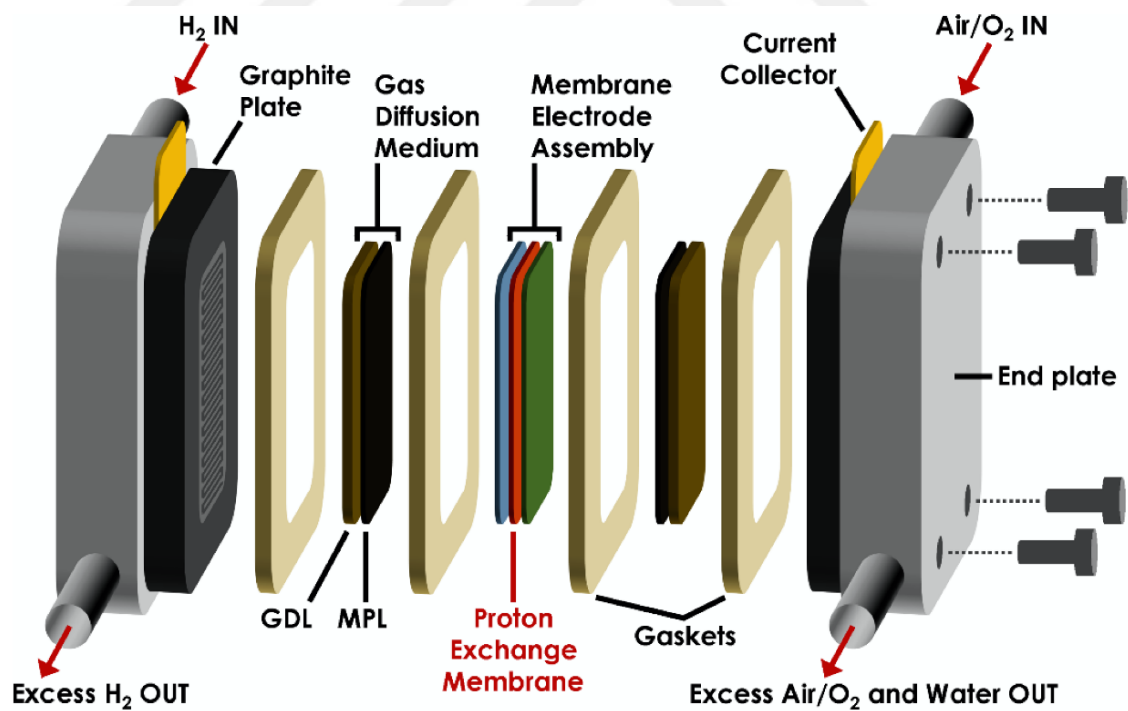


Figure 2.2. The multilayer structural view of a single-cell [31].

2.2.1. Membrane Electrode Assembly (MEA)

The MEA is the core component of a PEMFC, where power-generating electrochemical processes occur. The fundamental components of a standard MEA are a membrane, anode, and cathode (CLs), and (GDLs) linked to each CL. However, different MEA structures are also available. Firstly, a conventional two-layer MEA is created by applying a catalyst ink to the GDL. A Gas Diffusion Electrode (GDE) is the name given to this particular structure. Both sides of the membrane are coated immediately with the catalyst ink in the second configuration. This structure, known as the Catalyst Coated Membrane (CCM), creates the three-layer MEA. Finally, the third kind of MEA consists of either two GDEs sandwiched by a membrane or the CCM sandwiched by two GDLs to create a five-layer MEA, as represented in Figure 2.3 [32].

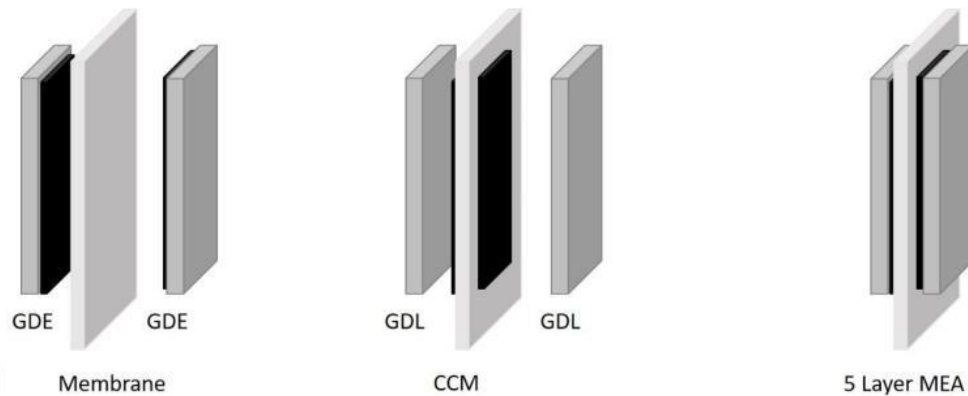


Figure 2.3. Different configurations of MEA structures [32].

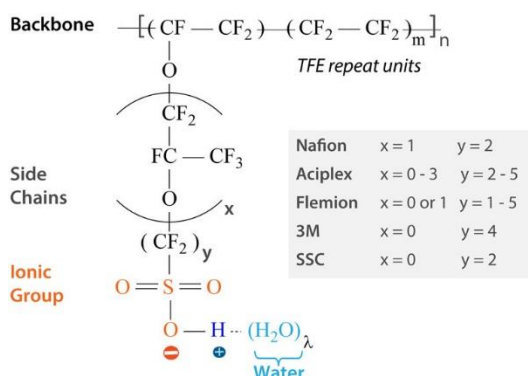
2.2.1.1. Polymer Electrolyte Membrane (PEM)

The membrane is a polymer structure with a thickness of approximately 50 to 254 μm placed between the anode and cathode CLs in a PEMFC and whose main function is to provide ionic interaction between the anode and cathode [33]. Another important role of the membrane is to provide H^+ ions to drift from the anode to the cathode and act as an insulator for electrons and a barrier for reactants by separating the reacting gases (hydrogen and oxygen). Therefore, the membrane material must be an excellent

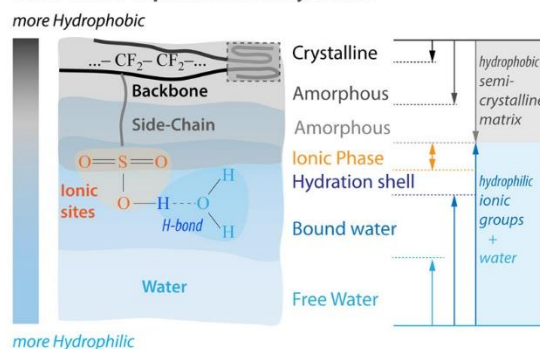
insulator, have strong ionic conductivity, limit gas cross-over, inhibit electron exchange, and have great mechanical and chemical stability.

PEMs may be fabricated from pure polymer membranes or composite membranes in which additional materials are inserted inside a polymer matrix. As mentioned earlier, the polystyrene sulfonic acid (PSA), whose salts are polystyrene sulfonates with the idealized chemical formula of $(\text{CH}_2\text{CHC}_6\text{H}_4\text{SO}_3\text{H})_n$, was the first membrane employed in LT-PEMFCs. However, this membrane was discovered fragile and operable for only up to 500 hours. In the mid-1960s, DuPont developed the first ion-conductive polymer membrane based on the perfluorocarbon-sulfonic acid (PFSA) ionomer, recognized by the tradename of Nafion®. It is a copolymer of polytetrafluoroethylene (PTFE or Teflon) by adding sulfonic acid ($\text{SO}_3^- \text{H}^+$) groups and perfluorinated chains to its structure [33]. The PTFE polymer is the structural backbone of the membrane and provides mechanical strength and functions as a barrier to prevent hydrogen and oxygen from mixing and reacting in an uncontrolled manner. Due to the sulfonic acid group's ionic interaction, an SO_3^- ion is present at the end of the side chain. The PTFE polymer structure enables the Nafion® membrane to be inherently hydrophobic. While the sulfonic acid group is crucial for membrane hydrophilicity and proton conductivity, the resulting structure is known as the ionomer. Its high conductivity is attributable to the binding strength of the sulfonic acid group. The C-F bonds are much stronger than the C-H bonds, and the F bonds protect the C-C bonds appropriately. Due to their increased electron affinity, the presence of F-atoms in sulfonic acid raises its acidity. Therefore, the proton conductivity increases in the case that the acidity of sulfonic acid rises. Furthermore, a perfluorinated polymer side chain provides greater mechanical and chemical stability. The length of the side chain has a considerable impact on the membrane's mechanical stability. In compared to larger length side chains, shorter length side chains are more crystalline. As a result, shorter side chains have high mechanical characteristics, which are advantageous in the construction of efficient membranes [17]. The typical chemical structure of PFSA ionomers produced by various institutions is depicted in Figure 2.4 (a). The phase separation in the membrane is a significant parameter governing the ionomer's chemistry (Figure 2.4 (b)). The impact of EW and sidechains is also illustrated in Figure 2.4 (c).

PFSA Ionomers: General Chemical Structure



Nano-Phase-Separation with Hydration



PFSA Structures: Comparison

Equivalent Weight: EW

$$\text{EW} = \frac{\text{g polymer}}{\text{mol SO}_3} = \frac{1000}{\text{IEC}}$$

$$\text{EW} = 100m + \text{MW}_{\text{side-chain}}$$

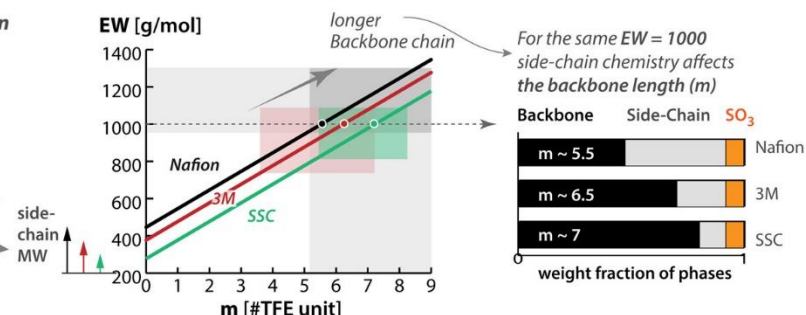


Figure 2.4. The illustrative view of (a) the chemical structure of PFSA ionomers, (b) non-phase separation, and (c) the impact of EW and sidechains [34].

The Nafion® is the most widely used and researched PFSA-based membrane for PEMFCs. However, other chemical companies, including Asahi, Chlorine Engineers, Dow, Fumatech, Gore, Solvay, etc., are also producing and commercializing this kind of polymer membrane [22,35]. Therefore, various series have been manufactured to date, including the Nafion 200, Nafion 115-117, HP, and XL. Among these series, Nafion-115 and Nafion-117 are the most used types, with thicknesses of 127 and 183 μm . The corresponding weights are 250 g/m^2 and 360 g/m^2 , respectively [13].

Nafion® membranes are typically stable over a restricted temperature range. The need for membrane humidification determines the upper-temperature limit since water is necessary for proton transport. This is because the performance of PEMFCs is directly related to the proton conductivity of the membrane that provides proton transfer. The proton conductivity of a membrane changes directly with its water content, which is a function of the temperature and relative humidity inside the cell. Since the membrane would dry out in the absence of water, the operation of the system is not suitable at temperatures above 80-90 $^{\circ}\text{C}$.

Protons transfer across a membrane in three ways: surface diffusion, Grotthuss hopping, and vehicular diffusion. The surface diffusion process occurs when the hydration level is low or close to the pore wall. Protons jump from one sulfonic site to another in this method. The Grotthuss hopping and vehicular diffusion processes are in charge of proton transfer at greater hydration levels. Protons move from one hydrolysed site to another in the first mechanism. On the other hand, the vehicular diffusion process includes the diffusion of hydrated protons through electroosmotic drag [17]. Figure 2.5 depicts potential proton diffusion processes in a Nafion membrane [36].

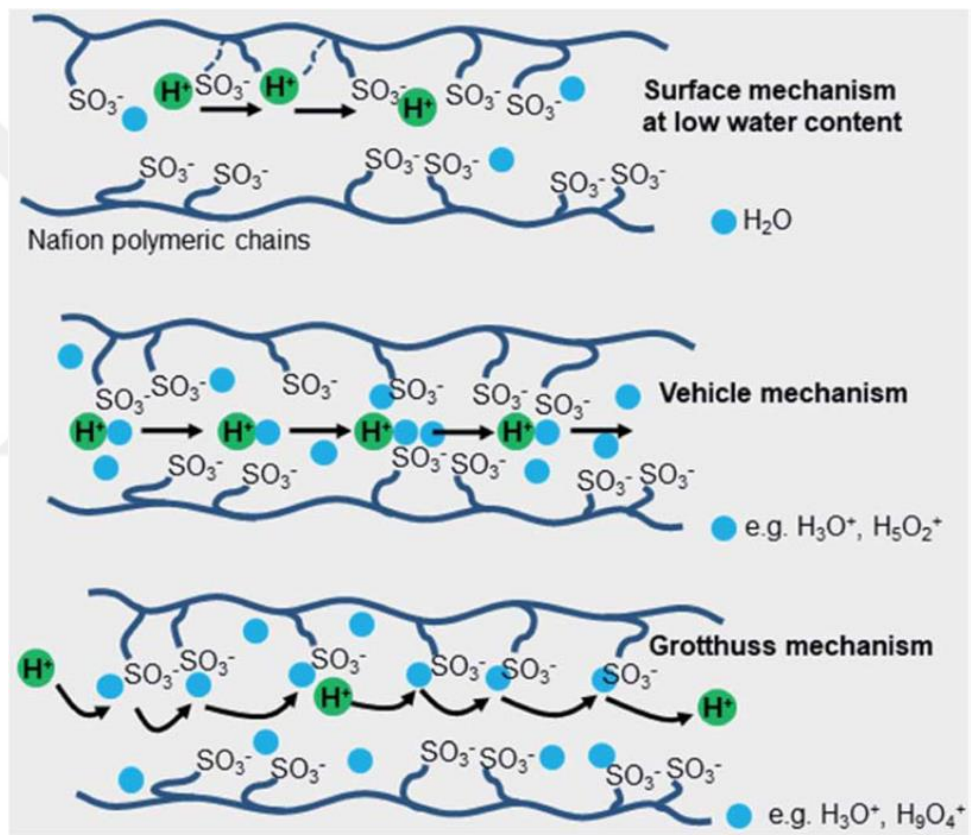


Figure 2.5. Different proton diffusion processes in a Nafion membrane [36].

The most significant issue with these Nafion® membranes used in PEMFCs is the reduction in proton or H^+ ion conduction caused by membrane drying. In the case that these membranes operate at temperatures over 80°C , the proton conductivity of the membrane and, hence, the performance of the PEMFC decrease substantially due to dehydration. The excess amount of water produces overflow and the formation of back pressure at the electrodes. Therefore, effective water management on the membrane is

necessary. It is also essential to remove the heat generated by the electrochemical reactions occurring in the fuel cell from the system. Keeping the temperature of the fuel cell constant requires an appropriate cooling system, particularly for medium and large-scale applications. As a remedy for these issues, several studies are being conducted on Nafion® membranes with enhanced chemical and mechanical stabilities and better water retention capacities. Thus, some alternative membrane materials used for PEMFCs have been extensively tested and investigated as follows [37]:

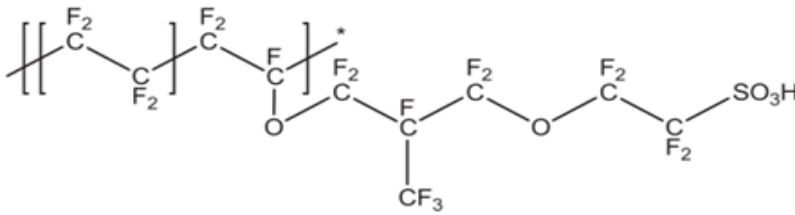
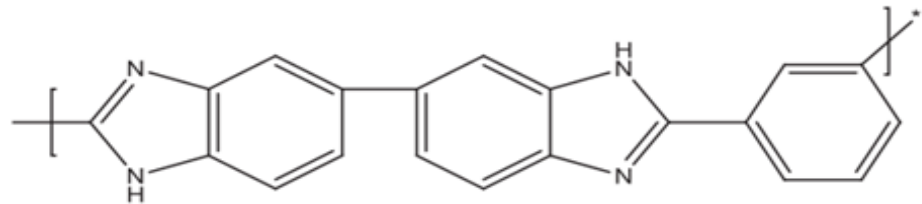
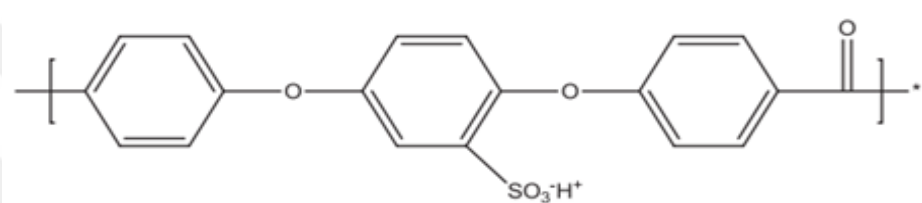
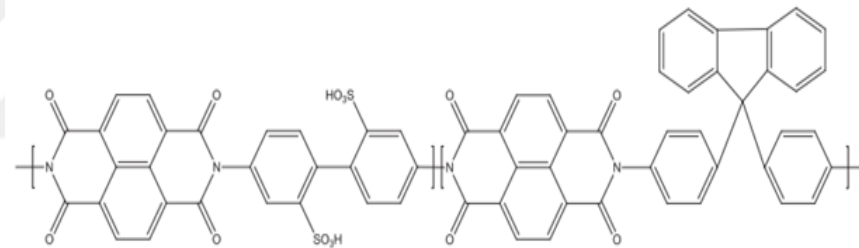
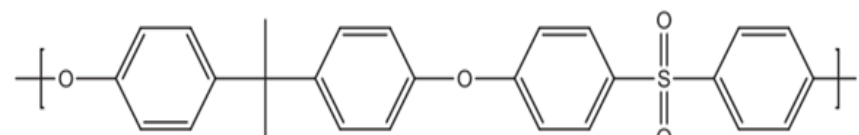
- Perfluorinated ionomers, including PFSA, perfluorocycloalkene (PFCA), perfluoro-sulfonyl imide (PFSI), and Grove-select.
- Partially fluorinated polymers, including sulfonated trifluoro styrene-grafted poly(tetrafluoroethylene) (PTFE-g-TFS) and polyvinylidene difluoride grafted polystyrene sulfonic acid (PVdF-g-PSSA).
- Non-fluorinated hydrocarbons, including aliphatic or aromatic structures.
- Acid-base blends, including sulfonated poly (ether ether ketone) (SPEEK)/polyethyleneimine (PEI), sulfonated polyphenylsulfone (SPPSU)/PEI, SPEEK/PBI/poly (4-vinyl pyridine) (P4VP), SPPSU/PEI, and PVA/H₃PO₄.
- Other composite and poly-organic membranes.

Among these options, the proper choice depends on the distinguishing features of the membranes, e.g., chemical and electrochemical stability, high proton conductivity, and sufficient mechanical integrity. Table 2.1 lists the classification of membrane materials. Besides, Table 2.2 presents the chemical structures of these PEM materials.

Table 2.1. The classification of membrane materials [38].

Perfluorinated	Partially fluorinated	Non fluorinated	Acid-base blends	Others
PFSA	PTFE-g-TFS	NPI	SPEEK/PBI/P4VP	Composite membrane Poly-AMPS
PFCA	PVdF-g-	BAM3G	SPEEK/PEI	
PFSI	PSSA	SPEEK	SPEEK/PSU(NH ₂) ₂	
Grove-select		SPPBP	SPSU/PBI/P4VP	
		MBS-PBI	SPSU/PEI	
			SPSU/PSU(NH ₂) ₂	
			PVA/H ₃ PO ₄	

Table 2.2. The chemical structures of common PEM materials [39].

Membrane type	Chemical structure
Nafion®/PFSA	
PBI	
SPEEK	
SPI	
SPSU	

2.2.1.2. Catalyst Layer (CL)

The catalyst layer (CL) is an active layer with a direct connection to the membrane and GDL. It is a critical component of the PEMFC because of the triple phase boundary (TPB), where the electrolyte, catalyst, and reactants combine and, therefore, where the electrochemical reactions occur, as illustrated in Figure 2.6 [39]. The role of catalysts with a thickness range of 5-25 μm in the fuel cell is to transport gases to the reaction region and accelerate the reaction, which occurs more slowly at low temperatures. For this reason, they are located at both poles, next to the electrodes and are produced larger than the geometric areas of the electrodes to achieve the desired reaction rate.

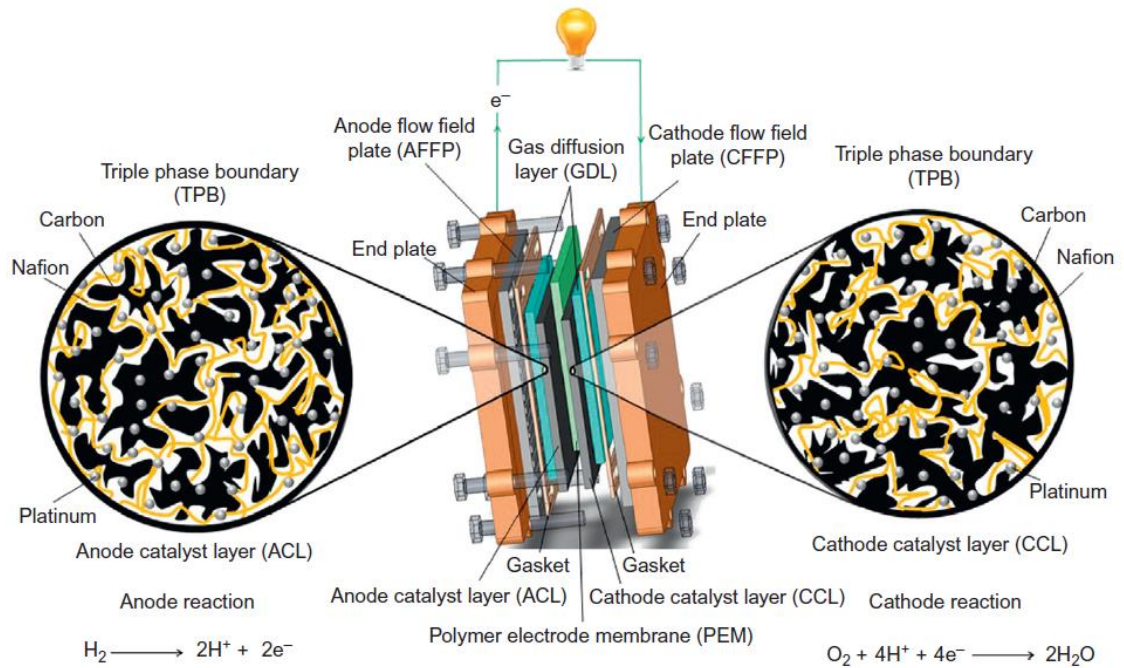


Figure 2.6. The exploded view of a TPB for a PEMFC [39].

The catalyst accelerates the chemical process without participating in the reaction itself. Since oxygen and hydrogen are inactive at low temperatures, fuel cells operating at low temperatures need extremely active catalysts. For this reason, platinum (Pt), the most active electrocatalyst to catalyse both anode and cathode reactions, is utilised for fuel cells operating on pure hydrogen and air. Pt nanoparticles are usually loaded on carbon support to reduce the cost because Pt is a quite expensive metal due to its extremely rare availability in nature. Therefore, Pt-based alloys are used nowadays to reduce platinum content. In fuel cells, carbon-supported platinum (Pt/C), platinum black (Pt/B), and platinum ruthenium (Pt/Ru) are the most prevalent catalyst types. For instance, Pt/Ru is used at the anode, whereas Pt/B or Pt/C is utilised at the cathode of DMFC. By converting CO to CO₂, Ru is used to reduce the poisoning effects of carbon monoxide on platinum. Although Pt offers outstanding catalytic properties, one of the major disadvantages of using it as a catalyst is its tendency to degrade. In order to overcome this issue, Curnick et al. [40] described novel techniques for manufacturing LT-PEMFC catalyst layers that improve the active Pt surface area and, thus, reduce the total Pt concentration. Using the ionomer Nafion® as a surfactant, they were able to stabilise the platinum particles through steric and electrostatic mechanisms. Thus, it

was discovered that strong interfacial contact could be achieved between these two phases, which persisted when the carbon support was added, as plotted in Figure 2.7.

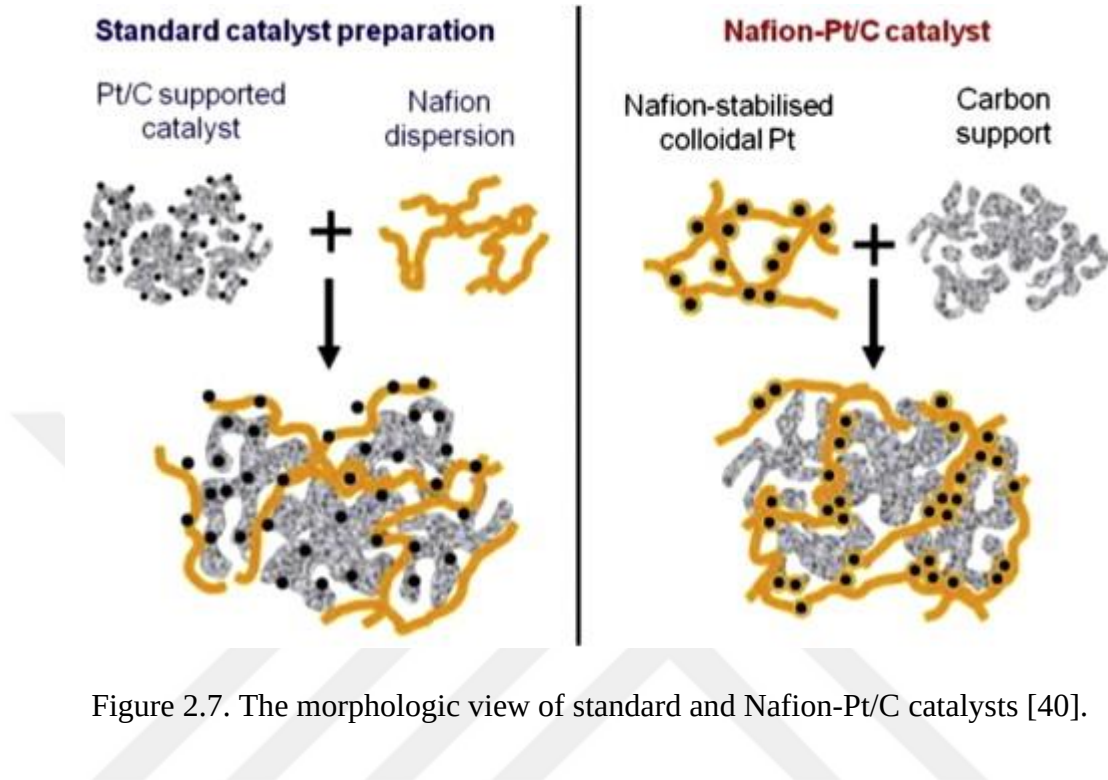


Figure 2.7. The morphologic view of standard and Nafion-Pt/C catalysts [40].

2.2.1.3. Gas Diffusion Layer (GDL)

The gas diffusion layer (GDL) located between the CL and the bipolar layer, is made of carbon fabric and paper. Its primary function is to ensure homogeneous concentration distribution of reactants throughout the CL, establish an electrical connection with the bipolar layer, and carry electrons to the bipolar layers on the anode and cathode sides. For this reason, it has a porous structure with a diameter of 0.1-0.5 μm , and its porosity varies between 70% and 80%. In addition, it is made of highly electrically conductive and chemically resistant materials. The GDL must be electrically and thermally conductive because electrical conductivity is required for electron transfer, and thermal conductivity is required for the dissipation of the generated heat from the catalyst to other fuel cell components.

The GDL also provides structural support to the CL and contributes to removing water produced as a by-product from the catalyst layer. In order to minimise the flooding problem, which leads to poor cell performance of the GDL with a thickness of

100- 500 μm , hydrophobic (water-repellent) materials are generally preferred. For this purpose, the GDLs produced as standard today consist of two main layers: a macroporous substrate (MPS) and a microporous layer (MPL), as displayed in Figure 2.8, and together with the CL, they constitute the GDE. The MPS, with a thickness of 100-500 μm , follows the gas flow field and operates by providing gas diffusion and collecting the current, usually through carbon paper or carbon fabric [41]. In addition, the carbon MPL minimises the contact resistance between the GDL and the CL, limits catalyst loss in the GDL interior, and helps improve water management by providing efficient water transport. The MPL naturally offers a smooth layer with sufficient surface area for the catalyst, as presented in Figure 2.9, and excellent membrane contact and usually employs PTFE as a binder that promotes hydrophobicity. This situation prevents water from escaping the membrane, the dehydration of the membrane, and the development of more resistance, which means lower performance. It is also often coated with PTFE (Teflon) to further increase its hydrophobicity. Thus, the water produced on the catalyst surface is transferred by diffusion through its hydrophilic channels to the water outlet gas channels, as represented in Figure 2.10. Therefore, species transport is stabilised without interference. The effective water management is essential to maintain gas transport and prevent waterlogging.

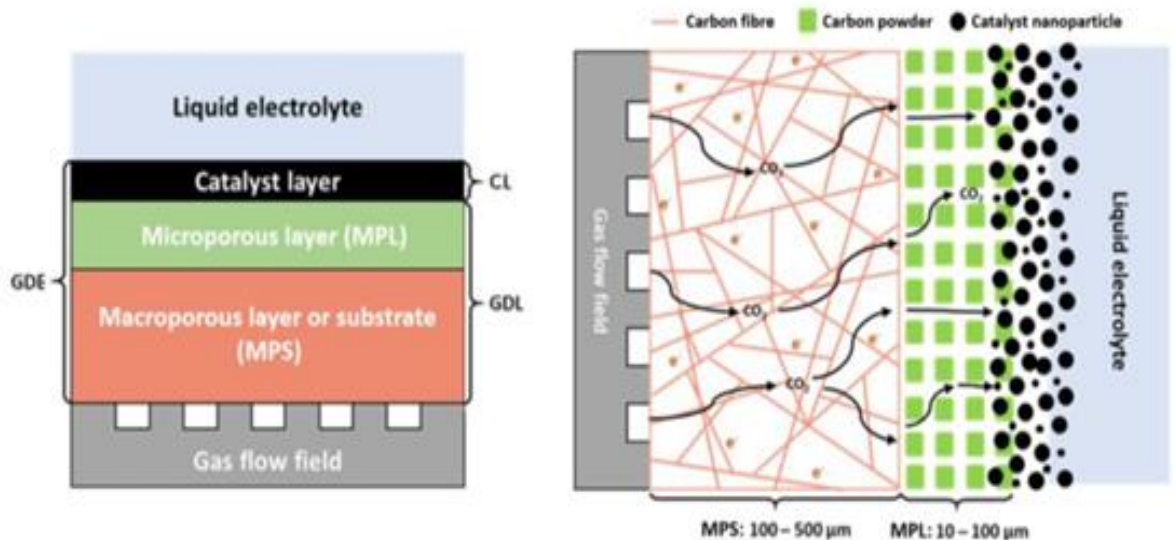


Figure 2.8. The schematic view of the GDL and GDE [41].

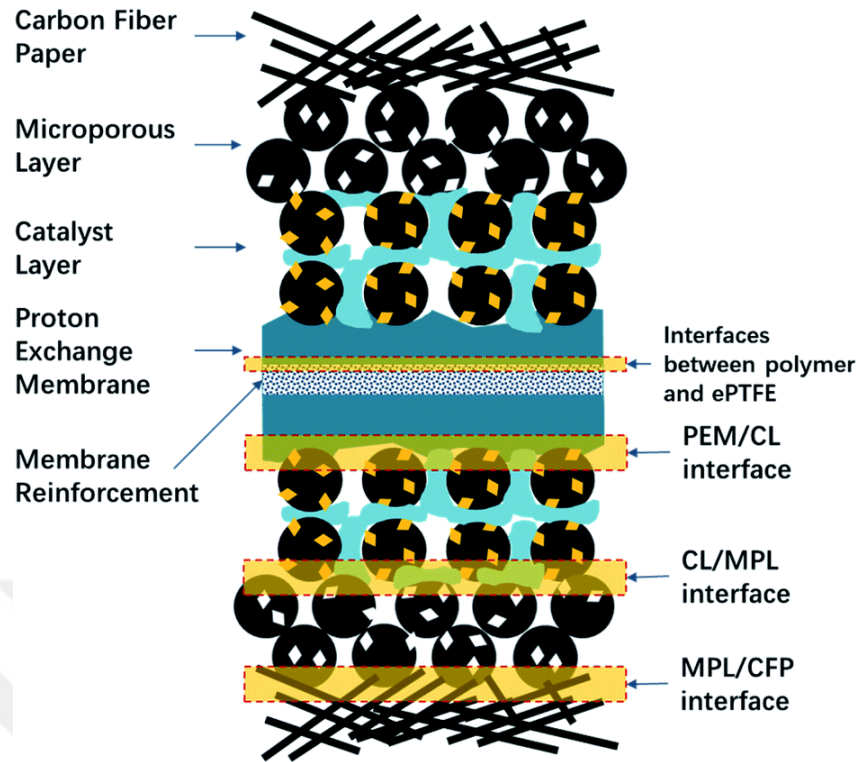


Figure 2.9. The structural view of MPS and MPL with different interfaces [42].

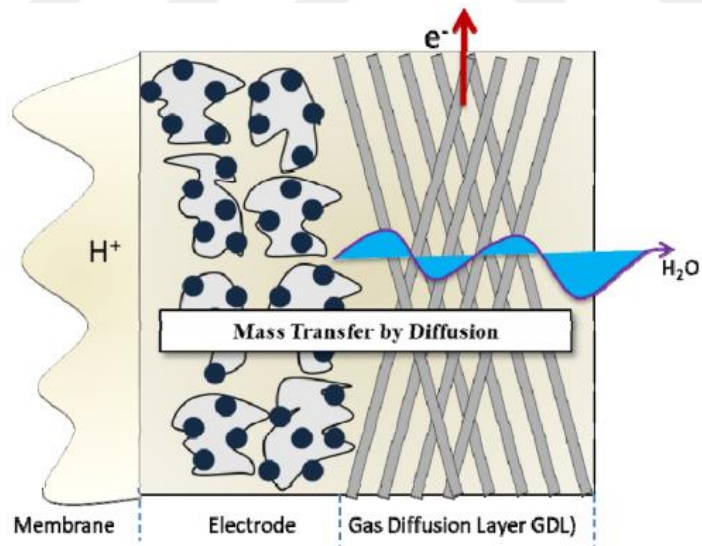


Figure 2.10. The water transport across the membrane to the GDL [43].

2.2.2. Sealing Gasket (SG)

Sealing gaskets (SGs) are intermediate components that prevent fuel leakage and help to distribute the pressure evenly. In PEMFCs, Teflon and silicone gaskets are generally

employed; however, other elastomeric gasket materials, including fluor elastomer copolymer, fluor silicone rubber, liquid silicone rubber, and ethylene propylene diene monomer rubber, can also be applicable. The specific properties provided by these materials are listed below [44]:

- Prevent leakage of gases
- Absorb vibration and shocks
- Chemically inert even in long-term use
- To be resistant to acids
- To be resistant to compression (200 N/cm²)
- Not reacting with hydrogen and oxygen
- To be resistant to melting and rupture
- Not containing materials that can poison catalysts

2.2.3. Bipolar Plate (BP)

Bipolar plates (BPs) are a significant component of PEMFCs, accounting for 60%– 80% of the overall stack weight, as plotted in Figure 2.11, and around 40%– 50% of the total stack cost. They are designed to implement many vital functions, as outlined below [17]:

- Uniform distribution of reactive gases on the active surface of the GDL
- Preventing reactant and coolant leakages
- Transporting the produced current from one cell to the another
- Ability to be connected in series to obtain higher voltage
- Transfer of reaction-generated heat from the fuel cell to the environment
- Facilitation of water and heat management inside the fuel cell
- Acting as a fuel and oxidant separator in the PEMFC stack
- Creating a manifold for oxidizing and fuel as well as cooling fluid
- Undertaking the mechanical maintenance of the MEA

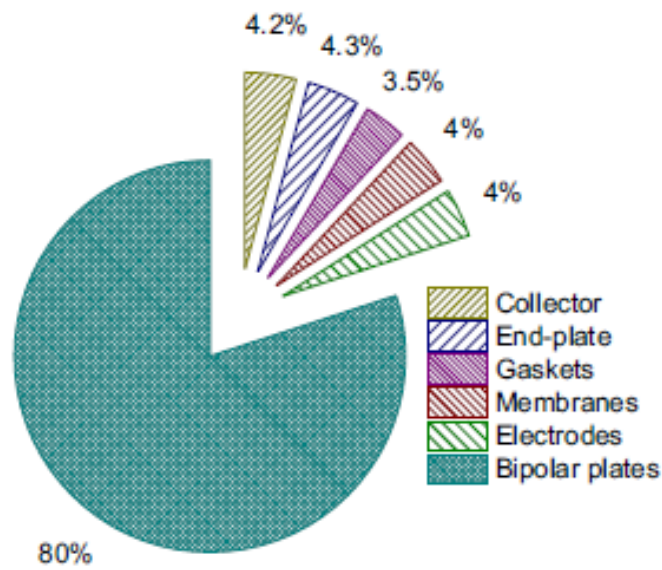


Figure 2.11. The percentage by weight of PEMFC components [17].

Considering these significant functions mentioned above, it is comprehensible that BPs should have certain characteristics. For instance, high thermal and electrical conductivity and low electrical resistance are required for fully functioning BPs. Herein, in terms of the electrical conductivity of BPs, the contact resistance is more significant than bulk resistance, particularly in terms of long-term behaviour. For long-term stability, a combined standard of less than $50 \text{ m}\Omega\text{cm}^2$ is used for the anode and cathode compartments, which should be maintained for at least 5000 hours of operation, whereas an initial resistance of $10 \text{ m}\Omega\text{cm}^2$ has been recommended as a standard [45]. Apart from these characteristics, BPs have other key physical features, including the density, hydrophobicity, and thermal expansion coefficient. The density should be low, less than $5\text{gm}/\text{cm}^3$; hence the weight of the BPs must be light yet resilient enough to withstand high stresses [46]. In addition, the following features are frequently sought in plate selection:

- Conformability [46].
- High compressive strength: $> 22 \text{ psi}$ [47].
- Hydrogen/gas permeability: $< 10^{-4} \text{ cm}^3/\text{s}\cdot\text{cm}^2$ [47].
- Low cost [17].
- Sufficient corrosion resistance: corrosion rate $< 0.016 \text{ mA}/\text{cm}^2$ [47].

In general, these plates should not only be composed of inexpensive and lightweight materials but also materials that are simple to produce. The primary materials include electro-graphite, sheet materials (both coated and uncoated), and graphite polymer composites. However, some attempts are currently being made to manufacture these plates that meet the abovementioned characteristics. The materials investigated to date, as presented in Figure 2.12 [47], can be broadly classified as:

- Non-metal: non-porous graphite/electrographite
- Metals: non-coated and coated
- Composites: polymer–carbon and polymer–metal

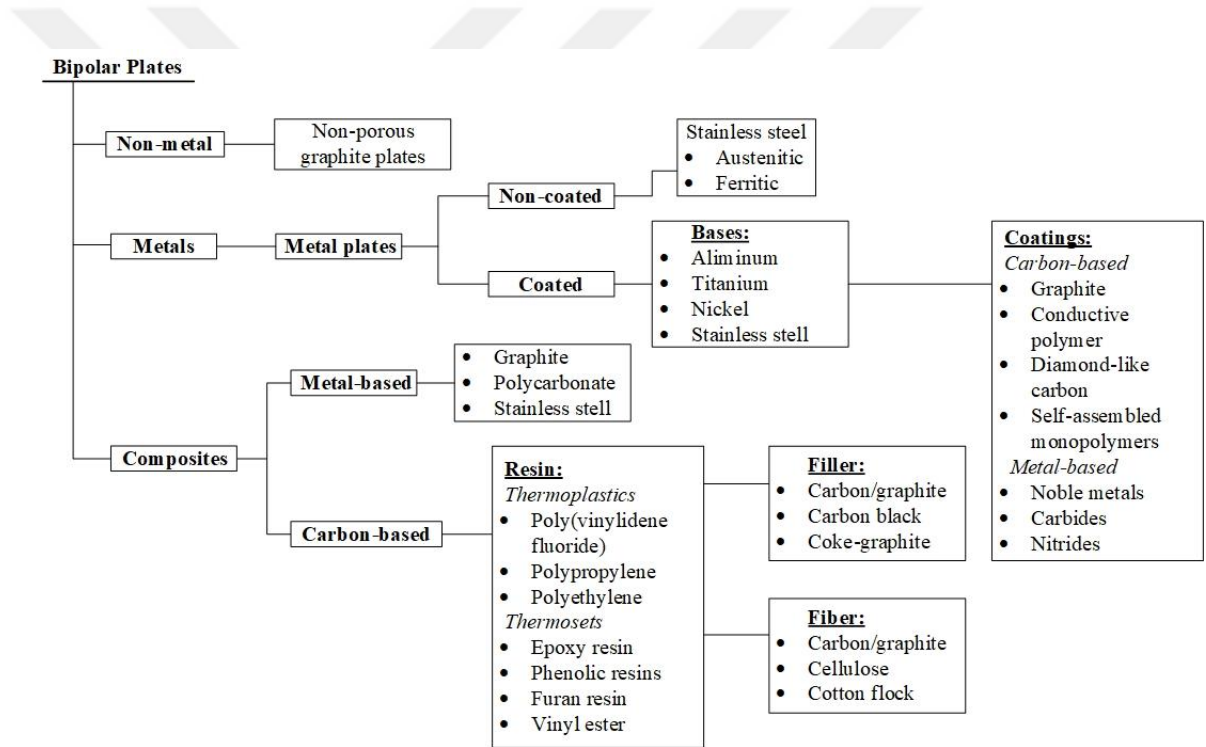


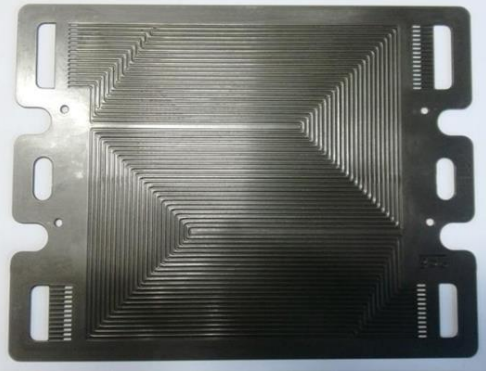
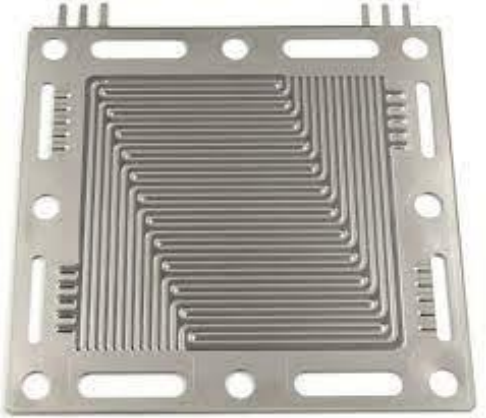
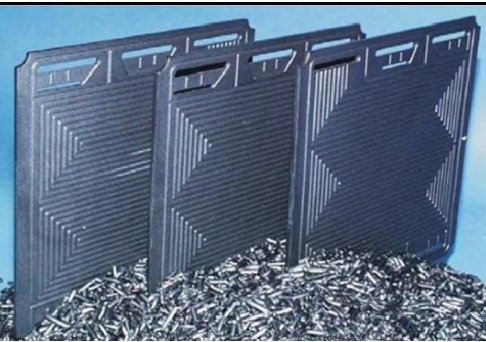
Figure 2.12. The general classification of BP materials employed for PEMFCs [47].

Non-porous graphite, both natural and synthetic, has traditionally been the most often utilised BP material due to its exceptional chemical stability in the fuel cell environment. The low electrical resistance of graphite materials enables the achievement of large power densities. Nevertheless, it is expensive, has little mechanical strength, and requires CNC machining and grinding for flow channel construction. Due to experiments conducted in recent years, these drawbacks have been overcome by using moulds to shape the channels on graphite plates.

Metals have begun to be employed as BP materials due to their excellent mechanical strength, high thermal conductivity, formability, and low weight when used as sheet metal and BPs. However, metal plates are susceptible to corrosion or dissolving when exposed to a fuel cell environment with a low temperature and a pH of 2-3. Dissolved metal ions and oxides poison the polymer membrane, resulting in a reduction in its ionic conductivity. In addition, the corrosion layer on the BP increases electrical resistance and decreases cell performance. In fuel cells, the use of uncoated metal plates or specific alloys is thus undesirable. As for basic metals, aluminium, titanium, and steels such as 304, 316L, and 301 are used. However, specific alloys such as Inconel may also be utilised as the material for BPs. The coatings applied on metal plates must be conductive and cling flawlessly to the metal's surface. Furthermore, the thermal expansion coefficients of the base metal and the covering material must be as similar as feasible. Otherwise, microcracks will form on the plate surfaces due to the disparate expansion rates. For coatings, carbon-based and metal-based coatings are recommended. Graphite, conductive polymer, diamond-like carbon, and organic mono-polymers are examples of carbon-based coatings. Metal-based coatings include noble metals, metal nitrides, and metal carbides [47].

Polymer composites are provided as an alternative to BP materials. Composites are excellent for PEMFC stacks because of their low weight and malleability. Composite plates can be categorized as metal-based and carbon-based. Los Alamos National Laboratory has developed a metal-based composite BP composed of porous graphite, polycarbonate plastic, and stainless steel. Since it is less time-consuming and less expensive to produce porous graphite plates than their nonporous counterparts, porous graphite plates may be used in conjunction with stainless steel and polycarbonate components to provide impermeability. Stainless steel provides the structure with rigidity, while graphite provides corrosion resistance. Polycarbonate's chemical resistance and formability make it appropriate for gaskets and manifolds. The multilayer plate appears to be a cost-effective and stable alternative. The comparison of these BP materials, focusing on advantages and disadvantages, is presented in Table 2.3 [48].

Table 2.3. The advantages and disadvantages of BP materials [48].

BP Materials	Advantages	Disadvantages	Sample Picture
Graphite	• Chemical resistance • Corrosion-resistance • Electrical conductivity • Low density	• Brittleness • Expensive • Porous • Time-consuming	
Metals	• Batch production • High strength • High rigidity • Mechanical/electrical/thermal properties	• Corrosion problem	
Composites	• Airtightness • Corrosion-resistance • Inexpensive • Lightweight • Mechanical property	• Low conductivity	

Bipolar plates have independent gas flow channels for both anode and cathode electrodes of the PEMFC. After fabricating the bipolar plates at high temperature and pressure, various designs of gas flow channels are machined, as illustrated in Figure 2.13.

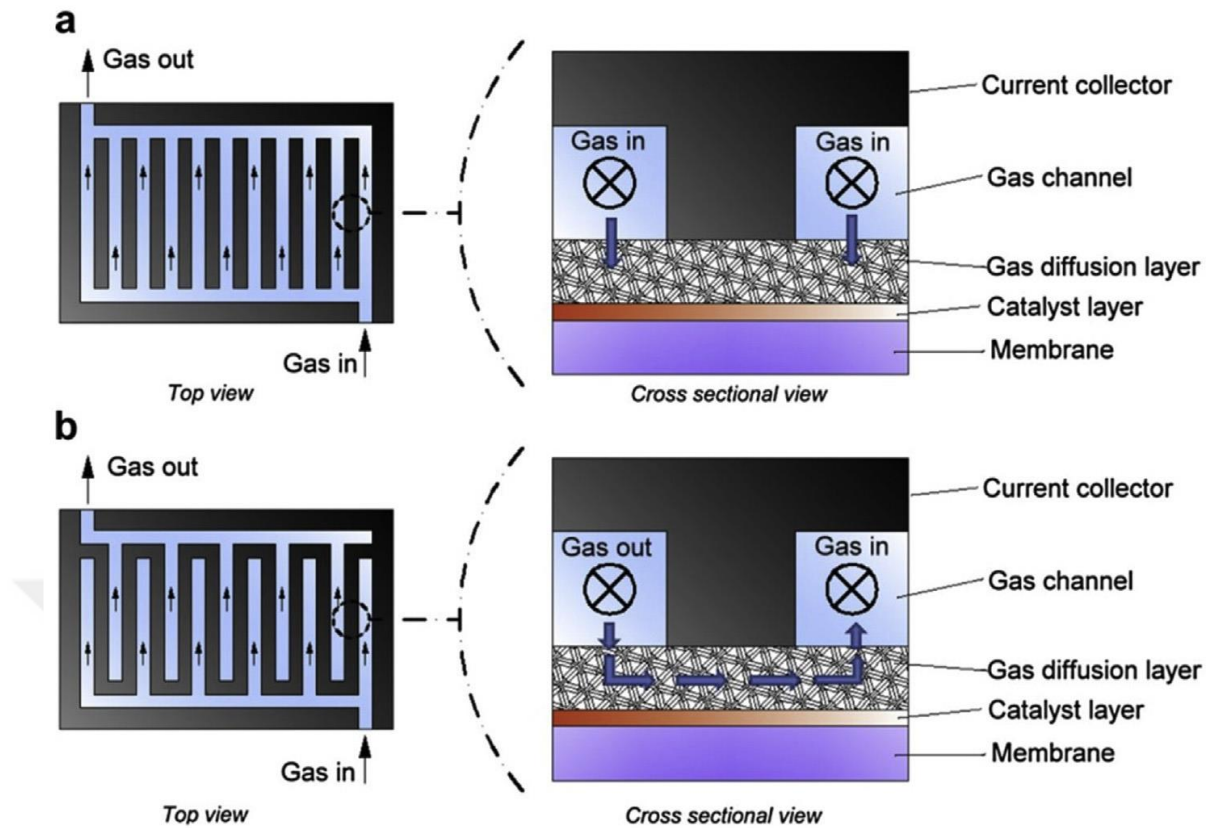


Figure 2.13. The structural view of gas flow channels for a) parallel b) interdigitated geometry design [46].

As discussed earlier, the gas flow channels are an essential component built with distinct geometries and machined to feed the reactants to the GDL and CL with minimal pressure drop on the cathode and anode sides, respectively. For the uniform distribution of reactive gases, the design of these channels is crucial. In the absence of consistent flow distribution, the use of catalysts and energy efficiency is diminished. Besides, the uneven current density distribution reduces the cell lifespan. In contrast, in circumstances where the gases are uniformly dispersed due to excellent and effective BP design, the current density will likewise be evenly spread, resulting in an evenly distributed cell operating temperature. The overall performance of the fuel cell will rise by around 50% in this case [46].

For the design of gas flow channels or flow fields, different configurations, including single straight, parallel, serpentine, interdigitated, pin, spiral, cylindrical, radial, natural or bio-inspired, square tubular, and fractal, are utilized for PEMFC. However, the most prevalent PEMFC flow field configurations are presented in Figure 2.14.

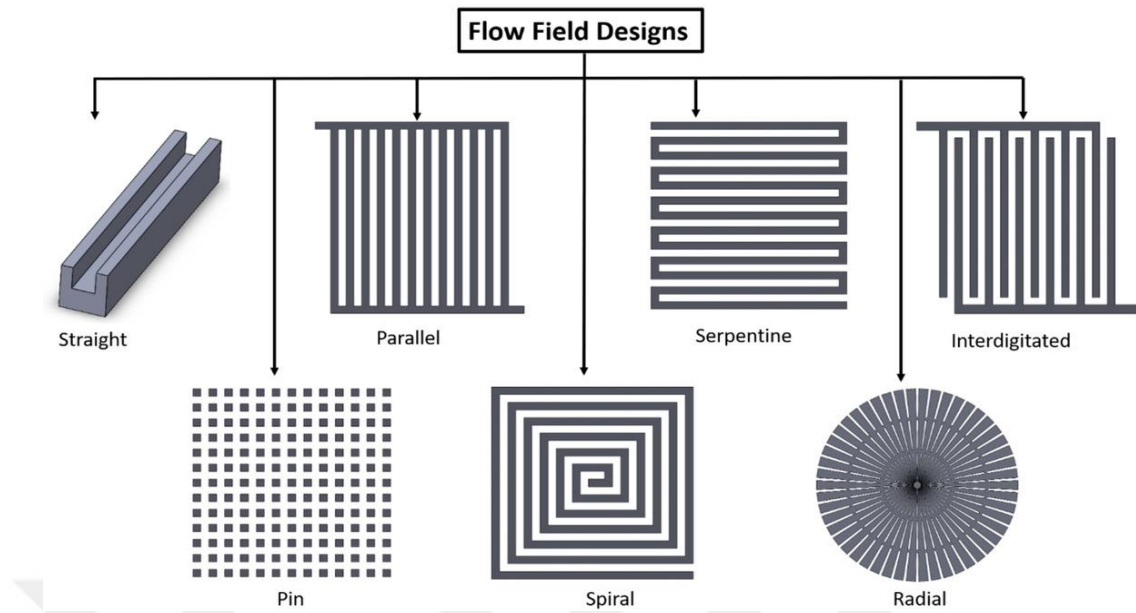


Figure 2.14. The major flow field desings employed in PEMFCs [49].

In the straight flow field, there is only one channel with a straight path. It has uniform cross-section (normally rectangular or square, trapezoidal, and parallelogram shapes) throughout the path [49], as illustrated in Figure 2.15 [46]. The structural view of other different configurations is presented in Table 2.4. In addition, a comprehensive comparison of other flow field designs focusing on the advantages, and disadvantages of each configuration is given in Figure 2.16.

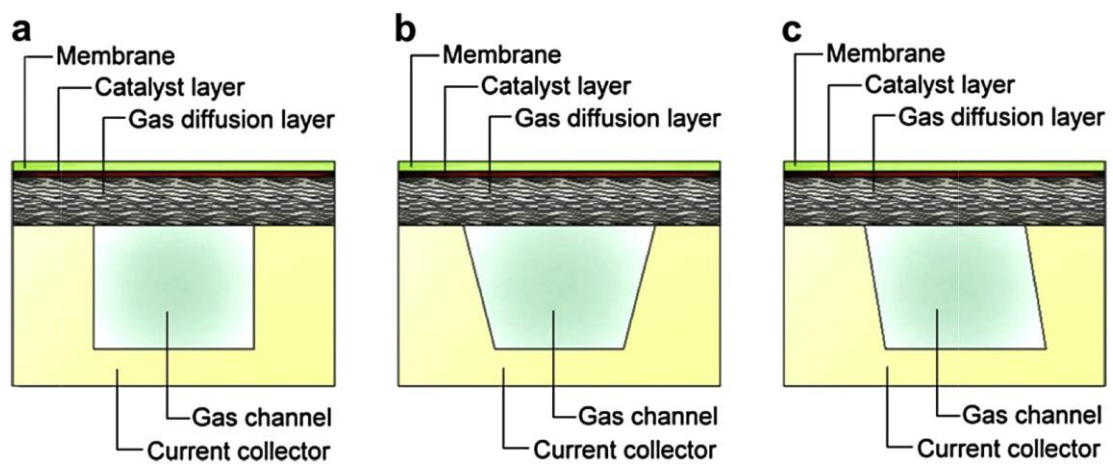


Figure 2.15. The cross-sectional view of a) rectangular, b) trapezoidal, and c) parallelogram shape gas flow channels [46].

Table 2.4. The structural view of different configurations of flow fields [50].

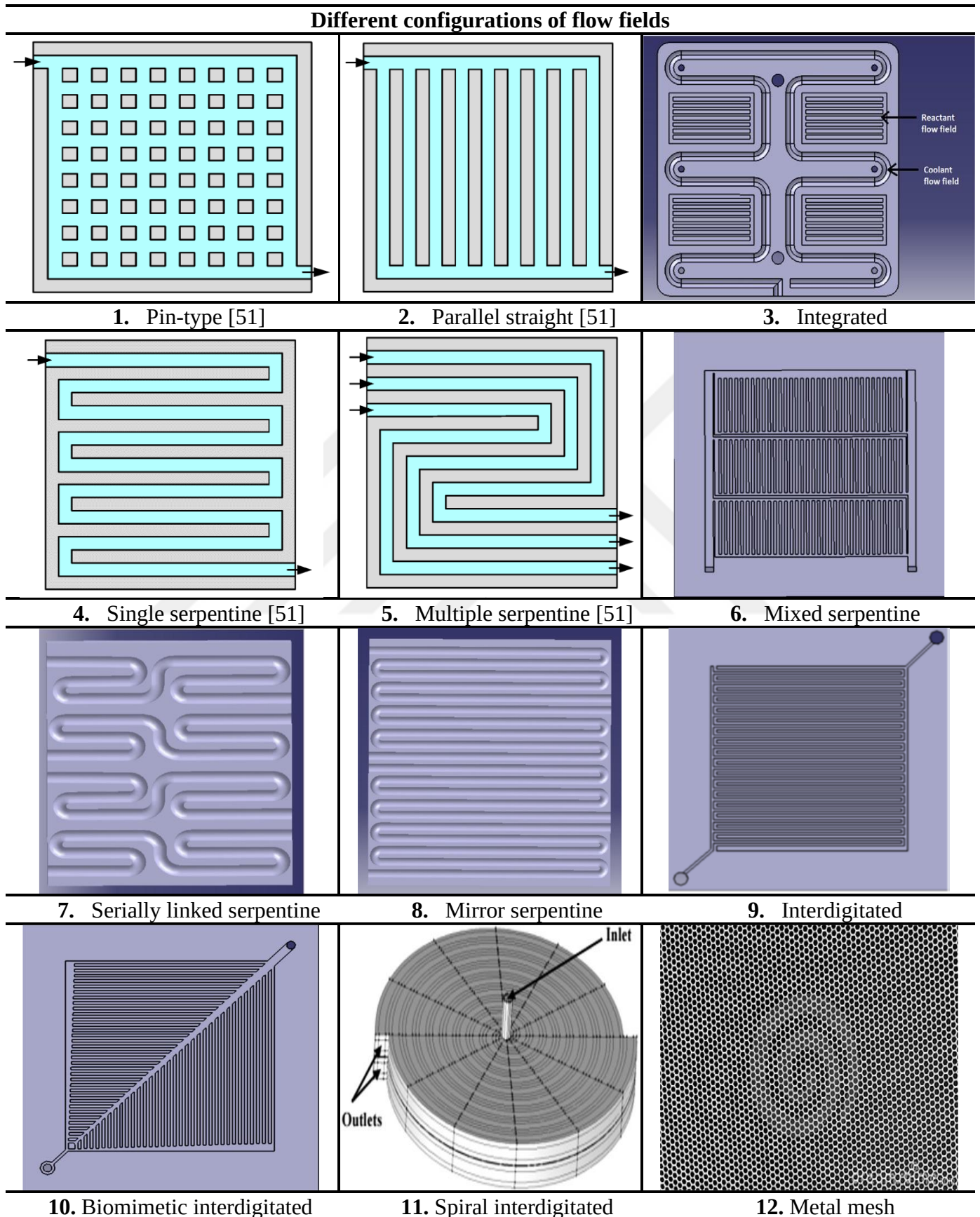


Table 2.5. The comparison of different flow field configurations [17].

Flow field configurations	Advantages	Disadvantages
Pin-type	• Utilizable for reactants with low consumption and high flow rates • Lower pressure reductions	• Non-uniform current density distribution • Insufficient water discharge • Unequal distribution of reactants
Parallel straight type or	• Uniform gas circulation • Lower pressure reductions	• Unsteady voltage after long-term usage • Lower channel velocity • Pressure drops • Insufficient water discharge • Water blockage in the canal
Integrated	• Higher power density	• More enhanced thermal gradient across the fuel cell
Single serpentine	• Suited for smaller active spaces • Completely covers all dynamic regions • Enhanced water discharge	• At larger current densities, more increased flood risk • Air oxidant concerns • High-pressure reductions • Non-uniform current density distribution
Multiple serpentine	• Useful for large active spaces • Completely covers all dynamic regions • Higher efficiency • Adequate water discharge • Lower pressure reductions	• Non-uniform current density distribution • High-pressure reductions
Mixed serpentine	• Combining the benefits of single and multiple serpentine • Uniform distribution of reactants • Lower pressure reductions	• Combining the drawbacks of single and multiple serpentine
Serially linked serpentine	• Combining the benefits of single and multiple serpentine • Lower pressure reductions	• Combining the drawbacks of single and multiple serpentine
Mirror serpentine	• Combining the benefits of single and multiple serpentine • Uniform distribution of reactants • Lower pressure reductions	• Combining the drawbacks of single and multiple serpentine

Table 2.5. Continued.

Interdigitated	• Enhanced performance • Uniform gas distribution • Limits the flooding • Exceptional mass transfer • Enhanced water discharge	• Negatively influence the gas diffusion layer • Large pressure reductions
Biomimetic Interdigitated	• Enhanced performance at higher temperatures • Outstanding current density • Less pressure reductions • Lower humidity necessity	• Water flooding problems • Insufficient water discharge
Spiral interdigitated		• Large pressure reductions • Bypass of reactants between inlet and outlet channels
Metal mesh	• Controls on contact area • Enhance performance at low current density • Lower pressure reductions	• Complex manufacturing • Corrosion • Non-uniform gas distribution • Insufficient water discharge

2.2.4. Current Collector Plate (CCP)

The current collectors between the end plate and the BP can be constructed of copper, titanium, aluminium, and many other conductive metals. Besides, the gold-plated copper plate, as illustrated in Figure 2.16, is also commonly utilised. The gold coating protects the graphite separator (bipolar) plate from corrosion and ensures excellent electrical contact. Therefore, current collectors have great electrical conductivity and facilitate electron transfer in the fuel cell. The GFCs and a manifold are constructed on a high purity graphite plate with high electrical conductivity (900 Scm^{-1}) and thermal conductivity ($117 \text{ Wm}^{-1}\text{K}$). A gasket is supplied with the MEA to create a secure seal. At both ends of the fuel cell, high-powered silicon rubber heaters are fitted to maintain a consistent cell temperature [52]. Apart from metals, some materials are also utilised as current collector plates. Particularly, graphiolo grabs notice with its strong performance.

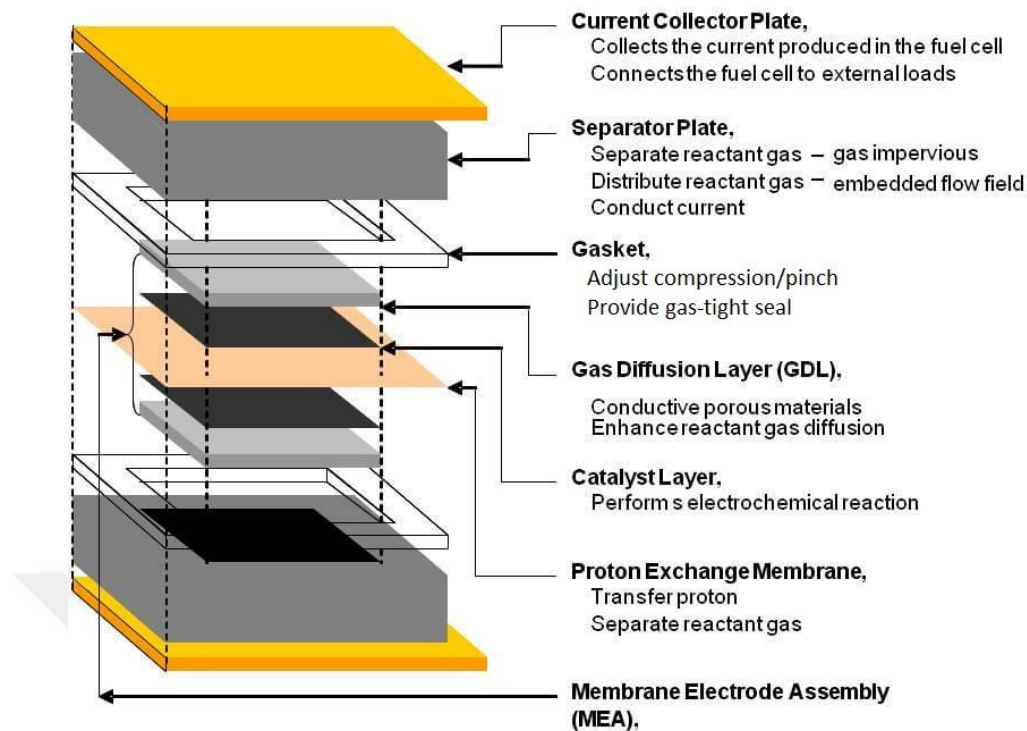


Figure 2.16. The shematic view of CCP [52].

2.2.5. End Plate (EP)

End plates (EPs), also known as clamp plates, are required at both ends of the stack, as depicted in Figure 2.17, and are a key component of PEMFCs. The primary function of these plates is to distribute the pressure uniformly across the different fuel cell components (e.g., BPs). Another pivotal role is to stack and stabilise each cell layer, decrease contact pressure and provide a seal between other plates and the MEA, and regulate the movement of reactant gases and refrigerants. Hence, they need adequate mechanical strength to withstand pressure, low weight to obtain high energy densities, stable chemical and electrochemical characteristics, and sufficient electrical insulation. The three design requirements for EPs are material, method of attachment, and form. Currently, metals, including aluminium, titanium, and stainless steel, are the predominant materials for constructing EPs. However, due to corrosion issues and heat losses, alternate materials such as polymers are being examined in place of these materials. In order to boost the mechanical strength of EPs, plastics and composite materials consisting of a combination of two or more components have also been suggested for supplanting metal EPs [53].

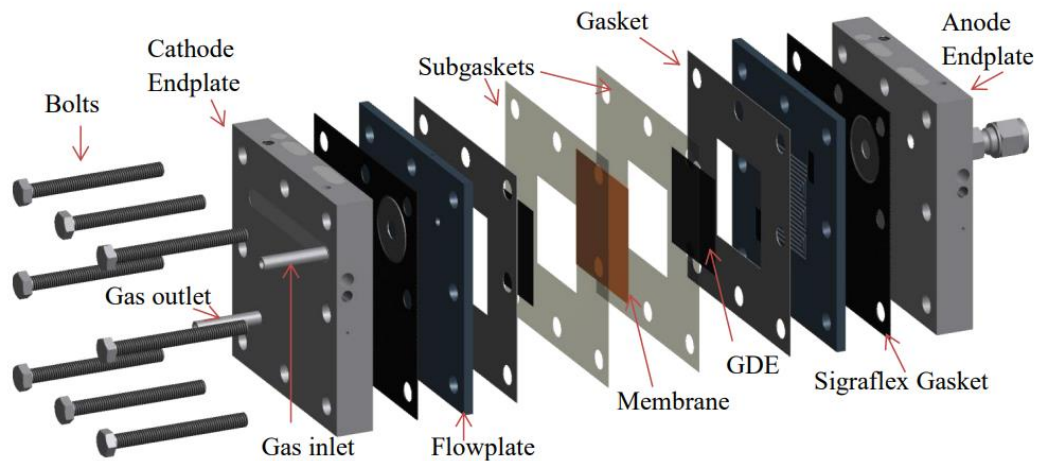


Figure 2.17. The schematic view of EPs [7].

2.3. ADVANTAGES AND DISADVANTAGES OF PEMFCS

There are several advantages of employing PEMFCS, as outlined below:

- They do not release harmful gases into the atmosphere (CO, NO_x etc.).
- They are tolerant to CO₂. Thus, PEMFCs may utilise unfiltered air as an oxidant and recycle the fuel.
- They function silently and have a long lifespan due to the absence of moving components.
- They are very efficient and able to function at low temperatures. This reduces material issues, allows for a quicker start-up (shorter warm-up time), and improves safety.
- A solid and dry electrolyte is used. This removes issues such as hydration management, electrolyte loss, and electrolyte replacement.
- They employ an electrolyte that is noncorrosive. Pure water treatment reduces corrosion issues and improves security.
- The voltage, current, and power density are all elevated.
- Their low operating pressure promotes safety.
- Their tolerances for differential reactive gas pressures are high.
- They possess a rather straightforward mechanical design.
- They use durable construction materials. Hence, they are little and sturdy.

Unfortunately, the utilization of PEMFCs also brings some important disadvantages, as follows:

- They are costly to manufacture and study.
- They can only withstand 50 ppm of CO₂ and a little amount of sulphur.
- As a catalyst, they use the platinum, a costly material.
- Due of the necessity for advanced technology in their creation, mass manufacturing is not readily.

Apart from these disadvantages, PEMFCs have also other drawbacks, mainly due to the polymer membrane. Firstly, the Nafion® must always be maintained by a highly hydrated condition with liquid water to keep and continue the ionic conductivity since it strongly depends on the humidity [15]. Besides, a case of excess humidification on the cathode compartment would cause flooding by blocking pores in the electrodes and or GDLs. As a result, the transferring of oxygen through the GDL would be interrupted [54]. Therefore, the water management have always become a vital concern in LT-PEMFCs [55]. In addition, for improving the kinetic reaction of the catalyst, elevated temperatures are required, but the Nafion® membrane suffers to get dry if they are operated at temperatures above 100 °C. This causes internal resistance in the fuel cell, resulting in energy loss during the transport of the proton and thus a decrease in electrical efficiency [56]. Therefore, the operation of these membranes at higher temperatures (e.g., above 100 °C) is restricted to prevent dehydration and excessive swelling [57]. As a solution, alternative membranes have begun to be investigated and tested to overcome the above issues. Therefore, the next chapter is devoted to the introduction of the high-temperature PEM fuel cells (HT-PEMFCs). The structural differences and distinctive features compared to the low-temperature counterpart will be comprehensively discussed.

CHAPTER 3

HIGH-TEMPERATURE PEM FUEL CELLS (HT-PEMFCs)

High-temperature PEMFCs (HT-PEMFCs) have drawn immense attention since their invention, dating back to the early 1990s, owing to their potential to resolve many crucial problems associated with conventional LT-PEMFCs. Due to this huge potential, numerous patent applications have been submitted, and thousands of academic articles have taken place in the literature during the past a few decades. As a result, several components, including high-temperature polymer electrolyte membranes (HT-PEMs), electrodes, cells, stacks, and other auxiliary systems, have become available on the market today [57].

The operating principles of HT-PEMFCs are the same as their low-temperature counterparts, except for a higher operating temperature, often between 160 and 180 °C, and the same half-cell processes govern them [20]. In these fuel cells, a phosphoric acid (PA, H_3PO_4) doped polybenzimidazole (PBI) membrane, generally between 40–60 μm in thickness, is employed, providing a high operating temperature of up to 200 °C and acting as a proton conductor [54]. Apart from the membrane, each cell comprises of two CLs, generally between 13–30 μm in thickness, two GLs, generally between 170–250 μm in thickness, and two BPs for conducting and distributing electron flow, as illustrated in Figure 3.1. The GLs and BPs are identical to those employed in LT-PEMFCs [39]. However, since the operating temperature is increased to allow the use of lower purity hydrogen in the HTPEMFC, the components to be employed must adapt to high-temperature conditions. Therefore, HT-PEMFC components exhibit some fundamental differences in terms of the type of membrane employed, the corrosion environment depending on the membrane used, and the design and durability of the CL. Therefore, the next chapter is devoted to the introduction of the critical components of the HT-PEMFC.

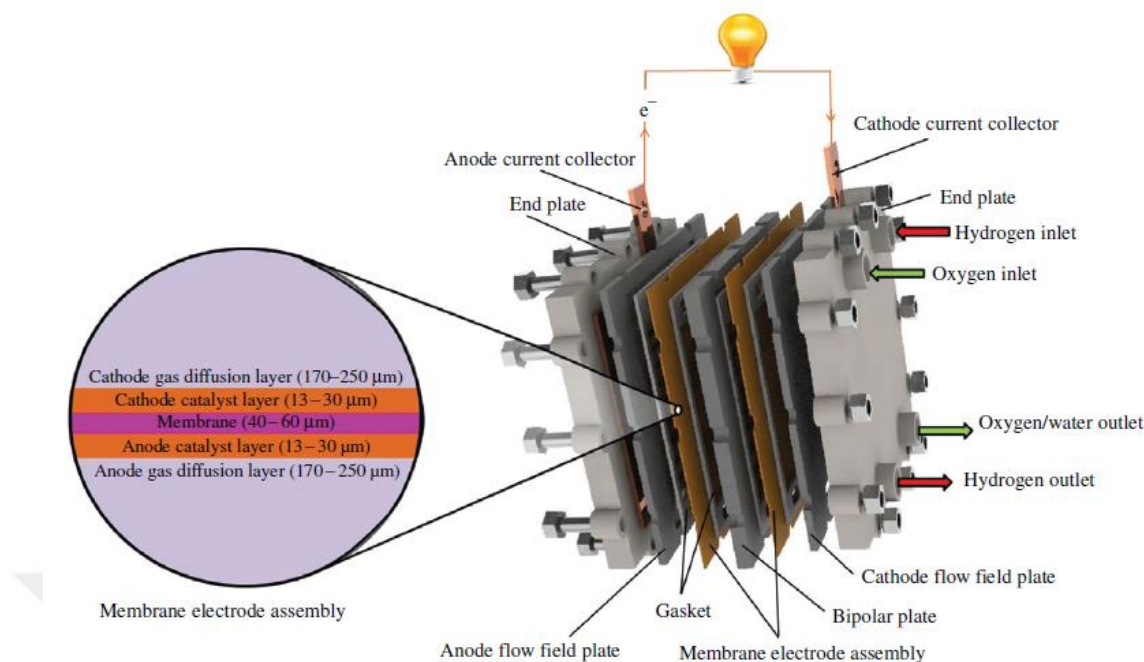


Figure 3.1. The structural view of an HT-PEMFC stack [39].

3.1. HT-PEMFC COMPONENTS

3.1.1. High-temperature PEMs (HT-PEMs)

As discussed earlier, polybenzimidazoles (PBIs) are extensively preferred membranes in HT-PEMFCs, particularly when doped with oxo-acids such as H_3PO_4 or H_2SO_4 [58]. These membranes were proposed by Litt and first employed in HT-PEMFCs by Wainright et al. [59] in 1995 at an operating temperature of 150 °C, with humidified reactants at room temperature and atmospheric pressure. This study aimed to create an alternative to Nafion®-based low-temperature membranes since they can only operate optimally below 100 °C and in a humid environment and hence have a higher electro-osmotic drag number [60]. The experiments have proved that acid-doped PBI membranes are a good alternative to low-temperature counterparts.

The PBIs refer to a broad family of aromatic linear heterocyclic semi-crystalline polymers containing repeated benzimidazole units. Due to the unique alkaline structure of the benzimidazole rings and superior distinguishing features, the PBIs have become the most effective and hottest membrane material among HT-PEMs

[60,61]. Apart from PBIs, non-PBI-based proton-conducting polymers, including aromatic polymers, composites, and fluorinated polymers, as depicted in Figure 3.2, can also be employed as HT-PEMs since they provide sufficient electrical conductivity and mechanical stability [60]. However, PBI membranes have come to the forefront more because they outperform and have many advantages over other HT-PEMs [62].

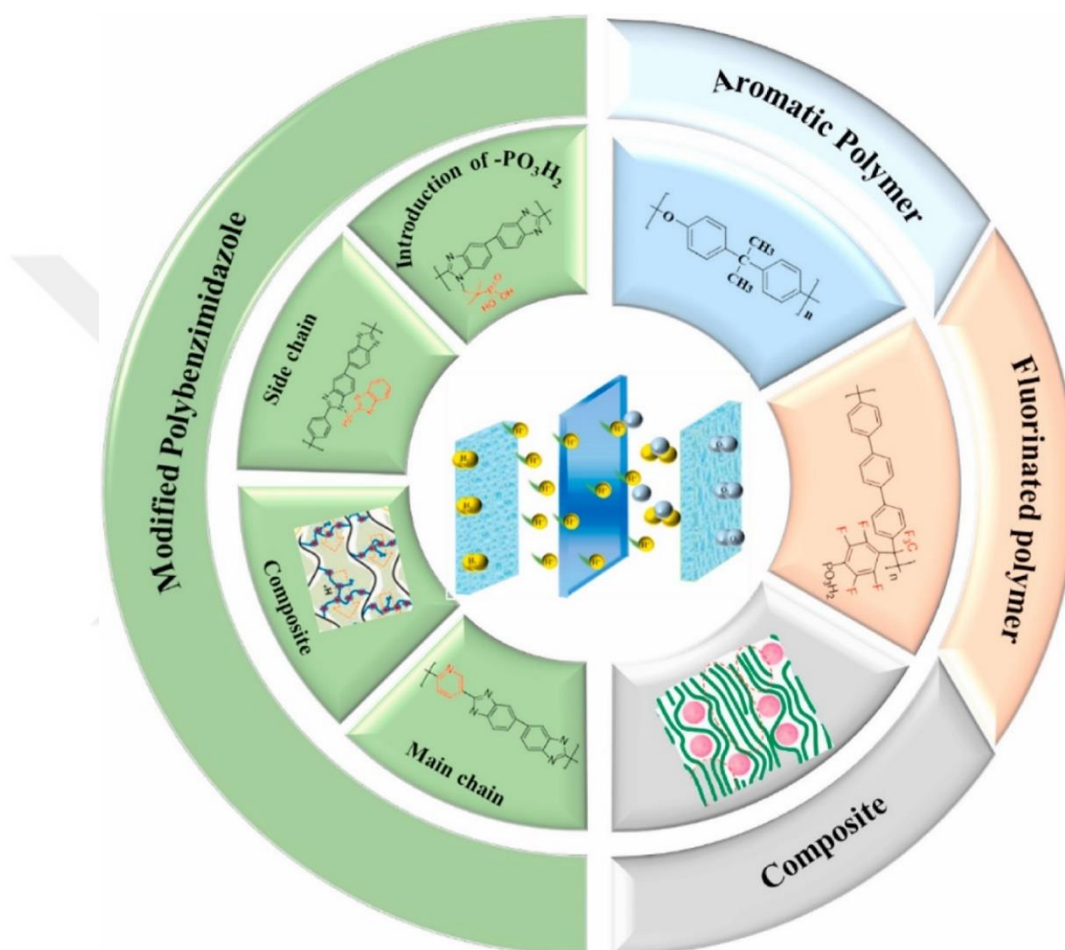


Figure 3.2. The classification of HT-PEMs for HT-PEMFCs [61].

As an example of superior features, PBI membranes exhibit high mechanical strength, excellent chemical resistance, sufficient moisture restitution, and exceptional thermo-chemical stability over 80 °C [63]. The PBI polymer is not conductive itself due to very low intrinsic proton conductivity, however when it is processed and impregnated with the PA (H₃PO₄), the most successful non-volatile proton carrier, as depicted in Figure 3.3, it transforms into a proton conductor with high conductivity even in the absence of water at elevated temperatures without losing thermal and chemical

stability, whereas simultaneously ensuring the low gas permeability [64,65]. These superior features enable the PA-doped PBI membranes to operate under anhydrous conditions at higher temperatures [65]. Therefore, water management is significantly easier in PBI/H₃PO₄ fuel cells since they are not dependent on water in liquid form to conduct protons, simplifying the system and reducing the system cost [21].

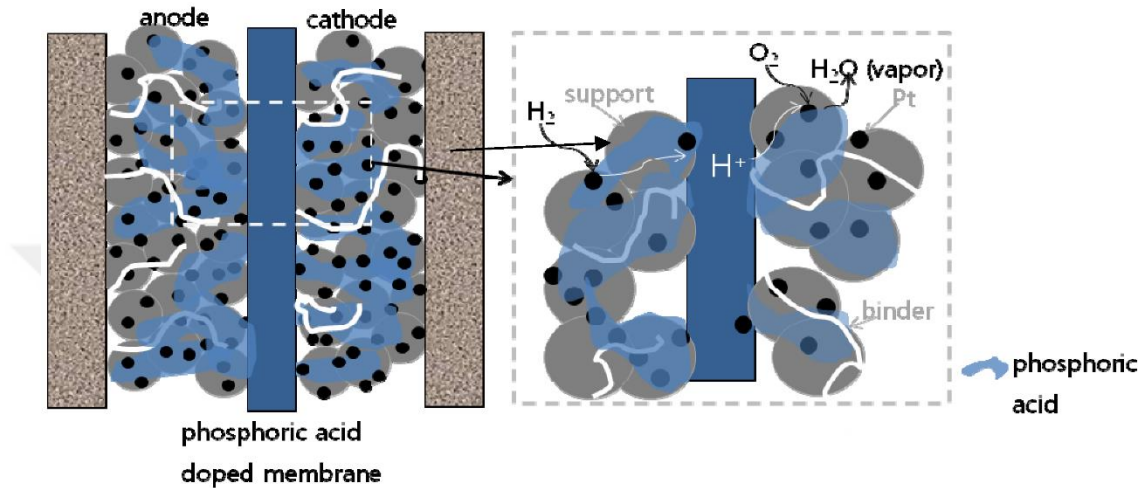


Figure 3.3. The schematic view of the PA-doped membrane [66].

The doping process of PA onto the PBI membrane occurs as follows. One repeating unit of PBI contains two Lewis basic nitrogen atoms (pyridine–N =) that may combine with the protonated PA molecule, thereby generating bound acid. Protons, positively charged hydrogen ions, are formed in the anode HOR and diffuse the molecules by hydrogen bonding [67]. Thus, they adhere to the PA and eject another hydrogen ion, as plotted in Figure 3.4. Since the proton transfer is performed by “hopping” along the hydrogen bond network, the acid doped PBI conductivity is guided by an activation process that conforms to the Arrhenius equation. In contrast, the Nafion’s proton conductivity is due to the vehicle mechanism, which has a reduced temperature dependency. In addition, the conductivity of acid doped PBI is less sensitive to the relative humidity, but there is still a discernible influence [68].

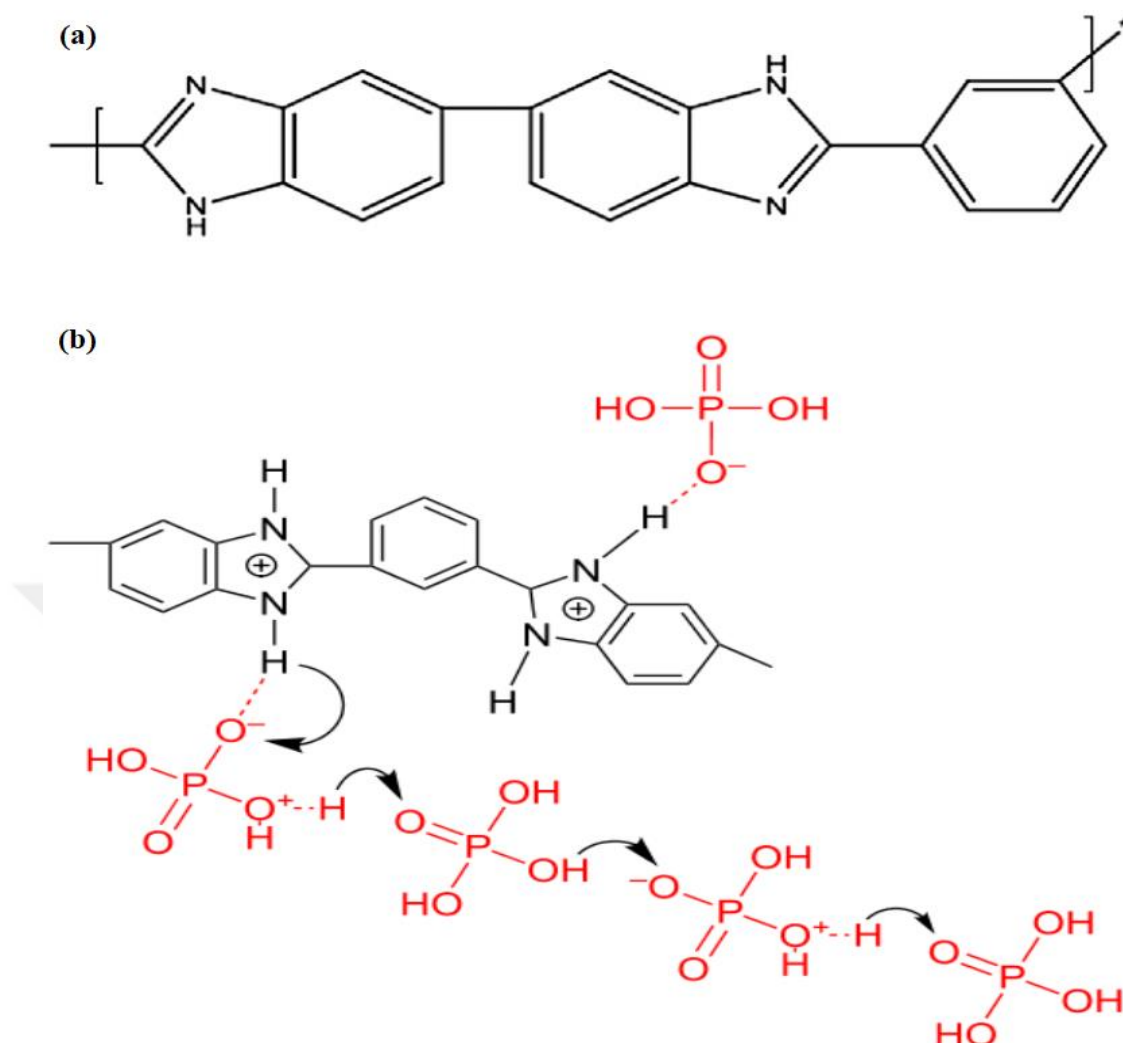
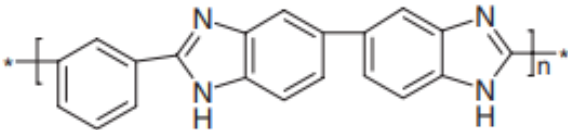
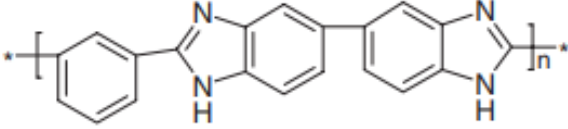
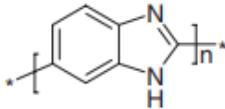
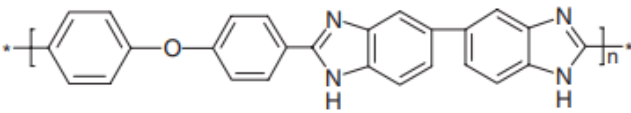
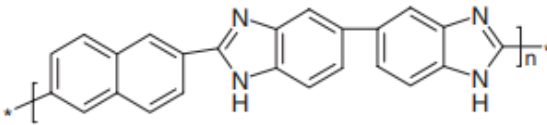
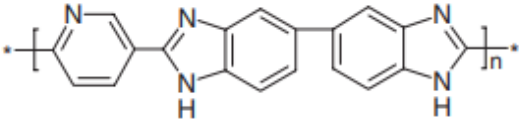
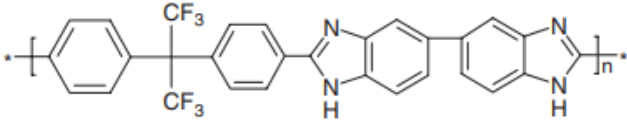


Figure 3.4. The chemical structure of (a) pure PBI [39] and (b) PA-doped PBI along with the proton transfer path [68].

The PBIs have many derivatives due to small modifications in their side chains. However, these derivatives are costly and difficult to produce, yet they possess exceptional qualities. For instance, the PBI, with a chemical structure of (poly [2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]), denoted by *m*-PBI, is the most frequently researched PBI polymer, although the term PBI itself commonly refers to this polymer. However, several other PBIs have also been investigated, including poly(2,5-benzimidazole), denoted as AB-PBI, which does not contain a connecting phenyl group but includes benzimidazole moieties solely. Another form of PBI, abbreviated as *p*-PBI, has a similar chemical structure to *m*-PBI. Other derivatives and their chemical structures are presented in Table 3.1.

Table 3.1. The chemical structures of different PBI derivatives [69].

PBI types	Chemical structure
PBI (<i>m</i> -PBI)	
<i>p</i> -PBI	
AB-PBI	
OPBI	
PBI-4N	
PBI-5N	
F ₆ -PBI	

3.1.2. HT-PEMFC Catalysts

The catalyst particles are positioned on the ionic conducting membrane and the support material, creating vital active sites where reactions occur. In PEMFC, catalysts primarily lower the activation energy of HOR and ORR processes at the anode and cathode, respectively. Platinum (Pt) and its alloys are employed as electrocatalysts in PEMFCs on a carbon substrate. The goal of employing carbon as a support material is to lower the amount of Pt used and increase the efficiency of the catalyst in order for it to be used. The support material is anticipated to be electrically conductive and has a wide surface area. A robust, cost-effective GDE is essential for high-temperature

applications. While the surface area of the CL is significant for long-term operations below 100 °C, the chemical and morphological degradation become crucial at higher temperatures. Carbon support corrosion may occur if the production of oxygen atoms in the catalyst results in an extremely high oxidation potential at the cathode. Carbon oxidation reactions are affected by the operating temperature, interface electrode potential and water vapour pressure. Studies on carbon supported Pt degradation have reported that carbon corrosion increases with Pt loading and temperature [70]. The aggregation of Pt particles and the increase in particle size during PEMFC reactions should also be noted.

In order to minimise the catalyst agglomeration and improve the performance of HT- PEMFCs, a thin CL with greater activity must be used at higher temperatures. The optimal particle size for ORR reactions on the Pt/C catalyst surface is determined as 3–5 nm. The ORR reactions on the Pt/C catalyst surface highly depend on the particle size. In the case that the particle size of Pt grows, the ORR rate and the efficiency of Pt use drops. Consequently, a highly active and thin CL is required to achieve the desired outcomes for the fuel cell. Since the CO tolerance of HT-PEMFCs increases from 10–20 ppm at 80 °C to 1000 ppm at 130 °C and 30,000 ppm at 200 °C [71], there is no need to build catalysts (PtRu/C, PtSn/C) with high CO tolerance. However, in the case that a metal bipolar layer is employed in the HT-PEMFC, the corrosion of the metal might limit the efficiency of the catalyst due to the dissolved ions that may form as a consequence of the corrosion of the metal. In order to prevent this situation, different resistant coatings must be used.

3.2. ADVANTAGES OF HT-PEMFCs

3.2.1. Improved Electrode Kinetics

The electrochemical ORR, generally between 10^{-8} and 10^{-9} A/cm², has a substantially lower exchange current density than HOR, generally between 10^{-3} and 10^{-4} A/cm². Due to the reversible nature of HOR at the Pt nanoparticle/PEM interface, the overpotential for HOR is much smaller than that of ORR in the case where the anode is sufficiently hydrated. Therefore, the comparatively slow ORR process governs the

overall electrochemical kinetics of the PEMFC. In this case, as the operational temperature rises, the anodic and cathodic exchange current densities rise, improving both electrodes' reaction kinetics. Nevertheless, it is worth noting that anode dehydration may become a serious obstacle at operating temperatures exceeding 100 °C [71].

3.2.2. Improved Contaminant Tolerance

A significant number of recorded statistics on the performance of H₂/air fuel cells are performed by using pure hydrogen as the reactant, although from a technological perspective, this is impractical since hydrogen of such high purity may not be easily accessible. As a fuel option, hydrogen-rich gases may be preferable. On-site hydrogen production from different organic fuels, including methanol, natural gas, and gasoline via reforming processes, including the water–gas shift reaction, preferential oxidation, membrane separation, and methanol oxidation, are desirable alternatives to the ‘stored’ hydrogen. As depicted in Figure 3.5, reformat gases often include carbon monoxide (CO) traces strongly adsorbed on Pt’s surface, occupying HOR sites. The trace CO drastically lowers the anode’s Pt or Pt-alloys’ activity.

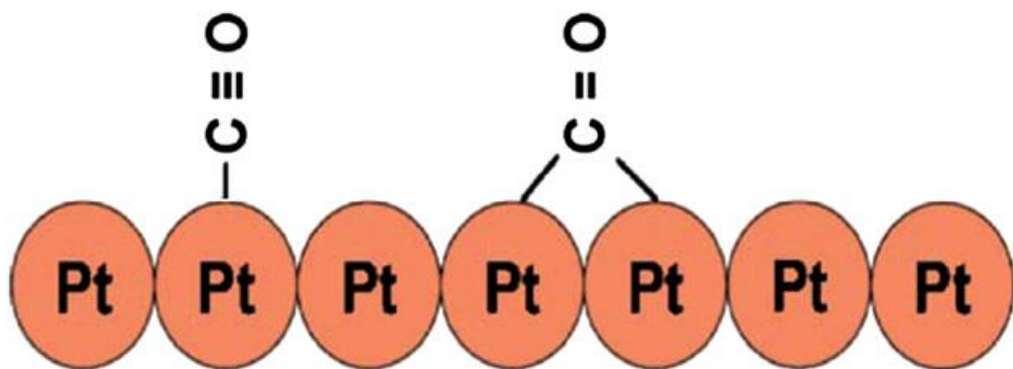


Figure 3.5. Different types of CO adsorption on the Pt surface [29].

As a consequence of the poisoning of the anodic Pt catalysts, even a fuel CO concentration as low as 10–20 ppm may result in a considerable reduction of cell performance for LT-PEMFCs typically operated at 80 °C. In order to keep the CO concentration below 10 ppm, the reformat gas must be purified. Qi et al. [15] showed that very low CO levels poison the cathode, too, after passing through the membrane.

Numerous efforts have been made to diminish the harmful effects of CO. These are some examples as follows [71]:

- Injecting an oxidant (O_2 or H_2O_2) into the fuel
- Enhanced purification of reformat gas
- The development of CO-tolerant electrocatalysts, including PtRu/C and PtSn/C

Nevertheless, every solution introduced to date has substantial disadvantages and/or performance concerns. Adding an oxidant to the fuel stream, for instance, reduces fuel usage and compromises safety; further fuel processing raises system complexity and causes additional costs, and the performance of modern CO-tolerant electrocatalysts is far from adequate. Alternatively, increasing the operating temperature of the fuel cell may efficiently reduce CO adsorption on the catalyst.

3.2.3. Simplified Water and Heat Management

In PEMFCs, water management is crucial since it impacts the system's efficiency and total power output. For PFSA membrane based PEMFCs operating below 100 °C, complex humidification subsystems are required to humidify the reactant gases (pure H_2 and O_2 or air) to keep the water level high enough for ionic conduction in the membrane. Nevertheless, excess water in the electrode often results in flooding, particularly in the cathode, where an electrochemical process produces water. This excess water in the electrode clogs the pores in the CL and GDL or blocks the channels in the gas flow fields, thus impeding gas transport and drastically reducing cell performance. The high-temperature operation of a PEMFC might alleviate the potential problems associated with water inundation. Due to the need for water in a PFSA-based membrane, it is not possible to eliminate the humidifier in a PEMFC, diminishing the advantage of high-temperature operation. An increase in operating temperature from 80 to 200 C, for instance, may result in a saturated water vapour pressure as high as 15 atm, which would significantly complicate the system if a high relative humidity had to be reached during operation. Therefore, PFSA-based membranes are not suitable for use at high temperatures [29].

Fortunately, in acid-base polymer membranes, including the PBI, protons are transferred by a doped acid, e.g., H_3PO_4 , via a solid PBI matrix, whose conductivity is less reliant on the water concentration than in a PFSA-membrane. An H_3PO_4 /PBI membrane-based HT-PEMFC may function at temperatures as high as 200 °C without humidification. This situation eliminates the risk of flooding in such a fuel cell system and allows for a more straightforward system design. In addition, water management is simplified due to the absence of liquid water at the electrode. Furthermore, the high-temperature operation offers two additional advantages in this case, as follows:

- Significantly reduced mass transport limitations in the CL and GDL
- Simpler flow-field design since only one phase flows through the flow channels

Rapid heat removal is another advantage of high-temperature operation since it minimises the demand for the cooling system. Even at low temperatures, e.g., 80 °C, a PEMFC with an efficiency of 40–50% may generate a significant amount of heat, which must be dissipated to maintain the fuel cell stack within a safe operating range. Therefore, a cooling subsystem is required to ensure the stack's continued functioning, performance, efficiency, and longevity. Nevertheless, if the fuel cell stack is driven at a high temperature, e.g., 200 °C, its heat dissipation rate will be much quicker than at a low temperature; this will result in a large decrease in the heat exchanger size in the cooling subsystem. For instance, the frontal area of radiators may be lowered by a factor of three to four when the operating temperature rises from 80 to 200 °C. This decrease will simplify the cooling subsystem and boost the fuel cell system's mass- and volume-specific power density. In addition, the high-temperature operation of PEM fuel cells may produce beneficial high-temperature water, which can be reused for various purposes and contribute to the system's overall efficiency [29].

3.2.4. Other advantages

Some critical problems may emerge when residual water created during fuel cell operation persists in the electrodes after the stack has been turned down, especially when the ambient temperature is below 0 °C. When the stack is subjected to sub-zero temperatures, the residual water will freeze, causing the volume of the electrodes

(particularly the catalyst layers) to swell owing to ice formation. This situation will cause structural damage and reduce the electrochemically active surface area. This is an additional degradation process revealed for PEMFCs [72]. However, if the PEMFC is driven at high temperatures, less liquid water will remain in the electrode, reducing the effect of frozen water-induced fuel cell structural failure. In addition, if a PEMFC is operated at around 200 °C, near the temperature for methanol-reforming, the fuel cell may be integrated with a methanol-reformer. It is anticipated that such integration would boost the overall efficiency of the power system and alleviate the challenges related to hydrogen storage [73].



CHAPTER 4

ENERGY AND EXERGY ANALYSIS OF HT-PEMFC

In order to better understand the transport phenomena occurring within the fuel cell, which are difficult to detect using experimental techniques, many researchers have concentrated on the mathematical modelling of HTPEMFCs. Compared to experimental investigations, these models give more insight into the design and optimisation of fuel cells [74]. For this reason, the number of mathematical model studies has increased significantly in recent years, and different models that can be either solved numerically or analytically have been proposed. For instance, numerical approaches are used for two-dimensional (2-D) and three-dimensional (3-D) models, whereas analytical methods are generally favoured for zero-dimensional (0-D) and one-dimensional (1-D) models. Each method has different computational approaches and hence has diverse results. Therefore, this chapter presents different mathematical models, including 0-D and 1-D, intending to determine the performance characteristics of HT-PEMFC. In order to analyse and discuss the performance characteristics under variable conditions, electrochemical and thermodynamic analyses based on these models have been applied, respectively. In the electrochemical analysis, some critical concepts have been derived first, including the reversible or open-circuit voltage and irreversible voltages; in other words, overpotentials, such as activation, concentration, and ohmic. Then, the details of all governing equations, assumptions, and other boundary conditions have been applied, and the polarisation curve has been analysed. As a second stage, comprehensive energy, entropy, and exergy analyses have been conducted, and significant concepts in thermodynamics (e.g., energy/exergy efficiency, entropy production, and exergy destruction) have been analysed and discussed according to the variation of operating and design conditions. Thus, a complete performance assessment of a single cell has been adopted according to the different models and variable conditions.

4.1. LITERATURE REVIEW

Despite their many successes in operating at elevated temperatures, further development and widespread commercialisation of HT-PEMFCs are hindered by technical obstacles connected with membrane durability [75,76]. In parallel to this issue, the performance of HT-PEMFC is deteriorated by other problems, including mechanical and membrane oxidative degradation and PA leaching [77]. Several research endeavours on these difficulties are comprehensively described in the present literature. However, relatively few studies analyse the fuel cell performance using thermodynamic principles. Some prominent studies are elaborately discussed. For instance, Bayat et al. [78] introduced a novel 0-D and isothermal model intending to determine the impact of several crucial factors, including operating temperature, pressure, membrane thickness, and relative humidity, on the energetic and exergetic performance of the HT-PEMFC. Accordingly, raising the operating temperature increases energy and exergy efficiency by 39.71% and 38.67%, respectively, relative to the baseline condition. However, raising the pressure increases these efficiencies only by 2.66%. In addition, a reduction in the membrane thickness raises energy and exergy efficiencies by 9.94% and 9.93%, whereas an increase in relative humidity boosts these efficiencies by 8.03% and 8.02%, respectively. Therefore, the operating temperature is the most influential parameter for the fuel cell performance, whereas the operating pressure influences the performance less than relative humidity and membrane thickness.

Guo et al. [79] conducted the 0-D and isothermal modelling of an HT-PEMFC using the PA-doped PBI membrane to determine energetic, exergetic, and ecological performance characteristics. In this study, some parametric analyses were performed to demonstrate the impact of operating and design conditions on the HT-PEMFC performance. Accordingly, the efficiency of the HT-PEMFC is considerably affected by operating temperature and doping level, whereas the operating pressure and relative humidity are less influential on the performance improvement.

Apart from these studies mentioned above focused on thermodynamic analyses, there are also other studies based on the 0-D and isothermal or semi-empirical

electrochemical models. For instance, Briceno-Mena et al. [80] presented a steady-state, 0-D and semi-empirical model of the HT-PEMFC to achieve high power density and also efficiency by using a machine learning tool. In the proposed model, different configurations are formed by employing several parameters, including the stoichiometric ratio of reactants, the operating temperature and pressure, the membrane and ionomer binder thickness, the CO/H₂ ratio, and the Pt loading, to predict the optimum net output voltage, while simultaneously aiming to reduce the fuel cell cost. Accordingly, the analysis results indicate that a power density above 1W/cm² can be achieved where CO-containing hydrogen and oxygen are fed as reactants. In this case, the operating temperature and pressure of 218 °C and 187 kPa, along with the proton conductivity of 0.2 S/cm in the electrode layers, are the optimum combinations for achieving this density.

Jannelli et al. [81] conducted a study focusing on the performance of a micro-cogeneration system based on a LT-PEMFC and two different HT-PEMFCs. The main objective of this study is to compare different configurations of this system in terms of performance, including a Nafion®-based LT-PEMFC operating at 340 K, a PA-doped PBI membrane-based HT-PEMFC operating at 423 K, and aromatic polyether polymers/copolymers bearing pyridine units-doped PBI membrane-based HT-PEMFC. According to this study, where the 0-D model was implemented for comparison, the highest electrical efficiency of 40% and cogeneration efficiency of 79% were achieved in the integrated systems based on HT-PEMFCs. Among these HT-PEMFC types, the one employing an aromatic polyether-doped PBI membrane has the highest electrical efficiency during all operational ranges, despite having the lowest stack efficiencies.

Zuliani and Tacconi [82] presented a 0-D and semi-empirical model to conduct the performance analysis of a micro-cogeneration system based on an HTPEMFC stack of 1 kW_{el} fed with natural gas. In this study, energy analysis was also performed to evaluate the system performance and to compare the performance of the HT-PEMFC-based system with its LT-PEMFC counterpart. Accordingly, the results reveal that the electrical efficiency of the HT-PEMFC-based system is determined as 26%, and the overall efficiency is calculated as 78% when operating at the design load. Table 4.1

lists the above studies conducted for energy and exergy analysis of HT-PEMFCs based on 0-D models.

Apart from these, many studies have been conducted on energy and exergy analysis of the HT-PEMFC by developing different 1-D, steady-state, and isothermal models. These studies will be comprehensively discussed. For instance, Amjad et al. [83] conducted energy, exergy, and economic analysis for a cogeneration system comprising an HT-PEMFC stack, an afterburner, a water gas shift reactor, and a coke oven gas steam reformer. In this paper, a genetic algorithm was used to conduct two-objective optimization to determine the ideal optimum point, indicating the minimum total product unit cost and maximum exergy efficiency. Accordingly, the optimal operating point for total product unit cost and exergy efficiency was determined to be 78.68 \$GJ⁻¹ and 32.86% when the current density, operating temperature, and cathode stoichiometric ratio were 0.12 A/cm², 198.7 °C, and 2.1, respectively.

Guo et al. [84] presented a new hybrid system consisting of a thermo-acoustic cycle (TAC) to recover the waste heat of an HTPEMFC. In order to analyse the performance of the hybrid system, a multi-objective optimisation based on the GA is employed. Accordingly, compared to a standalone HTPEMFC, the suggested system has the potential for a 33.3% improvement in maximum power density and a 34.5% increase in energy efficiency. In addition, the suggested system's optimum power density and energy efficiency are determined as 6147.8 W/m² and 53.9%, respectively, employing the ideal point method based on multi-objective optimisation.

Table 4.1. The list of present studies on the 0-D models of HT-PEMFC.

Authors	Year	Model	System	Electro-chemical	Energy	Entropy	Exergy	Ecological	Solution Technique
Bayat et al. [78]	2022	0-D & isothermal	Cell	+	+	+	+	-	EES
Briceno-Mena et al. [80]	2021	0-D & semi-empirical	Cell	+	-	-	-	-	Python
Guo et al. [79]	2020	0-D & isothermal	Cell	+	+	+	+	+	NA
Jannelli et al. [81]	2013	0-D	Stack	+	+	-	-	-	Numerical
Zuliani and Taccani [82]	2012	0-D & semi-empirical	Stack	+	+	-	-	-	Fortran/ Aspen Plus

Li et al. [85] conducted a complete performance assessment, including energy, exergy, ecological, and improvement potential analyses, for a vehicular HT-PEMFC system composed of an HT-PEMFC stack based on a PA-doped PBI membrane, a coolant pump, compressors, heat exchangers, and humidifiers. This study investigated the impact of various parameters, including stack inlet temperature, anode and cathode inlet pressure, and anode and cathode stoichiometric ratios, on the system performance. Besides, each system component's energy losses and exergy destructions were calculated, and improvement potentials were examined according to these losses. Consequently, energy and exergy efficiencies and net output power of the system are reached at their maximum in the case where the operating temperature of inlet gases is 406.1 K. At this point, the net output power, energy efficiency, and exergy efficiency are determined as 24907.4 W, 35.4%, and 33.3%, respectively. In the case where the cathode inlet pressure is comparatively small, the system performs the best ecologically. Furthermore, as the anode inlet pressure increases, the output performance of the system increases as well.

In another study by Li et al. [86], the performance analysis of an HT-PEMFC was conducted according to the variation of a novel parameter, the exergetic performance coefficient (EPC). In this study, the impact of several parameters, including inlet mass flow rate, doping level, inlet pressure, and membrane thickness, on the fuel cell performance is analysed, and the relationship between EPC and energy efficiency is also discussed. The results demonstrate that EPC is the superior performance criteria because it not only considers the exergy destruction to reduce exergetic loss but also considers the power density of HT-PEMFC to optimise its power density and increase its efficiency. In addition, EPC and, correspondingly, energy efficiency (both of which increase with increased intake pressure and doping level) are also enhanced.

Sun et al. [87] introduced a novel optimisation methodology for the exergetic assessment of an HT-PEMFC. In this methodology, the Fractional-order Coyote Optimization Algorithm (COA) was employed in order to acquire advanced precision, consistent findings and higher efficiency. The optimisation process used three cost functions: irreversibility, work, and exergy. After constructing the algorithm, a comparison was made using actual data, the original COA, and the Genetic Algorithm

(GA) from the literature to establish the optimiser's superiority. Consequently, final results reveal that the proposed method provides the greatest experimental confirmation.

Li et al. [88] conducted the performance analysis of a fuel cell vehicle (FCV) powertrain based on an HT-PEMFC employing a PA-doped PBI membrane. In this study, the particle swarm optimisation (PSO) algorithm is utilised to optimise the power density and efficiency of the HT-PEMFC with a multi-objective optimisation method. In addition, the impact of operational (operating temperature, pressure, and relative humidity) and design parameters (doping level and membrane thickness) on the output performance of the fuel cell are also analysed and discussed. As a result, the performance of the optimised fuel cell increases via the PSO algorithm, acquiring a power density of 6848 kW/m^2 and an efficiency of 64.58%. In addition, the FCV using the improved HT-PEMFC has the greatest average efficiency, lowest energy loss, and lowest hydrogen consumption.

Erzen et al. [89] presented a study comparing different hybrid system configurations, including hybrid I, consisting of an HT-PEMFC stack and a thermo-capacitive cycle, and hybrid II, consisting of an HT-PEMFC stack and a thermoelectric generator. The main objective of this study is to determine the performance of these systems through energy, exergy, and economic analyses and to compare the results with each other to find which system would give a higher performance during parametric studies. Accordingly, the maximum energy efficiencies for hybrids I and II are determined as 51.6% and 50.4%, respectively. Therefore, the hybrid I system is more practical and preferable.

Li et al. [90] performed energy, exergy, and ecological analysis of an HT-PEMFC by employing a finite-time optimization to determine the optimum point for the energy efficiency, exergy efficiency, ecological coefficient of performance (ECOP), and, correspondingly, the maximum power density of the fuel cell. In addition, the impacts of different parameters, including operating temperature and pressure, doping level, and relative humidity, on the performance of HT-PEMFC were also investigated in this paper. As a result, the maximum output power density, output efficiency, exergy

efficiency, and ECOP increase by 72%, 19%, 21%, and 50%, respectively, as the operating temperature rises from 403 K to 473 K. In addition, the maximum power density is increased by 150% in the case where the PA doping level is raised from 2 to 10. Furthermore, operational pressure and relative humidity have a negligible impact on these parameters.

Sarabchi et al. [91] performed exergetic and exergoeconomic analyses of HT-PEMFC stack-based novel combined cogeneration cycles, including methanol steam reformers coupled with a catalytic combustor or parabolic trough solar collector. In the proposed systems, the HT-PEMFC stack, consisting of 1000 single cells, is fed with a hydrogen-rich reformat gas on the anode side and operates at a temperature and pressure of 180 °C and 2 bars, respectively. Accordingly, the exergy efficiency of the HT-PEMFC stack increases, and the total unit product cost decreases with increasing the fuel cell temperature from 165 to 200 °C in both configurations.

Lu et al. [92] presented a new method for exergy analysis of an HT-PEMFC-based power generation system where an Organic Rankine Cycle (ORC) is employed to recover the waste heat. In this study, a modified version of the Farmland Fertility Optimization (IFFO) Algorithm was used in the optimization process in order to produce more precise and reliable results. After validating this algorithm by comparing it to well-known algorithms, three significant parameters, including exergy efficiency, irreversibility, and work, were optimized to improve the fuel cell design. According to the simulation findings, the proposed IFFO achieves the best outcomes for all objective functions, reaching the optimized values of -0.446, 0.011, and -0.462 for the mentioned-above parameters, respectively.

Xu et al. [93] performed an exergy analysis of an HT-PEMFC to determine the effect of operating conditions and membrane thickness on some thermodynamic concepts (e.g., exergy efficiency, irreversibility, and work) by employing a Manta Ray Foraging Optimization (DMRFO) Algorithm. Based on the optimization for optimal design in the HT-PEMFC, the suggested algorithm was compared with other studies in the literature. As a result, the simulation results agree with the literature, and the DMRFO algorithm best fits for exergy analysis.

In another study of Lu et al. [94], an exergy analysis has been accomplished to achieve the optimum steady-state model of the HT-PEMFC by employing a Grass Fibrous Root Optimization Algorithm (IGRA). In this study, different single-objective functions, including exergy efficiency, irreversibility, and work, are employed for optimally designing the fuel cell. In addition, some benchmark functions have been used to test the proposed algorithm's performance. The results have been compared to those of other optimization techniques, including the Genetic Algorithm (GA) and the Grass Fibrous Root Optimization Algorithm (GRA). Accordingly, the performance of the HT-PEMFC is marginally enhanced by the GA-based approach. However, it is evident that, among all studied methods, the IGRA yields the highest actual output. In addition, increasing the current density causes a reduction in the exergy efficiency, whereas increasing the operating temperature provides a noticeable rise in the exergy efficiency, mass exergy, and work at the constant membrane thickness.

With a special focus on the Thomson effect, Guo et al. [95] performed energy and exergy analysis for a hybrid system consisting of a two-stage thermoelectric generator and an HT-PEMFC. In this study, power output, exergy destruction rate, and electrical and exergy efficiencies are all stated as mathematical formulas for the hybrid system and its components. Consequently, with the contribution of the Thomson effect, the proposed system's electrical efficiency, exergy efficiency, and maximum power density are 17.5%, 17.7%, and 11.8% greater than the standalone HT-PEMFC, respectively.

Guo and Zhang [96] discussed the energetic and exergetic performance characteristics of a combined system comprised of an HT-PEMFC, a thermally regenerative electrochemical cycle, and a regenerator. This study also provides mathematical models for the HT-PEMFC, the thermal regeneration electrochemical cycle subsystem (TRECS), and the HT-PEMFC/TRECS combination system, considering the numerous irreversible losses in the combined system. An analytical formula relating HT-PEMFC current density to TRECS electric current is derived. Power density, energy efficiency, exergy destruction rate, and exergy efficiency are used to assess the overall system performance. As a result, the maximum power density and energy and

exergy efficiencies are higher at 15.6%, 8.5%, and 11.7%, respectively, compared to the single HT-PEMFC.

Nalbant et al. [97] presented a natural gas-fed integrated cogeneration system consisting of an HT-PEMFC stack, the fuel processing system, and other auxiliary components to examine energetic and exergetic performance analysis results. In addition, this study discussed the effects of parameters, e.g., anode stoichiometric ratio, operating temperature, and steam-to-carbon ratio, on the system's performance. As a result, increasing the stoichiometric ratio from 1.2 to 2 causes a decrease in the electrical, cogeneration, and exergetic efficiencies by 42.04%, 33.15%, and 37.39%, respectively.

Chang et al. [98] proposed the thermal, economic, and environmental performance analysis of different micro-combined cooling, heating, and power (CCHP) system configurations. System I primarily consists of HT-PEMFC, ORC and vapour compression cycle (VCC) subsystems and is driven by solar energy, whereas System II is composed of the same subsystems but in the absence of solar energy, e.g., in the evening or on rainy days. Consequently, under identical operational circumstances, the coefficient of performance (COP) of System II is around 1.19 in summer and 1.42 in winter, always greater than that of System I. In addition, System I and System II have exergy efficiencies of 49.7% and 47.7%, respectively. In the summer, the primary energy savings rates (PESRs) of System I and System II are determined to be 64.9% and 31.8%, while in the winter, these rates are found to be 60% and 36.2%, respectively. Without government subsidies, System I and System II payback periods are 9.6 and 6.0 years, respectively.

Sarabchi et al. [99] introduced a novel cogeneration system consisting of an HT-PEMFC stack, an integrated solar methanol steam reformer, and a Kalina cycle, driven by solar energy to generate power and heat. The suggested system is examined through the perspectives of energy, exergy, economics, and environmental effects by utilizing energy, exergy, and cost balance. As a result, increases in current density and fuel cell temperature, as well as reductions in cathode stoichiometric ratio, are observed to decrease the total product unit cost. In addition, the suggested system

improves energy efficiency by up to 9.6% and exergy efficiency by up to 4.3%, compared to the standalone HT-PEMFC stack. Furthermore, it is determined that the best economic performance is achieved in the case of the cathode stoichiometric ratio of 2, fuel cell temperature of 200 °C, reformer temperature of 220 °C, the anode gas recirculation ratio of 0.72, and the turbine inlet pressure of 47.48 bar. In contrast, the best environmental performance is obtained with the same stoichiometric ratio, fuel cell temperature, and turbine pressure, along with a reformer temperature of 280 °C and an anode gas recirculation ratio of 0.7987.

Guo et al. [100] performed a performance analysis of a combined system composed of an HT-PEMFC, a thermoelectric generator (TEG) to recover the fuel cell's waste heat, and a regenerator. In this study, the combined system's power output and efficiency are calculated under various operating conditions, including the current density, doping level, the figure of merit of thermoelectric materials, operating temperature, relative humidity, and thermal conductivity, as a parametric study. Consequently, the maximum power density and efficiency of the HT-PEMFC/TEG system are 21.13% and 15.54% greater than a single HT-PEMFC, respectively.

In another study by Guo et al. [101], a novel general model for an integrated system composed of an HT-PEMFC, an absorption cycle (APC), and a regenerator is introduced to assess the system's performance. As a result, compared to a standalone HT-PEMFC system, the proposed system's maximum equivalent power density (P_{max}) is about 33.41% higher when the APC operates as an absorption heat pump with a target temperature of 300 K and an ambient temperature of 273 K. The P_{max} of the suggested system is about 19.34% greater than a standalone HT-PEMFC system when the APC operates as an absorption refrigerator with a target temperature of 273 K and an ambient temperature of 300 K.

Mamaghani et al. [102] presented the optimum solutions for an HT-PEMFC-based micro-cogeneration plant using a multi-objective optimisation approach with electrical and thermal efficiency as the objectives. Apart from the HT-PEMFC, the methane reformer, water-gas shift reactor, and balance of plant are the components that form the system. As a result, optimising the system at full load with electrical efficiency as

the main objective led to obtaining a 29.5% net electrical efficiency. At 60% partial load, the net electrical efficiency is determined as 33.3%, which is 1% higher than the efficiency acquired under typical operating circumstances. When the system is optimised at several degrees of partialization, a broad range of electrical (20.7%–33.3%) and thermal efficiencies (49.0%–61.1%) were found.

Authayanun and Hacker [103] performed energy and exergy analysis for a trigeneration system composed of a 5 kW_{el} HT-PEMFC stack, a biogas steam reformer, a Li-Br absorption chiller, and a biogas steam reformer. In this study, the impacts of the operating temperature, pressure, and anode and cathode stoichiometric ratios on the power production, net power consumption, electrical efficiency, and cell performance are examined. Accordingly, due to its low power consumption, HT-PEMFC operating at atmospheric pressure presents a maximum electrical energy efficiency of around 36%. In addition, in order to obtain the optimal electrical exergy efficiency and total system exergy efficiency, it is determined that HT-PEMFC is operated in the case of atmospheric pressure, a cathode stoichiometric ratio of 4, an anode stoichiometric ratio of 1.35, and an operating temperature of 180 °C.

Lee et al. [104] performed a performance analysis of a CCHP system composed of an HT-PEMFC and an absorption refrigerator (AR). As a result, it was determined that the combined system produced 24–50% more equivalent power than the standalone HT-PEMFC. Furthermore, the electrical efficiency increased by more than 8% under varying temperatures and loads. In order to accomplish its cooling targets under certain conditions, the absorption refrigerator should have a COP of between 1 and 1.2.

Chang et al. [105] studied the energetic and exergetic performance of an HT-PEMFC stack-based micro-CCHP system in combination with ORC and VCC subsystems. The performance of the CCHP system in terms of energy and exergy analyses is extensively investigated for a total of six organic working fluids. Among these fluids, R601 was ultimately selected for this system based on the cycle performance and its physical, safety, and environmental qualities. In addition, under normal operating circumstances, the average COP of the micro-CCHP system in the summer and winter is determined to be 1.19 and 1.42, whereas the average exergy efficiency in the

summer and winter is found to be 46% and 47%, respectively. Furthermore, the energetic performance of the micro-CCHP system is significantly affected by the current density and operating temperature, whereas the exergetic performance is only noticeably affected by the current density.

In another study by Lee et al. [106], the performance analysis of a combined power system composed of an HT-PEMFC based on a PA-doped PBI membrane and an ORC was conducted to recover the waste heat from the fuel cell stack and produce more power. In this study, the system's maximum power is determined according to whether the HT-PEMFC is fully or partially loaded. In order to optimally obtain the performance of the ORC, maximum power density and efficiency were considered. As a result, depending on the operating temperature and load circumstances, the combined system's power output is 17–21% higher than the standalone HT-PEMFC, and its overall electrical efficiency is enhanced by 5–7%. Under these conditions, the ORC achieves an electrical efficiency of 13%-17%.

Haghighi and Sharifhassan [107] performed an exergy analysis of an HT-PEMFC under steady-state conditions. In this study, the GA code was constructed by employing MATLAB to determine and optimize the exergy, exergy efficiency, irreversibility, and work. As a result, the optimal values for exergy efficiency, irreversibility, and work are determined as 0.46, 0.007 W/cm², and 0.496 W/cm² in the case of a current density of 1 A/cm², a membrane thickness of 0.016 cm, an operating temperature of 453 K, and a pressure of 2.6 atm. In addition, according to the multi-objective optimization, the optimum points of these parameters are also determined as 0.3545, 0.1542 W/cm², and 0.2767 W/cm² in the case of a current density of 0.49363 A/cm², a temperature of 451.231 K, a pressure of 2.5 atm, and a membrane thickness of 0.016 cm.

Table 4.2. The list of present studies on the 1-D models of HT-PEMFC.

Authors	Year	Model	System	Electro-chemical	Energy	Exergy	Exergo-economic	Ecological Analysis	Solution Technique
Amjad et al. [83]	2022	1-D & isothermal	Stack	+	+	+	+	-	EES
Guo et al. [84]	2022	1-D & steady-state	Cell	+	+	-	-	-	NA
Li et al. [85]	2022	1-D & steady-state	Stack	+	+	+	-	+	MATLAB
Li et al. [86]	2022	1-D & steady-state	Cell	+	+	+	-	-	NA
Sun et al. [87]	2021	1-D & steady-state	Cell	+	+	+	-	-	MATLAB
Li et al. [88]	2021	1-D	Cell	+	+	-	-	-	PSO Algorithm
Erzen et al. [89]	2021	1-D	Stack	+	+	+	+	-	NA
Li et al. [90]	2021	1-D & quasi-steady state	Cell	+	+	+	-	+	NA
Sarabchi et al. [91]	2021	1-D & semi-empirical	Stack	+	+	+	+	-	EES
Lu et al. [92]	2021	1-D & steady-state	Cell	+	-	+	-	-	MATLAB

Table 4.2. Continued.

Authors	Year	Model	System	Electro-chemical	Energy	Exergy	Exergo-economic	Ecological Analysis	Solution Technique
Xu et al. [93]	2020	1-D & steady-state	Cell	+	-	+	-	-	Manta Ray Algorithm
Lu et al. [94]	2020	1-D & steady-state	Cell	+	-	+	-	-	Grass Algorithm
Guo et al. [95]	2020	1-D & steady-state	Cell	+	+	+	-	-	MATLAB
Guo and Zhang [96]	2020	1-D & isothermal	Cell	+	+	+	-	-	NA
Nalbant et al. [97]	2020	1-D & semi-empirical	Stack	+	+	+	-	-	EES
Chang et al. [98]	2019	1-D	Stack	+	-	+	+	+	NA
Sarabchi et al. [99]	2019	1-D	Stack	+	+	+	+	+	EES
Guo et al. [100]	2019	1-D & steady-state	Cell	+	+	-	-	-	NA
Guo et al. [101]	2019	1-D & isothermal	Cell	+	+	-	-	-	NA

Table 4.2. Continued.

Authors	Year	Model	System	Electro-chemical	Energy	Exergy	Exergo-economic	Ecological Analysis	Solution Technique
Mamaghani et al. [102]	2018	1-D & steady-state	Stack	+	+	-	-	-	MATLAB
Authayanun and Hacker [103]	2018	1-D & isothermal	Stack	+	+	+	-	-	MATLAB
Lee et al. [104]	2017	1-D & isothermal	Cell	+	+	-	-	-	MATLAB
Chang et al. [105]	2017	1-D & steady-state	Stack	+	+	+	-	-	MATLAB/REFPROP
Lee et al. [106]	2016	1-D & isothermal	Stack	+	+	-	-	-	NA
Haghighi and Sharifhassan [107]	2016	1-D & steady-state	Cell	+	-	+	-	-	ANSYS/MATLAB

4.2. ZERO-DIMENSIONAL AND ISOTHERMAL MODEL

This section is devoted to describing the 0-D and isothermal model of the HT-PEMFC. As demonstrated in Figure 4.1, an HT-PEMFC contains cathode and anode plates with a PA-doped PBI membrane as an ion-conducting electrolyte in the form of a solid sandwiched between electro-catalysts (the electrodes) [108]. The operating principle of HT-PEMFCs is identical to their low-temperature counterparts, except for high temperatures ranging from 160 °C to 180 °C, and is governed by the same half-cell reactions. Pure oxygen or air is transmitted to the cathode, and the hydrogen is directed to the anode flow channel to arrive at the catalyst layers where the reduction and oxidation reactions occur. The oxidation reaction occurs at the anode after encountering the hydrogen; it divides into H^+ ions and free electrons. H^+ ions advance through the electrolyte, which encourages ionic movement. These ions are carried across the PEM membrane directly to the cathode, where they encounter oxygen to produce water. The flow of electrons through the external circuit closes a cycle. Thus, the water, heat, and electrical energy are obtained at the end as the products [109].

In order to simplify the modelling approach, the following general assumptions are taken into consideration:

- Hydrogen and air are utilized as reactants [104].
- All reactants are considered ideal gases [110].
- The HT-PEMFC fully operates in steady-state conditions [106].
- The flow of reactants is considered steady, incompressible, and laminar [101].
- The electrical energy required for compressing reactants is ignored [79].
- The operating temperature and pressure are constant at the initial state [79].
- The variation in kinetic and potential energy and exergy is not considered [97].
- The amounts of the reactants are supplied with respect to the electric current generated in the fuel cell [96].
- All overpotentials are considered and calculated to verify the model [111].

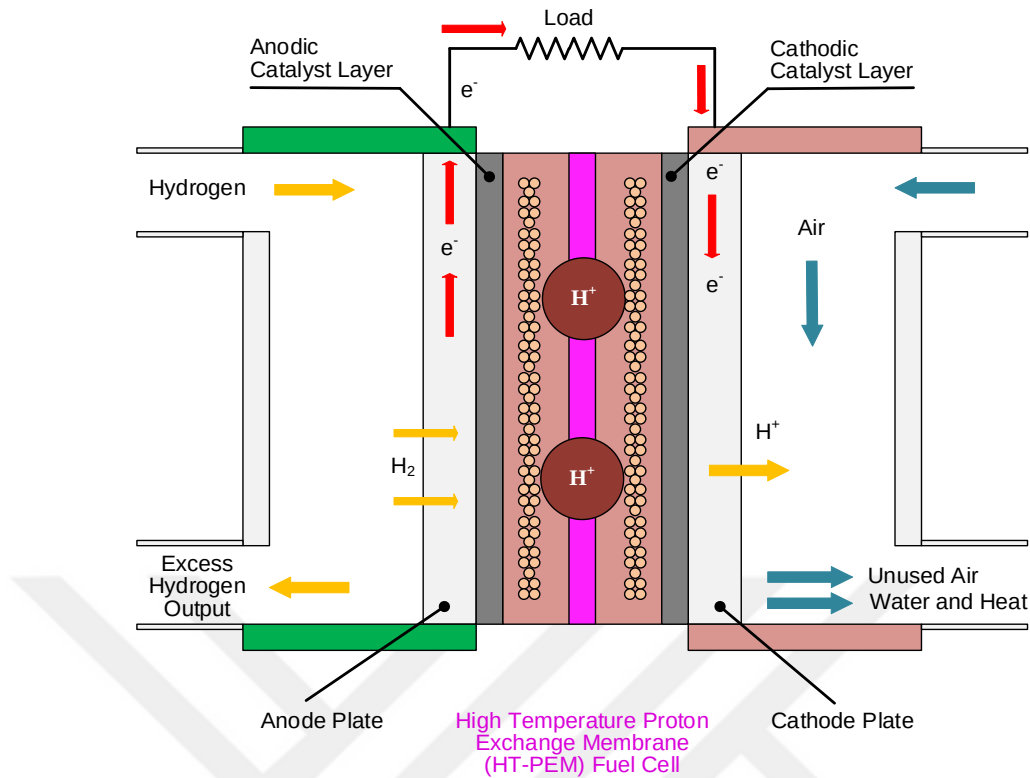


Figure 4.1. The schematic structure of an HT-PEMFC.

Considering these assumptions mentioned above, the electrochemical analysis will be applied to an HT-PEMFC first, and then thermodynamic analyses, including energy, entropy, and exergy analysis, will be added to the model. Therefore, the next chapter presents the principles and calculation procedures of the 0-D and isothermal model. In addition, significant concepts in electrochemical analysis, including reversible and irreversible voltages, net output voltage, and overpotentials, and other concepts in thermodynamics, including energy and exergy efficiency, entropy production, and exergy destruction, will be comprehensively analysed and discussed.

4.2.1. Electrochemical Analysis

The electrochemical reactions in the fuel cell happen in an exothermic process. The term “exothermic” describes a chemical process in which energy is released during the process as heat, as depicted in Figure 4.2. Therefore, the variation in the enthalpy, ΔH , is negative for an exothermic process. It may sound counterintuitive, but it should be remembered that system attributes are seen from the system’s perspective. As the

system loses heat (by releasing it into the environment), the change in enthalpy is negative. A negative value for ΔH indicates that the enthalpy of the products is less than that of the reactants, as demonstrated in Figure 4.3.

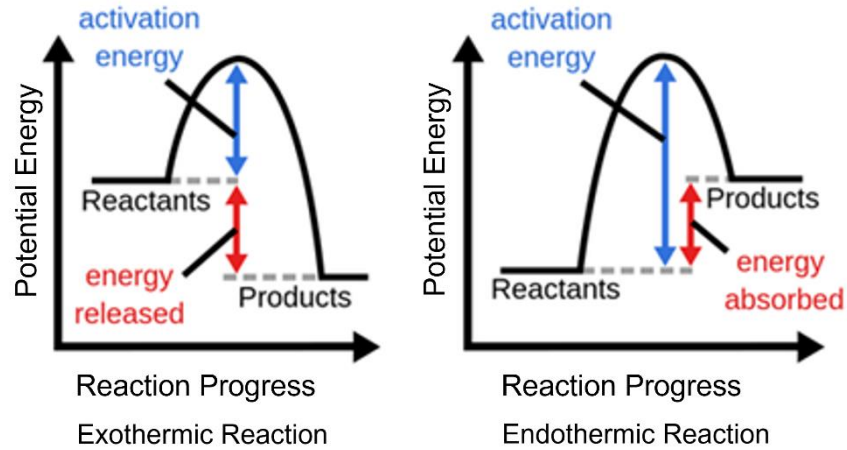


Figure 4.2. The difference between exothermic and endothermic reactions [112].

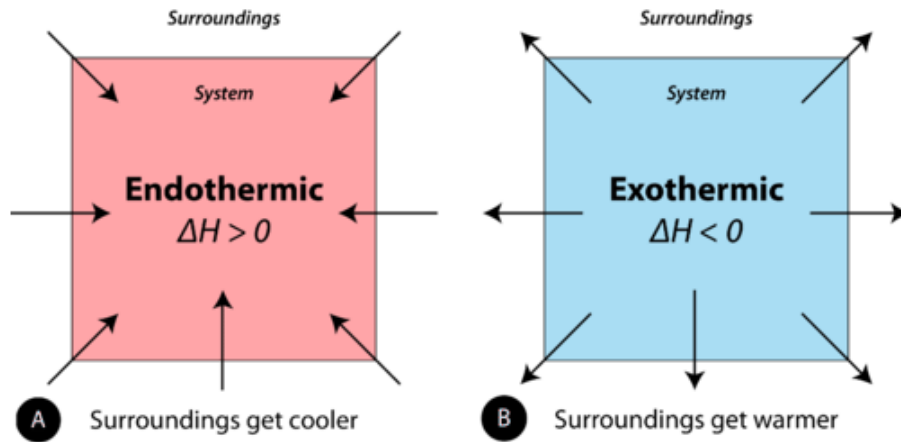
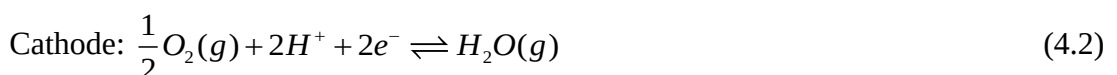
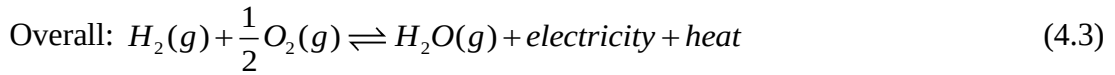


Figure 4.3. The enthalpy variation in endothermic and exothermic reactions [112].

Considering the anode and cathode compartments of the HT-PEMFC, these reactions can be summarized as:





The calculation procedure starts with determining the open-circuit cell voltage or ideal standard potential, E_0 , which equals 1.229 V for LT-PEMFCs at standard conditions (25 °C and 1 atm) due to the liquid phase of the produced water, given as:

$$E_0 = -\frac{\Delta g^0}{n_e F} \quad (4.4)$$

where Δg^0 stands for the variation in the molar Gibbs free energy for the electrochemical reaction at standard conditions, n_e for the electron number involved per mole of electrolysed component, and F for the Faraday's constant.

In addition, the maximum possible energy output and, correspondingly, the potential difference between the cathode and anode compartments can be achieved in the case that the fuel cell is operated in totally thermodynamically reversible conditions. The maximum electrical potential is known as the reversible voltage, E_{rev} , given by [79]:

$$E_{rev} = E_0 + \frac{\Delta s}{n_e F} (T_{fc} - T_0) + \frac{RT}{n_e F} \ln \left(\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}} \right) \quad (4.5)$$

where Δs stands for the variation in the molar entropy for the electrochemical reaction, T_{fc} for the operating temperature of the fuel cell, T_0 for the ambient temperature, and R for the universal gas constant. In addition, P_{H_2} , P_{O_2} , and P_{H_2O} signify the partial pressures of H_2 , O_2 , and H_2O , respectively. Both Δs and Δg^0 will be comprehensively discussed in this section.

Here, it is worth noting that the reversible voltage is the maximum theoretical value. However, in practice, the cell voltage is much lower than the reversible voltage and typically stands between 0 and 1.0 V. The actual output voltage, U , can be defined as the difference between the reversible and irreversible voltages caused by

electrochemical losses due to the overpotentials. Therefore, the irreversible voltage, E_{irr} is the sum of all overpotentials, including the activation, concentration, and ohmic, as follows:

$$U = E_{rev} - E_{irr} \quad (4.6)$$

$$E_{irr} = E_{act} + E_{con} + E_{ohm} \quad (4.7)$$

The activation overpotential, E_{act} , occurs due to low reaction speeds in anode and cathode compartments. The correlation between the current density and the activation overpotential is logarithmic [113]. Namely, it increases with increasing the current density and is expressed by a modified version of the Tafel equation [114]:

$$E_{act} = \frac{RT}{n_e \alpha F} \ln \left(\frac{j + j_{leak}}{j_0} \right) \quad (4.8)$$

where α denotes the charge transfer coefficient, whereas j , j_0 , and j_{leak} stand for the current density, the exchange current density, and the leak current density due to the internal current and the leakage of the reactant, respectively.

The concentration overpotential, E_{con} , is due to mass transfer limitations and voltage drops. At high current densities, especially approaching the current density limit [113] the concentration gradient between the reaction sites and the bulk phase becomes sky-high and limits the rate of the reactions. This situation causes a rapid increase compared to the ohmic overpotential and is determined by [115]:

$$E_{con} = \frac{RT}{n_e F} \ln \left(\frac{j_L}{j_L - j} \right) \quad (4.9)$$

where j_L denotes the limiting current density. The ohmic overpotential, E_{ohm} , is due to the resistance to the protons' flow and the resistance of the electrodes. The total ohmic polarization loss through the membrane can be given as [101]:

$$E_{ohm} = j \frac{t_{mem}}{\sigma_{mem}} \quad (4.10)$$

where t_{mem} denotes the membrane thickness, and σ_{mem} stands for the proton conductivity of the PBI membrane, which is written as [96]:

$$\sigma_{mem} = \frac{A_0 B_0}{T} e^{-\frac{b_{act}}{RT}} \quad (4.11)$$

where A_0 and B_0 denote pre-exponential coefficients for PA doping level and humidity, respectively. These coefficients are determined by [116]:

$$A_0 = 168DL^3 - 6324DL^2 + 65750DL + 8460 \quad (4.12)$$

$$B_0 = \begin{cases} 1 + (0.01704T - 4.767)RH & 373.15 \text{ K} \leq T \leq 413.15 \text{ K} \\ 1 + (0.1432T - 56.89)RH & 413.15 \text{ K} < T \leq 453.15 \text{ K} \\ 1 + (0.7T - 309.2)RH & 453.15 \text{ K} < T \leq 473.15 \text{ K} \end{cases} \quad (4.13)$$

where DL denotes the PA doping level, whereas RH stands for the relative humidity of the electrolyte. The activation energy of the membrane, b_{act} in Eq. (4.11), can be given as [116]:

$$b_{act} = -619.6DL + 21750 \quad (4.14)$$

Considering Eqs. (4.6-4.10), U can be rewritten as:

$$U = E_{rev} - \left\{ \frac{RT}{n_e \alpha F} \ln \left(\frac{j + j_{leak}}{j_0} \right) + \frac{RT}{n_e F} \ln \left(\frac{j_L}{j_L - j} \right) + j \frac{t_{mem}}{\sigma_{mem}} \right\} \quad (4.15)$$

The equivalent internal resistance arising from overpotentials, R_I , can be expressed as [79]:

$$R_i = \frac{E_{irr}}{A_j} \quad (4.16)$$

As depicted in the polarisation curve of a typical PEMFC in Figure 4.4, the cell voltage decreases with increasing these overpotentials. In the low current density region (Region 1), it is mainly affected by the activation loss, whereas the effect of ohmic loss is more visible in the medium region (Region 2). In addition, the effect of concentration loss becomes dominant in the high-current density region (Region 3). Therefore, all these parameters significantly influence the precision and accuracy of the results. In order to derive the following curve, some parameters, including operating temperature and pressure, must be considered constant at the beginning stage. Therefore, Table 4.3 demonstrates some of these parameters used in the electrochemical analysis.

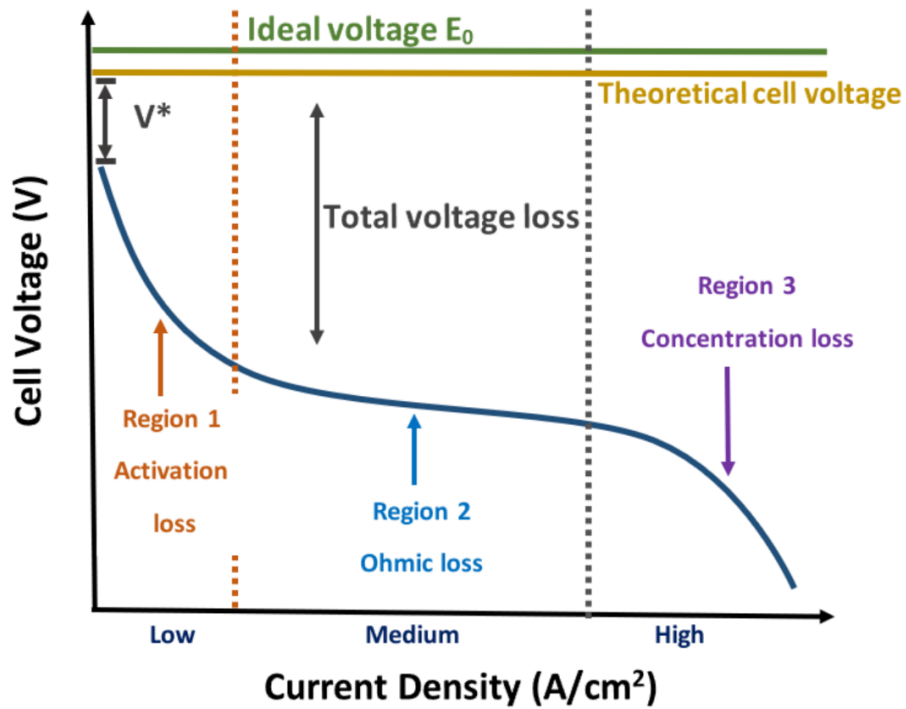


Figure 4.4. The polarisation curve of a typical PEMFC [117].

Table 4.3. Some parameters used in the electrochemical analysis [78].

Parameters	Symbol	Value	Unit
Faraday constant	F	96,485	C.mol ⁻¹
Universal gas constant	R	8.314	J. mol ⁻¹ K ⁻¹
Operating temperature	T	448	K
Ambient temperature	T_0	298	K
Leak current density	j_{leak}	50	Am ⁻²
Thickness of the membrane	t_{mem}	0.05	cm
Anode pressure	P_{H2}	1	atm
Cathode pressure	P_{O2}	1	atm
Relative humidity	RH	3.8	%
Charge transfer coefficient	α	0.5	-
Number of electrons	n_e	2	-
Doping level	DL	10	-

4.2.2. Thermodynamic Analysis

The thermodynamic analysis covers a study in which the electrochemical, thermal, and electrical reactions are evaluated together to demonstrate the performance of the HT- PEMFC. In order to apply the thermodynamic laws and determine the efficiency, a thermodynamic potential that can be used to calculate the maximum reversible work is needed. This phenomenon is called the Gibbs free energy of formation, ΔG , as follows [118]:

$$\Delta G = \Delta G_{(products)} - \Delta G_{(reactant)} \quad (4.17)$$

Considering the products and reactants, Eq. (4.17) can be rewritten as:

$$\Delta G = \Delta G_{(H_2O)} - \Delta G_{(H_2)} - \Delta G_{(O_2)} \quad (4.18)$$

The released energy or reaction enthalpy in the fuel cell is not transformed into useful work or electricity since the entropy is generated due to irreversibilities, as in every chemical reaction. Therefore, ΔG may be rewritten to indicate the reaction enthalpy and some irreversible losses during the energy conversion due to the formation of entropy given by:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4.19)$$

The molar enthalpy changes of a chemical reaction, ΔH^0 , is the difference between the heats of formation of products and reactants as follows [118]:

$$\Delta H^0 = (h_f)_{H_2O} - (h_f)_{H_2} - \frac{1}{2}(h_f)_{O_2} \quad (4.20)$$

Similarly, molar entropy changes of the electrochemical reaction, ΔS^0 , is determined by:

$$\Delta S^0 = (s_f)_{H_2O} - (s_f)_{H_2} - \frac{1}{2}(s_f)_{O_2} \quad (4.21)$$

where h_f and s_f stand for reaction reactants and products under standard circumstances, as given in Table 4.4.

Table 4.4. Enthalpy, Entropy, and Gibbs Free Energy for reactants and products at standard conditions, where (g) and (l) denote the gas and liquid phases, respectively [119].

Chemical Species	h_f (kJ/kmol)	s_f (kJ/kmol.K)	ΔH^0 (kJ/kmol)	ΔS^0 (kJ/kmol.K)	ΔG^0 (kJ/kmol)
Hydrogen (H ₂)	0	0.13066	-	-	-
Oxygen (O ₂)	0	0.20517	-	-	-
Water (H ₂ O) (l)	-286.02	0.06996	-286.02	-0.1633	-237.34
Water (H ₂ O) (g)	-241.98	0.18884	-241.98	-0.0444	-228.74

In order to determine the energy and exergy efficiency, new correlations identifying the molar enthalpy and entropy variations according to temperature are still needed. Here, it is worth noting that the expressions mentioned above were valid at a constant temperature, but a fuel cell can work at any temperature. Therefore, for proper modelling, both ΔH and ΔS should be specified as a function of temperature given as:

$$\Delta H = \Delta H^0 + \int_{298.15}^T C_p dT \quad (4.22)$$

$$\Delta S = \Delta S^0 + \int_{298.15}^T \frac{1}{T} C_p dT \quad (4.23)$$

An empirical expression can be utilized since the specific heat, C_p , may be written as a function of temperature as given below:

$$C_p = a + bT + cT^2 \quad (4.24)$$

where a , b , and c denote empirical coefficients of each substance given in Table 4.5.

Table 4.5. Empirical coefficients for the temperature dependence of C_p for each component [119].

Chemical Species	a (J/mol.K)	b (J/mol.K)	c (J/mol.K)
Hydrogen (H ₂)	28.91404	-0.00084	2.01×10^{-6}
Oxygen (O ₂)	25.84512	0.012987	-3.9×10^{-6}
Water (H ₂ O) (l)	75.42546	0	0
Water (H ₂ O) (g)	30.62644	0.009621	1.18×10^{-6}

Considering the above equation and the table, the heat capacity of each substance can be determined. The variation in the heat capacity is negligible at temperatures below 100 °C, but it cannot be ignored in the case that a fuel cell operates at higher temperatures [35]. Figure 4.5 presents the variation of the heat capacity as a function of temperature for both reactants and products.

Substituting Eq. (4.24) into Eqs. (4.22-4.23), these equations can be rewritten as:

$$\Delta H = \Delta H^0 + \Delta a(T - 298.15) + \Delta b \frac{(T^2 - 298.15^2)}{2} + \Delta c \frac{(T^3 - 298.15^3)}{3} \quad (4.25)$$

$$\Delta S = \Delta S^0 + \Delta a \ln \frac{T}{298.15} + \Delta b(T - 298.15) + \Delta c \frac{(T^2 - 298.15^2)}{2} \quad (4.26)$$

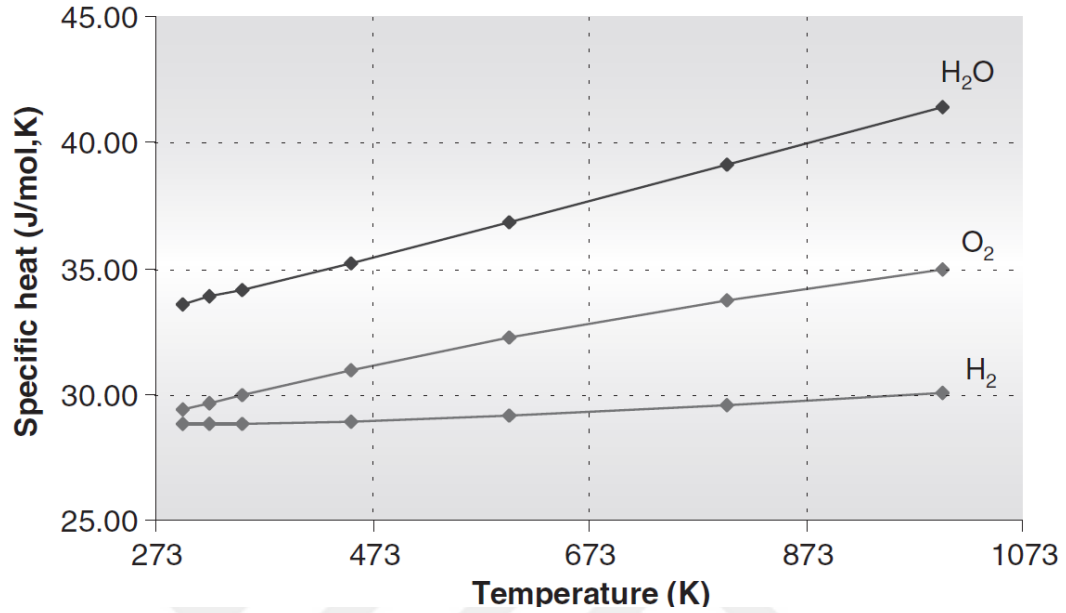


Figure 4.5. The variation of C_p as a function of operating temperature for reactants and products in the gas phase [35].

where Δa , Δb , and Δc are the differences between the coefficients of a , b , and c , respectively, for both products and reactants given as:

$$\Delta a = a_{H_2O} - a_{H_2} - \frac{1}{2}a_{O_2} \quad (4.27)$$

$$\Delta b = b_{H_2O} - b_{H_2} - \frac{1}{2}b_{O_2} \quad (4.28)$$

$$\Delta c = c_{H_2O} - c_{H_2} - \frac{1}{2}c_{O_2} \quad (4.29)$$

4.2.2.1. Energy Analysis

The energy disposition in either physical or chemical processes involving the transfer or conversion of energy is based on the first law of thermodynamics. Considering the

conservation of energy principle, the traditional method of process analysis in terms of thermodynamics has two major steps. This method usually entails to perform energy balance and evaluate process effectiveness. Using this balance, the unaccounted heat transfer between system and environment is determined at first. Secondly, the efficiency analysis relevant to the system under consideration is calculated. Accounting of the performance analysis for any process can be helpful in evaluating the level of thermodynamic perfection. More specifically, it may give sufficient data for identifying heat loss and can be utilized for enhancing heat recovery by applying the system specification. However, it does not provide details on internal losses occurring in the process and the reason of energy degradation, besides does not quantify the usefulness of the various energy and material streams [120].

The maximum efficiency of a fuel cell is identical to the thermodynamic efficiency of energy conversion, defined as the ratio between the variation of ΔG and the variation of ΔH . The thermodynamic efficiency of the fuel cell, η_{th} , is denoted by the expression, given as:

$$\eta_{th} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (4.30)$$

Assuming that all of the ΔG is transformed into electrical energy, as depicted in Figure 4.6, the maximum possible theoretical efficiency can easily be determined as:

$$\eta_{th} = \frac{237.13 \text{ kJ / mol}}{285.83 \text{ kJ / mol}} \cong 83\% \quad (4.31)$$

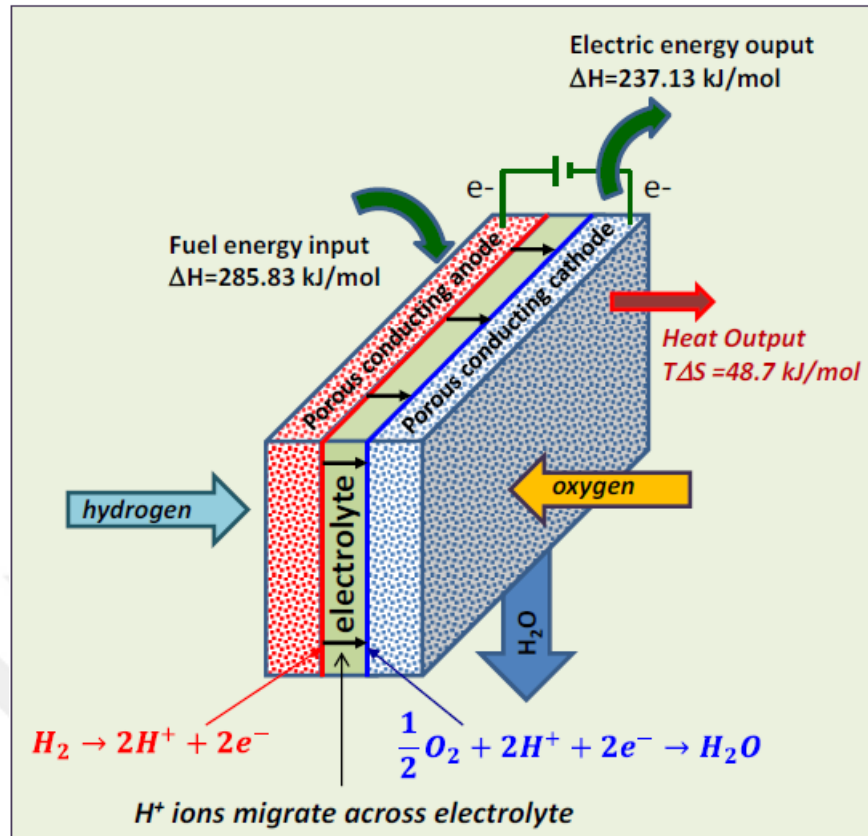


Figure 4.6. The input and output energy balance of a PEMFC [14].

The efficiency rate given in Eq. (4.29) is valid only under standard conditions, including the ambient temperature of 25 °C and an atmospheric pressure. As the temperature increases, the maximum theoretical efficiency decreases, as demonstrated in Figure 4.7, depending on whether the reactants are in the liquid or gas phase.

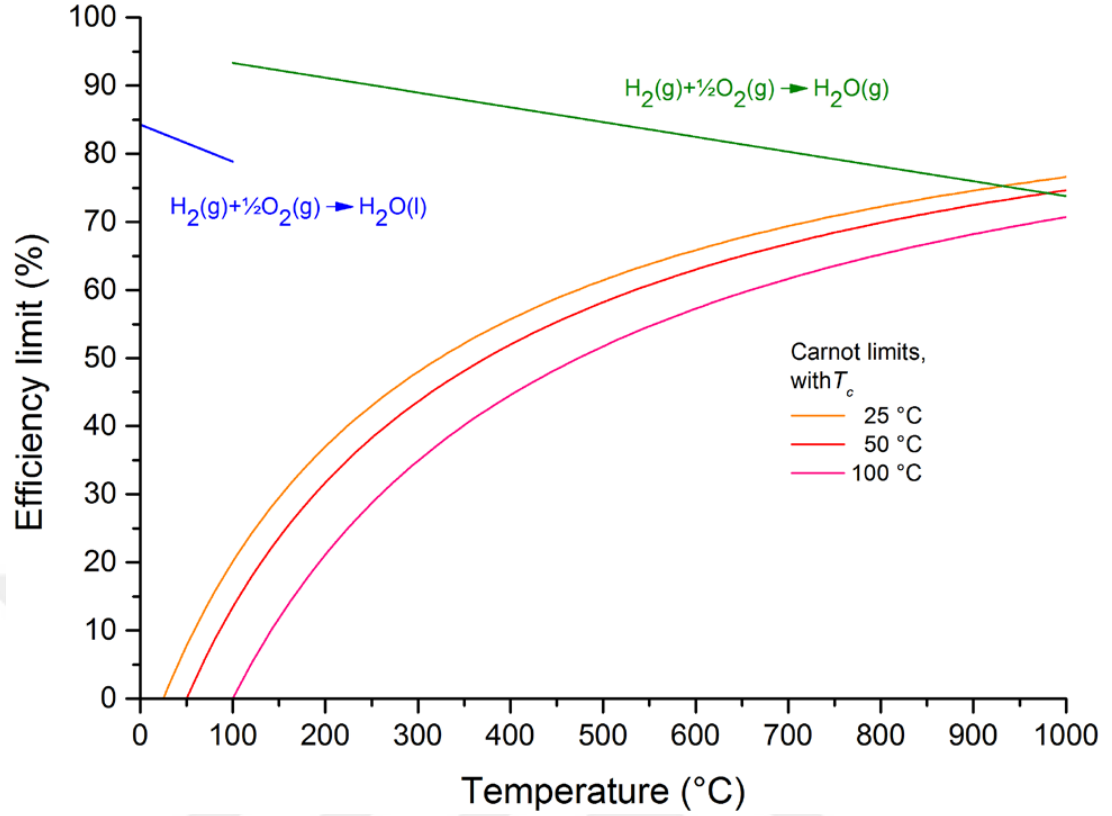


Figure 4.7. The variation of efficiency limit for H₂/O₂ fuel cells with different product phases at atmospheric pressure and Carnot cycle with different operating temperatures [21].

Considering the fuel cell, the actual power output, P_{fc} , derived from the HT-PEMFC in real operation, can be determined as [121]:

$$P_{fc} = IV = jA(E_{rev} - E_{act} - E_{con} - E_{ohm}) \quad (4.32)$$

where I and V stand for the operating electric current, and the output voltage, respectively. The variation of theoretical efficiency and cell voltage as a function of power density is also presented in Figure 4.8.

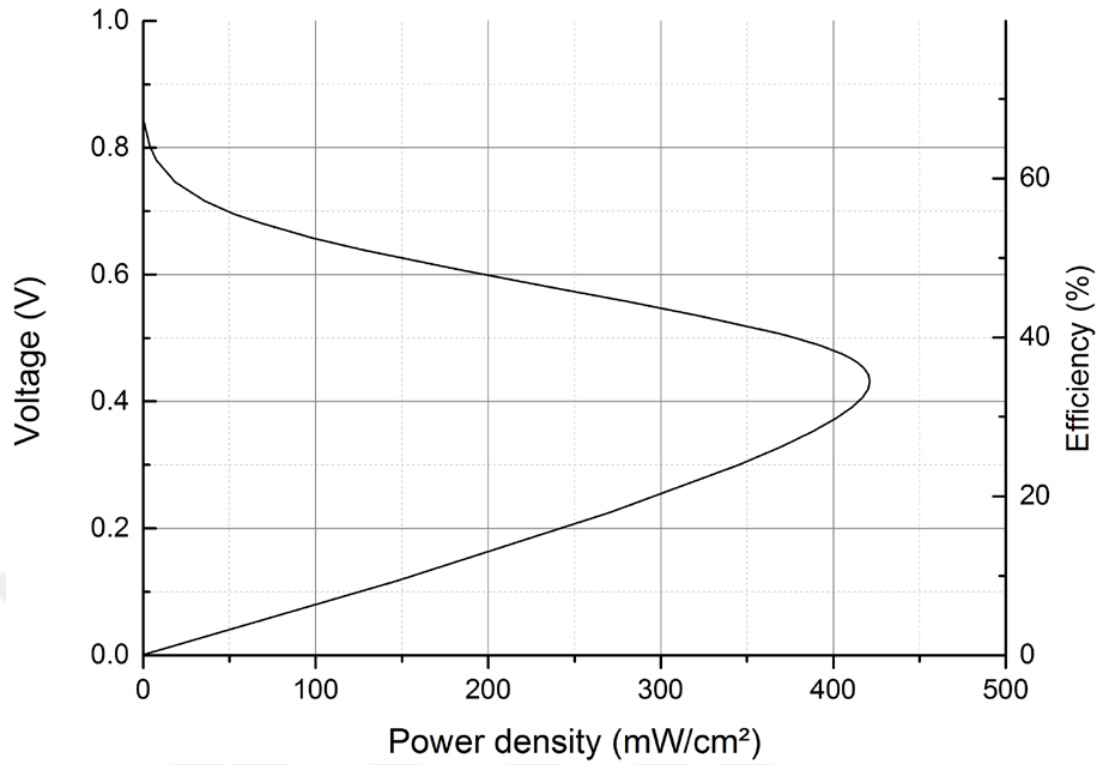


Figure 4.8. The variation of efficiency and cell voltage as a function of power density [21].

The energy efficiency of the HT-PEMFC, η_{fc} , is the ratio of the output power to the total energy realized per unit of time, $(-\Delta \dot{H})$, given as [96]:

$$\eta_{fc} = \frac{P_{fc}}{-\Delta \dot{H}} \quad (4.33)$$

The term, $(-\Delta \dot{H})$ in the previous equation, can be written as [96]:

$$(-\Delta \dot{H}) = -\dot{q}_{H_2} \Delta h_T = -\frac{jA \Delta h_T}{n_e F} \quad (4.34)$$

where $\dot{q}_{H_2}$ stands for the hydrogen consumption rate during the energy conversion.

Based on the first law of thermodynamics, the entire waste heat generated in the HT- PEMFC can be split into two parts. The first part is the heat dissipation from the fuel cell to the environment via conductive and/or convective heat losses as indicated [122]:

$$\dot{Q}_L = K_L A_L (T_{fc} - T_0) \quad (4.35)$$

where K_L and A_L denote the conductive and/or convective heat dissipation coefficient and the heat transfer surface, respectively.

The second part is the waste heat from the HT-PEMFC to the surroundings, which can be determined by [121]:

$$\dot{Q}_H = -\Delta \dot{H} - P_{fc} - \dot{Q}_L \quad (4.36)$$

4.2.2.2. Entropy Analysis

Entropy can be characterized as an extensive property that becomes somewhat more meaningful when the microscopic state of the system and its surroundings is considered. Thus, the entropy changes of the system during an irreversible process are directly associated with increasing of molecular chaos of a substance. From a more fundamental point of view, the second law of thermodynamics gives us a clear picture of where entropy is generated from. Accordingly, for an HT-PEMFC, the entropy production rate, $\dot{\delta}$ is determined as:

$$\dot{\delta} = \frac{-\Delta \dot{H} - P_{fc}}{T_{fc}} \quad (4.37)$$

4.2.2.3. Exergy Analysis

Exergy is defined as a universal measure of the work potential or the maximum amount of work which can be obtained from great variety of streams (mass, heat, and work) that flow through a system. The concept of exergy comes from the second law of thermodynamics in which both the quality and quantity of different forms of energy (ordered or disordered) are taken into consideration together. The ability to account for a quantitative measure of the usefulness of an energy or a substance provides this concept to become the most natural and convenient standard for analyzing a process or system. Because of this distinctive feature, exergy gives more insight than energy concept for understanding the physical basis of the system behavior using environmental parameters as the reference state. Therefore, it is not only a significant principle for evaluating thermodynamics systems, but also a co-property of a system and reference environment, combining the extensive properties of the system with the intensive properties of the environment [120].

Considering the fuel cell, the total exergy of stream for any matter can be written as:

$$\dot{E}x = \dot{E}x_{pe} + \dot{E}x_{ke} + \dot{E}x_{phy} + \dot{E}x_{chm} \quad (4.38)$$

The kinetic and potential exergy rate are given as follows [123]:

$$\dot{E}x_{pe} = PE = g(z - z_0) \quad (4.39)$$

$$\dot{E}x_{ke} = KE = \frac{1}{2}(V^2 - V_0^2) \quad (4.40)$$

where g , z , and V stand for the gravity, velocity, and elevation, respectively. Since the system under consideration is a fuel cell, thus kinetic and potential exergy changes are not taken into consideration, the total flow exergy rate becomes as the sum of its physical and chemical exergy rates given by [124]:

$$\dot{E}_x = \dot{E}_{x_{phy}} + \dot{E}_{x_{chm}} = \dot{n}(\overline{ex}_{phy} + \overline{ex}_{chm}) \quad (4.41)$$

where $\dot{n}$, $\overline{ex}_{phy}$ and $\overline{ex}_{chm}$ denote the molar mass flow rate of species, the specific physical exergy, and the specific chemical exergy of a substance, respectively. $\overline{ex}_{phy}$ is defined as the maximum theoretical useful work obtained as a system when it is brought from the dead state to the unrestricted dead state and is determined by the following equation in the absence of the velocity and elevation.

$$\overline{ex}_{phy} = (\overline{h} - h_0) - T_0(\overline{s} - s_0) \quad (4.42)$$

where $\overline{h}$ and $\overline{s}$ stand for the specific enthalpy and entropy of species at the operating cell temperature, respectively. In addition, $\overline{ex}_{chm}$ is defined as the chemical flow exergy and is associated with the departure of the chemical composition of a system from its chemical equilibrium. For an ideal gas mixture, $\overline{ex}_{chm}$ is determined on the molar basis as follows [124]:

$$\overline{ex}_{chm} = \sum x_i \overline{ex}_{chm,i}^0 + RT_0 \sum x_i \ln x_i \quad (4.43)$$

where x_i denotes the molar fraction and $\overline{ex}_{chm,i}^0$ is the standard chemical exergy of species at the reference conditions. The standard chemical exergies of H₂, O₂, and H₂O (l) are estimated as 236900, 3970, 9500 (J/mol), respectively as given in Ref [79].

The general form of the steady-state control volume exergy balance for an HT-PEMFC can be written as [125]:

$$\sum \dot{E}_{x_{in}} + \sum \dot{E}_{x_{heat}} = \sum \dot{E}_{x_{out}} + \sum \dot{E}_{x_{work}} + \dot{E}_{x_D} \quad (4.44)$$

where $\dot{E}x_{in}$ and $\dot{E}x_{out}$ stand for the inlet and outlet exergy transfer by mass, while $\dot{E}x_{heat}$ and $\dot{E}x_{work}$ denote exergy transfer by the heat and work, respectively. In addition, $\dot{E}x_D$ is the exergy destruction rate of the system.

Here, it is worth to noting that $\sum \dot{E}x_{work}$ and $\dot{E}x_{heat}$ can be determined as follows [125]:

$$\sum \dot{E}x_{work} = \dot{W}_{fc} \quad (4.45)$$

$$\sum \dot{E}x_{heat} = \left(1 - \frac{T_0}{T_{fc}}\right) \dot{Q}_H \quad (4.46)$$

Finally, the exergy efficiency of the HT-PEMFC can be written as [122]:

$$\psi_{fc} = \frac{P_{fc}}{\left(-\Delta \dot{G}\right) - T \Delta \dot{S} \cdot \left(1 - \left(T_0 / T_{fc}\right)\right)} \quad (4.47)$$

4.2.3. Statistical Analysis

In order to certify the validity of the presented model, different statistical methods were applied. These methods were primarily used to present the statistical results of each experimental or numerical data in itself. Then, experimental and numerical results were evaluated integrally, and model performance analyses were performed to find the best fit.

First of all, the mean value of each data, either experimental or numerical, can be determined as:

$$\bar{y}_i = \frac{\sum y_i}{n} \quad (4.48)$$

where y_i , $\bar{y}_i$, and n denote the real observed value, the mean value of each data, and the number of observations, respectively.

In the case that n is odd, the median of the given dataset (M) can be calculated as:

$$M = \frac{n+1}{2} \quad (4.49)$$

The standard deviation of the dataset (S) can be written as [126]:

$$S = \sqrt{\frac{\sum (y_i - \bar{y}_i)^2}{n-1}} \quad (4.50)$$

The variance (S^2) is equal to the square of the standard deviation and is therefore calculated as follows:

$$S^2 = \frac{\sum (y_i - \bar{y}_i)^2}{n-1} \quad (4.51)$$

The coefficient of variance (CV) can be determined as:

$$CV = \frac{\sqrt{\frac{\sum (y_i - \bar{y}_i)^2}{n}}}{\bar{y}_i} \quad (4.52)$$

The coefficient of skewness (δ_s) measures the departure from normality. Symmetric distributions have zero skewness, as given in the following equation [126]:

$$\delta_s = \frac{\frac{1}{n} \sum_{i=1}^n (y_i - \bar{y}_i)^3}{S^3} \quad (4.53)$$

The data significance for which the coefficient of kurtosis (δ_s) equals zero mainly refers to the normal distribution. Distributions that peaked more than normal have kurtosis >0 ; flatter ones have kurtosis <0 , given by:

$$\delta_k = \frac{\frac{1}{n} \sum_{i=1}^n (y_i - \bar{y})^4}{S^4} \quad (4.54)$$

Apart from these aforementioned statistical approaches, the model performance between the experimental and numerical results was applied. Multiple indicators, including the ratio of means, the mean absolute error, the mean fractional error, the mean square error, the root mean square error, the R-squared, the adjusted R-squared, the normalised mean bias, the normalised mean error, the mean fractional bias, the mean fractional error, the standard error of the mean, and uncertainty values, were used to evaluate the performance of the model.

The mean zero bias demonstrates that any residuals in the model's predictions are cancelled. Time series are computed from the residuals determined by the difference between the observed and fitted values. The average difference, $\bar{\varepsilon}$, (the first moment of distribution, mean bias, or mean error) can be calculated by [127]:

$$\bar{\varepsilon} = \frac{1}{n} \sum (y_i - \hat{y}_i) \quad (4.55)$$

where $\hat{y}_i$ stands for the predicted value.

The ratio of the means (*Rat*) signifies overprediction or underprediction. *Rat* values larger than 1 represent an overprediction, while those less than 1 represent an underprediction. This value can be determined by [127]:

$$Rat = \sum_{i=1}^n \frac{y_i}{\hat{y}_i} \quad (4.56)$$

The Mean absolute error (*MEA*) is a statistical measure of how far off the mark the dataset's predictions were from the actual values. The *MEA* considers the mean absolute difference between the dataset's real observed and predicted values and is calculated as follows [128]:

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i| \quad (4.57)$$

The mean fractional error (*MFE*) is another statistical method and is determined as:

$$MFE = \frac{2}{n} \sum_{i=1}^n \frac{(y_i - \hat{y}_i)}{y_i + \hat{y}_i} \quad (4.58)$$

The average squared difference between the actual and projected values is described as the mean squared error (*MSE*). It is a statistical metric that quantifies the residuals' variance, given as [128]:

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (4.59)$$

The root mean square error (*RMSE*) is an excellent general-purpose error metric used to measure the difference between projected values by a model and actual values from an observation, e.g., an experimental study, as given:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (4.60)$$

The R-squared (R^2), or the coefficient of determination, is an essential statistical metric that indicates the ratio of the difference or variation in statistical terms for a dependent variable in a regression model. This method establishes how well- modelled data fit the regression model or observation data. It ranges from 0

to 1 and indicates how accurate the proposed modelling is as it approaches 1, given by [128]:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \bar{y})^2}{\sum_{i=1}^n (y_i - \bar{y}_i)^2} \quad (4.61)$$

The adjusted R^2 is the modified version of R^2 and is always smaller than or equal to the R^2 . In the following formulation, k represents the number of independent variables.

$$R_{adj}^2 = 1 - \frac{(1 - R^2)(n - 1)}{n - k - 1} \quad (4.62)$$

The normalised mean bias (*NMB*) and normalised mean error (*NME*) are the differences between fitted and observed values relative to the total of observed values. These indications prevent an overestimation of the observed range of values and are derived using the following equation [126]:

$$NMB(\%) = \frac{\sum_{i=1}^n (y_i - \hat{y}_i)}{\sum_{i=1}^n y_i} \times 100 \quad (4.63)$$

$$NME(\%) = \frac{\sum_{i=1}^n (|y_i - \hat{y}_i|)}{\sum_{i=1}^n y_i} \times 100 \quad (4.64)$$

Due to having equally weighted positive and negative biases with error estimates, as demonstrated in the following equation, the mean fractional bias (*FBIAS*) and the mean fractional error (*FERR*) are important indicators. Both formulations are given as [126]:

$$FBIAS(\%) = \frac{2}{n} \sum_{i=1}^n \left(\frac{y_i - y_i}{y_i + y_i} \right) \times 100 \quad (4.65)$$

$$FBIAS(\%) = \frac{2}{n} \sum_{i=1}^n \left(\frac{|y_i - y_i|}{y_i + y_i} \right) \times 100 \quad (4.66)$$

The standard error of the mean (*SEM*) and the uncertainty are calculated using the student t-table values based on the degrees of freedom (*df*) and 0.05 (95% of confidence interval), as follows [127]:

$$SEM = \frac{S_{\varepsilon}}{\sqrt{n}} \quad (4.67)$$

$$Uncertain(\%) = \frac{2 \cdot SEM \cdot t_{0.05, df}}{y_i} \times 100 \quad (4.68)$$

Where S_{ε} and $t_{0.05, df}$ denote the standard error of residuals and student t-table value due to *df* and 0.05 probability of an absolute value.

4.3. ONE-DIMENSIONAL AND SEMI-EMPIRICAL MODEL

This section is devoted to describing the 1-D and semi-empirical model of the HT- PEMFC. In this model, as depicted in Figure 4.9, only the thickness of the polymer membrane in the y plane is considered, and the length in the x and z coordinates is not considered.

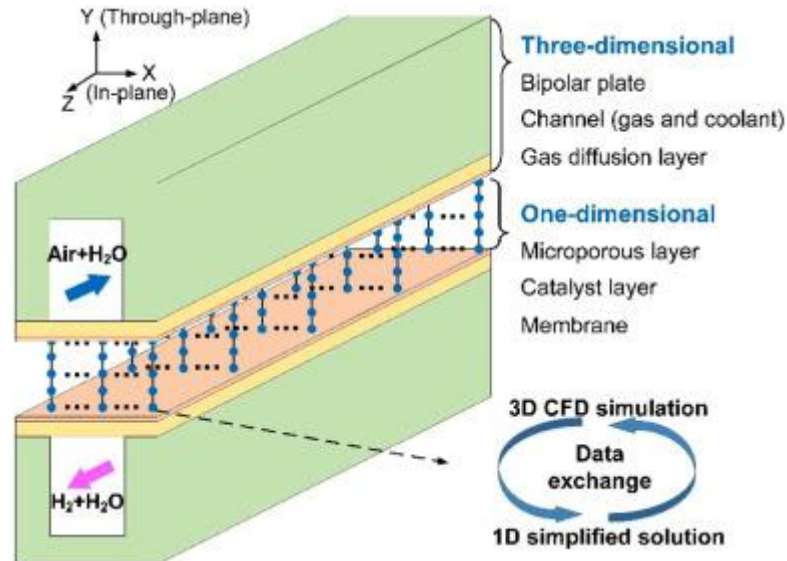
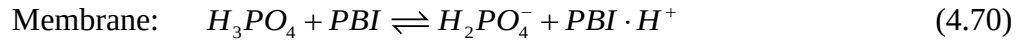
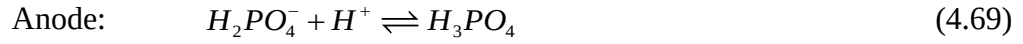


Figure 4.9. The coordinates of a sample HT-PEMFC [129].

In order to simplify the modelling technique, some common assumptions are considered, as in 0-D modelling. As reactants, hydrogen and air are regarded as ideal gases. The fuel cell functions under steady-state conditions, and it is assumed that the reactant flow is laminar, steady, and incompressible. The electrical energy needed for reactant compression is disregarded, and the reactants are supplied proportionally to the electrical flow produced by the fuel cell. At the initial condition, the operational pressure and temperature are constant. The variance in potential energy and kinetic energy, as well as exergy, is ignored. In order to verify the model, all overpotentials are accounted for and calculated. Finally, there is no predetermined net output voltage (such as 0.7 V) at the initial stage of the model. After performing the electrochemical analysis, thermodynamics analyses will be conducted as well.

4.3.1. Electrochemical Analysis

Since the main component of the HT-PEMFC is the PA-doped-PBI membrane, the only one that fulfils the US Department of Energy requirements among other HT-PEMs [130], it is widely believed that proton conduction in these membranes mostly occurs through the ‘Grotthus mechanism’ [65], as given by the following equation [131]:



Considering these electrochemical reactions and the assumption that HT-PEMFC operates under completely thermodynamically reversible circumstances, E_{rev} can be determined via the modified Nernst equation as given [132–134]:

$$E_{rev} = E_0 - 2.576 \cdot 10^{-4} (T_{fc} - 373.15) + 4.308 \cdot 10^{-5} \ln \left(\frac{P_{H_2} (P_{O_2})^{1/2}}{P_{H_2O}} \right) \quad (4.72)$$

Here, E_0 is normally accepted as 1.229 V at the standard temperature and pressure (1 atm, 25 °C). However, in this paper, E_0 is considered 1.1885 V [88,90] since the fuel cell operates above 100 °C and the Gibbs free energy changes concerning the temperature.

Before introducing the net output voltage and overpotentials, critical parameters for determining the polarisation curve, the significant correlation between the current density and exchange current density should be determined. The Butler-Volmer equation is used to describe the electrochemical kinetics for both the anode and cathode as follows [135]:

$$j_a = j_0 \cdot \exp \left(\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} \cdot \eta \right) \quad (4.73)$$

$$j_c = -j_0 \cdot \exp \left(\frac{-\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta \right) \quad (4.74)$$

where j_a and j_c signify anode and cathode current densities, whereas η defines the activation overpotential caused by slow reaction rates in the anode and cathode.

Considering Eqs. (4.52-4.53), the Butler-Volmer equation can be given in a more compact form to explain the correlation between the j and j_0 in a case at equilibrium [135].

$$j = j_0 \left(\exp \left[\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta \right] - \exp \left[-\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} \cdot \eta \right] \right) \quad (4.75)$$

Here, j_0 for the ORR over a Pt catalyst in contact with acid doped PBI is relevant to that of H_3PO_4 solution, given as [64,136]:

$$\log(j_0^{PBI}) = \log(j_0^{H_3PO_4}) - 4.16(1 - \varepsilon_{PBI}) \quad (4.76)$$

where ε_{PBI} defines the volume fraction of amorphous H_3PO_4 that is present in the membrane, and it is proportional to the number of moles of free acid as follows:

$$\varepsilon_{PBI} = \left(\frac{4.81}{X - 2} + 1 \right)^{-1} \quad (4.77)$$

Here, X represents the doping level characterized by the number of moles of acid absorbed in every PBI repetition unit. The PBI unit comprises two bonding sites for H_3PO_4 ; hence, two moles of acid may be bound to PBI [136].

The doping level has the greatest impact on the performance of a PBI membrane, and it is determined by the concentration of acid used in the doping procedure. Therefore, the following correlation is utilized to demonstrate the relationship between X and the concentration of H_3PO_4 , M , presented as [64]:

$$X = 0.012 \cdot M^3 - 0.2111 \cdot M^2 + 1.2363 \cdot M + 0.7119 \quad (4.78)$$

In Eq. (4.55), j_0 was previously expressed as a function of temperature in the case of 85 wt.% H_3PO_4 given by [64,136]:

$$\log(j_0^{H_3PO_4}) = 3.509 - 2193 \cdot T^{-1} \quad (4.79)$$

In addition, in Eqs. (4.52-4.53), the activation overpotential, η_{act} , can be determined by the modified Tafel equation [137].

$$\eta_{act} = \frac{RT}{\alpha n F} \ln \left(\frac{j + j_{leak}}{j_0} \right) \quad (4.80)$$

where j_{leak} defines the leak or lost current density caused by the internal current and reactant leaking.

Apart from the activation overpotential, other types of overpotentials, namely the concentration overpotential (η_{con}) and ohmic overpotential (η_{ohm}), affect the polarization curve too. Due to voltage losses and mass transfer constraints in high current density, particularly near the current density limit, a rapid decrease is observed in the polarization curve due to a higher η_{con} rate, indicated as [78]:

$$\eta_{con} = \frac{RT}{nF} \ln \left(\frac{j_l}{j_l - j} \right) \quad (4.81)$$

In the above equation, j_l is generally defined as an appropriate value in the modelling stage.

Finally, as a consequence of the occurring resistance to the electron and proton transitions, the total ohmic overpotential across a membrane may be calculated as follows [137]:

$$\eta_{ohm} = j \frac{t_{mem}}{\kappa_{mem}} \quad (4.82)$$

Here, κ_{mem} denotes the membrane's proton conductivity (S/m), and it is determined by using the following semi-empirical correlation based on the Arrhenius Law [110]:

$$\kappa_{mem} = \frac{AB}{T} \exp\left(\frac{-E_a}{RT}\right) \quad (4.83)$$

where A denotes the pre-exponential coefficient for the doping level of H_3PO_4 , determined as [110]:

$$A = 168X^3 - 6324X^2 + 65750X + 8460 \quad (4.84)$$

and B represents the coefficient for the humidity, given as [110,138]:

$$B = \begin{cases} 1 + (0.01704T - 4.767)RH & 373.15 \text{ K} \leq T \leq 413.15 \text{ K} \\ 1 + (0.1432T - 56.89)RH & 413.15 \text{ K} < T \leq 453.15 \text{ K} \\ 1 + (0.7T - 309.2)RH & 453.15 \text{ K} < T \leq 473.15 \text{ K} \end{cases} \Rightarrow \quad (4.85)$$

where RH signifies the relative humidity of the electrolyte. In addition, in Eq. (12), E_a defines the membrane's activation energy (J/mol), written as [110,138,139]:

$$E_a = -619.6X + 21750 \quad (4.86)$$

The net output voltage of the cell, U , is always less than E_{rev} due to the overpotentials mentioned above, given by [134]:

$$U = E_{rev} - \eta_{act} - \eta_{con} - \eta_{ohm} \quad (4.87)$$

Substituting Eqs. (4.51-4.65) into Eq. (4.66), U may be reformulated as follows:

$$U = E_{rev} - \left\{ \frac{RT}{\alpha n F} \ln\left(\frac{j + j_{leak}}{j_0}\right) + \frac{RT}{n_e F} \ln\left(\frac{j_l}{j_l - j}\right) + j \frac{t_{mem}}{\kappa_{mem}} \right\} \quad (4.88)$$

4.3.2. Thermodynamic Analyses

Thermodynamic analyses encompass research that concurrently evaluates the electrochemical, thermal, and electrical processes to illustrate the fuel cell's performance. In order to thermodynamically assess the system and determine its efficiency, the maximum reversible work must be computed first. Herein, the Gibbs free energy is used to calculate the maximum amount of electrical work (W_{el}) a system can perform at a particular temperature and pressure, as follows [140]:

$$W_{el} = -\Delta G \quad (4.89)$$

The released energy is not converted into usable work owing to irreversibilities occurring in the fuel cell. Therefore, it is possible to reformulate the ΔG to represent irreversible losses owing to entropy formation along with the reaction enthalpy [78].

$$\Delta G = \Delta H - T\Delta S \quad (4.90)$$

where ΔH stands for the total enthalpy variation for a specified chemical reaction, and it can be determined by considering both products and reactants.

$$\Delta H = \Delta h_{H_2O} - \Delta h_{H_2} - \frac{1}{2} \Delta h_{O_2} \quad (4.91)$$

where Δh denotes the molar enthalpy of species, and it can be reformulated as a function of temperature with the assumption that the fuel cell operates at any temperature, given by [140]:

$$\Delta h_{sp} = \Delta h^0 + \int_{298.15}^T C_p dT \quad (4.92)$$

where Δh^0 and C_p stand for the molar enthalpy at standard conditions and the specific heat capacity of species, respectively. Thus, the absolute enthalpy of H_2 , O_2 , and H_2O can be determined, as follows [140]:

$$\Delta h_{H_2} = \Delta h_{H_2}^0 + C_p^{H_2} (T_{fc} - T_{ref}) \quad (4.93)$$

$$\Delta h_{O_2} = \Delta h_{O_2}^0 + C_p^{O_2} (T_{fc} - T_{ref}) \quad (4.94)$$

$$\Delta h_{H_2O} = \Delta h_{H_2O}^0 + C_p^{H_2O} (T_{fc} - T_{ref}) \quad (4.95)$$

An empirical correlation based on previous experimental data can be used for calculating C_p concerning the temperature for each species, given as [95,139,141]:

$$C_p^{H_2} = 27.28 + 0.00326T + 50,000 / T_{fc}^2 \quad (4.96)$$

$$C_p^{O_2} = 29.96 + 0.00418T - 167,000 / T_{fc}^2 \quad (4.97)$$

$$C_p^{H_2O} = 30.00 + 0.01017T + 33,000 / T_{fc}^2 \quad (4.98)$$

In Eq. (4.90), ΔS denotes the total molar entropy variation in the reaction, and it can be calculated as [78]:

$$\Delta S = \Delta s_{H_2O} - \Delta s_{H_2} - \frac{1}{2} \Delta s_{O_2} \quad (4.99)$$

where Δs denotes the molar enthalpy of each species, and it can also be reformulated as a function of temperature, given by [140]:

$$\Delta s_{sp} = \Delta s^0 + \int_{298.15}^T \frac{1}{T} C_p dT \quad (4.100)$$

where Δs^0 defines the molar entropy at standard conditions given in Table 4.4. Thus, Eq. (4.100) can be rewritten in a more compact form, as follows:

$$\Delta S_{H_2} = \Delta S_{H_2}^0 + \frac{C_p^{H_2} (T_{fc} - T_{ref})}{T_{fc}} \quad (4.101)$$

$$\Delta S_{O_2} = \Delta S_{O_2}^0 + \frac{C_p^{O_2} (T_{fc} - T_{ref})}{T_{fc}} \quad (4.102)$$

$$\Delta S_{H_2O} = \Delta S_{H_2O}^0 + \frac{C_p^{H_2O} (T_{fc} - T_{ref})}{T_{fc}} \quad (4.103)$$

After determining ΔH and ΔG , the maximum theoretical efficiency for a fuel cell can be calculated as [140]:

$$\eta_{\max} = \frac{-\Delta G}{\Delta H} \quad (4.104)$$

The energy efficiency of the HT-PEMFC can be determined by [141–143]:

$$\eta_{fc} = \frac{P_{fc}}{-\Delta \dot{H}} \quad (4.105)$$

where P_{fc} is expressed as [78,144]:

$$P_{fc} = IV = jAU \quad (4.106)$$

where A denotes the effective surface area of the electrode.

$(-\Delta \dot{H})$ in Eq. (4.105) defines the rate of overall energy released by the reaction, and it can be written as [141–143]:

$$(-\Delta \dot{H}) = -\dot{q}_{H_2} \Delta H = -\frac{jA\Delta H}{n_e F} \quad (4.107)$$

In addition, the thermal power output of the fuel cell, Q_{fc} , may be determined as [145]:

$$\dot{Q}_{fc} = (E_{rev} - U) jA \quad (4.108)$$

The entropy generation rate, $\dot{\delta}$, for the fuel cell may also be expressed as [78,143,144]:

$$\dot{\delta} = \frac{-\Delta \dot{H} - P_{fc}}{T_{fc}} \quad (4.109)$$

In order to perform an exergy analysis for a fuel cell, the total exergy transfer of a flowing stream should be determined first. In the absence of electrical, magnetic, nuclear, and surface tension effects, the total exergy rate, $\dot{Ex}$, is determined by the following equation [78]:

$$\dot{Ex} = \dot{E} x_{pe} + \dot{E} x_{ke} + \dot{E} x_{phy} + \dot{E} x_{chm} \quad (4.110)$$

$\dot{Ex}$ (kW) can be rewritten as the sum of the physical and chemical exergy rate since the variations in kinetic and potential exergies are excluded, given as [78,144]:

$$\dot{Ex} = \dot{E} x_{phy} + \dot{E} x_{chm} = \dot{n}(\overline{ex}_{phy} + \overline{ex}_{chm}) \quad (4.111)$$

where $\dot{n}$, $\overline{ex}_{phy}$, and $\overline{ex}_{chm}$ denote molar flow rate (kmol/s), specific physical exergy (kJ/kmol), and chemical exergy (kJ/kmol) of the substance. $\overline{ex}_{phy}$ is also known as the thermo-mechanical exergy of a flowing stream, and it can be determined in the absence of elevation and velocity, as follows [97,146]:

$$\overline{ex}_{phy} = (\bar{h}_i - \bar{h}_{0,i}) - T_0(\bar{s}_i - \bar{s}_{0,i}) \quad (4.112)$$

Here, $\bar{h}$ denotes the molar-specific enthalpy (kJ/kmol) and $\bar{s}$ stands for the species' molar entropy (kJ/kmol.K), where the subscript 0 represents the same parameters at the reference environmental conditions.

For an ideal gas mixture, $\bar{e}x_{chm}$ can be computed on a molar basis presented by Szargut, given as [147]:

$$\bar{e}x_{chm} = \frac{\sum x_i \bar{e}x_{chm,i}^0 + RT_0 \sum x_i \ln x_i}{M_{m,i}} \quad (4.113)$$

where $M_{m,i}$ and $\bar{e}x_{chm,i}^0$ represent the relative molecular mass (kg/kmol) and the standard chemical exergy of species at the reference environmental conditions. Here, x_i denotes the molar fraction of each gas component in the air given in Table 4.6.

The exergy rate balance for a steady-state control volume can be expressed given by the following equation [78,97]:

$$\sum \dot{E}x_{in} + \sum \dot{E}x_{heat} = \sum \dot{E}x_{out} + \sum \dot{E}x_{work} + \dot{E}x_D \quad (4.114)$$

where $\sum \dot{E}x_{in}$ and $\sum \dot{E}x_{out}$ denote the input and output exergy transferred by the mass, which can be determined as [148,149]:

Table 4.6. Molar fractions and standard chemical exergy of each species in the air [46,47].

Chemical Species	Molar fraction (x_i)	Standard chemical exergy (kJ/mol)
N ₂	0.7567	0.72
O ₂	0.2034	3.97
H ₂ O (g)	0.0303	9.49
CO ₂	0.0003	19.87
Ar	0.0092	11.69
Ne	0.000018	27.16
He	0.0000052	30.37
Kr	0.00000076	34.36

$$\sum \dot{E}x_{in} = \dot{E}x_{air,R} + \dot{E}x_{H_2,R} \quad (4.115)$$

$$\sum \dot{E}x_{out} = \dot{E}x_{air,P} + \dot{E}x_{H_2O,gen} \quad (4.116)$$

In Eq. (4.114), $\sum \dot{E}x_{heat}$ and $\sum \dot{E}x_{work}$ represent the exergy transfer by the heat and useful work, given by the following equations [78,97]:

$$\sum \dot{E}x_{heat} = \left(1 - \frac{T_0}{T_{fc}}\right) \dot{Q}_{fc} \quad (4.117)$$

$$\sum \dot{E}x_{work} = \dot{W}_{fc} \quad (4.118)$$

In addition, $\dot{E}x_D$ denotes the rate of exergy destruction, given as [95,138,143]:

$$\dot{E}x_D = -\Delta \dot{G} - T \Delta \dot{S} \left(1 - \frac{T_0}{T_{fc}}\right) - P_{fc} \quad (4.119)$$

Finally, the exergy efficiency can be determined as [150]:

$$\psi_{fc} = \frac{\dot{W}_{fc}}{(\dot{E}x_{air,R} + \dot{E}x_{H_2,R}) - (\dot{E}x_{air,P} + \dot{E}x_{H_2O,gen})} \quad (4.120)$$

Exergy contributes to determining efficiency improvements and reductions in thermodynamic losses attributed to a process. Reducing the harmful effects of a process or a system on the environment can only be achieved by taking measures to increase the exergy efficiency of that system. Therefore, the concept of exergetic improvement potential, which is a suggested statistic based on the exergy efficiency, was proposed by Hammond and Stapleton in 2001 [151]. This parameter seeks an answer to the question of how much improvement potential is possible in the efficiency

of a system. Therefore, it is highly useful because it can be used to evaluate the performance of any energy system and its components. For evaluating the potential, an empirical expression, providing to increase the efficiency and decrease exergy losses is utilized, given as [145,151]:

$$IP = (1 - \psi) \left(\dot{E} x_{in} - \dot{E} x_{out} \right) \quad (4.121)$$

The above expression indicates that a lower exergy efficiency would result in a greater improvement potential. In addition, for greater potential, it is necessary to minimise the difference between the input and output exergy rate of the system.

4.3.3. Ecological Analysis

The performance of the HT-PEMFC regarding energy conversion may also be evaluated according to some ecological criteria along with energetic and exergetic performance analyses. Angulo-Brown [152] proposed an ecological-optimization function to determine a heat engine's best mode of operation under more realistic circumstances than reversible operation. The main objective of this study was to find realistic boundaries for crucial process variables (e.g., work, power, and efficiency) and to use an ecological criterion for maximizing power and efficiency and minimizing entropy generation or the loss of available work, given as [152]:

$$EOF = \dot{W} - T_L \dot{\delta} \quad (4.122)$$

where T_L denotes the cold thermal-reservoir temperature.

Yan [153] examined the findings of Angulo-Brown subsequently and indicated that it might be more appropriate to utilize T_0 rather than T_L in the case that the temperature of the cold thermal reservoir differs from the ambient temperature. Thus, Eq. (45) started to be used for different thermal systems and processes, including heat engines [154], fuel cells [90,143,155], and other cycles [153], as follows:

$$EOF = P_{fc} - T_0 \dot{\delta} \quad (4.123)$$

Apart from the ecological-optimization function, EOF , another ecological function, E_f , focusing on the difference between the system output power and total exergy destruction rate, is proposed. The difference between the ecological function and the objective function is that it gives a better understanding of minimizing exergy losses and destruction occurring in the system while increasing the power output and reducing the environmental impact, given as [147,156,157]:

$$\dot{E}_f = P_{fc} - \dot{E} x_D \quad (4.124)$$

Finally, Ust et al. [153,158] presented a novel ecological coefficient of performance (ECOP), defined as the ratio of the power output per unit of loss availability. The link between output power and power dissipation is enhanced in comparison to the prior ecological functions, as follows [90,143,144,153,155,158,159]:

$$ECOP = \frac{P_{fc}}{T_0 \dot{\delta}} \quad (4.125)$$

CHAPTER 5

INTEGRATION OF HT-PEMFC INTO A SOLAR-BASED HYDROGEN PRODUCTION SYSTEM

This chapter presents the performance analysis of an HT-PEMFC stack in a solar-based hydrogen production system. In this study, a hybrid system consisting of a solar power plant (SPP), a PEM water electrolyser (PEME) stack, an HT-PEMFC stack, and other auxiliary equipment was designed with the aim of providing sufficient energy demand for residential buildings in a remote area. For the proposed hybrid system application, the province of Sakarya, located in the north-western part of Türkiye, was selected, as illustrated in Figure 5.1.



Figure 5.1. The location of the proposed hybrid system on the map [160].

Apart from the location, the global solar radiation intensity map of Sakarya province is illustrated in Figure 5.2. As can be obtained from the figure, the annual solar radiation remains between 1400 kWh/m^2 and 1500 kWh/m^2 . In addition, the radiation data for the specified location for each month is presented in Figure 5.3. Furthermore, the daily sunshine duration of the province is demonstrated in Figure 5.4. Moreover, other geographical information about the area is given in Table 5.1.

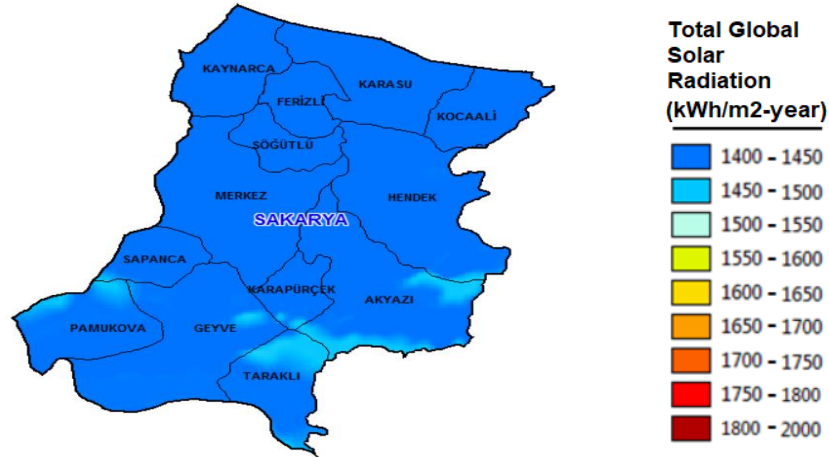


Figure 5.2. The annual global solar radiation intensity map of Sakarya province [160].

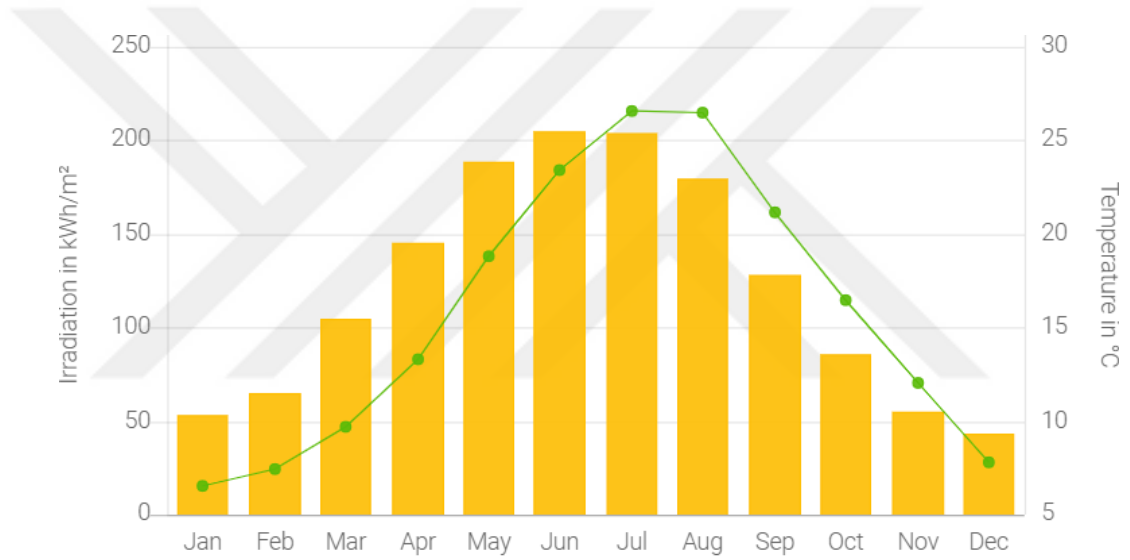


Figure 5.3. The global solar radiation at the specified location for each month [160].

Table 5.1. Other geographical information of the proposed system [160].

Info	Value
Latitude	40.68793505 °
Longitude	30.46699752528132 °
Annual global irradiation	1458.1 kWh/m²
Average temperature	15.9 °C

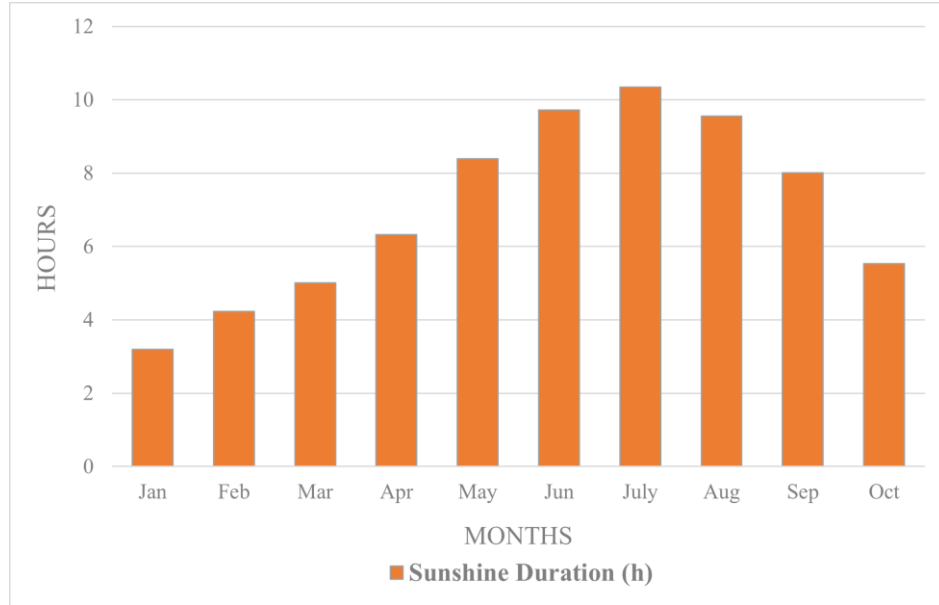


Figure 5.4. The daily sunshine duration of the province for each month [160].

In this study, a hybrid system consisting of a PEME with a power rate of 16.5 kW and a 4 kW HT-PEMFC integrated into an approximately 240 kWe grid-connected SPP comprising 720 solar PV modules is analysed and discussed. This PV/PEME/HT- PEMFC system is proposed to generate electricity to meet the seasonal demands of 15 residential buildings with a total of 4 people living in each house, with 2 children and 2 adults. In this system, the required energy is produced by a roof-mounted solar PV array, whereas an HT-PEMFC stack along with the PEME system serves as a backup. Going further in detail, the initial energy fed to the system is provided by converting sunlight into electricity through PV modules. However, before distributing this power to the consumer, DC/AC converters must convert the direct current (DC) generated by the PV modules and HT-PEMFC stack to an alternative current (AC). In the case where the produced power exceeds the user's needs (as is the case with the proposed system) and the hydrogen tank is not full, the excess energy is transferred to the electrolyser to decompose water and generate hydrogen, which is then stored for later use in the rigid hydrogen tank. In the event that sunlight is unavailable, and the PV system cannot supply enough power, the stored hydrogen and air are supplied to the HT-PEMFC stack, which operates continuously and without interruption. The HT-PEMFC stack thus generates electricity for the second time in the system by using the previously stored hydrogen, as depicted in Figure 5.5.

In order to evaluate the performance of the entire system given below, it is necessary to examine the system components separately. Therefore, in the next section, the components of the proposed system will be introduced first. Subsequently, the performance analysis of the solar PV system, the HT-PEMFC stack, and the PEME will be presented. In modelling the fuel cell stack, the 1-D and semi-empirical cell model will be considered.



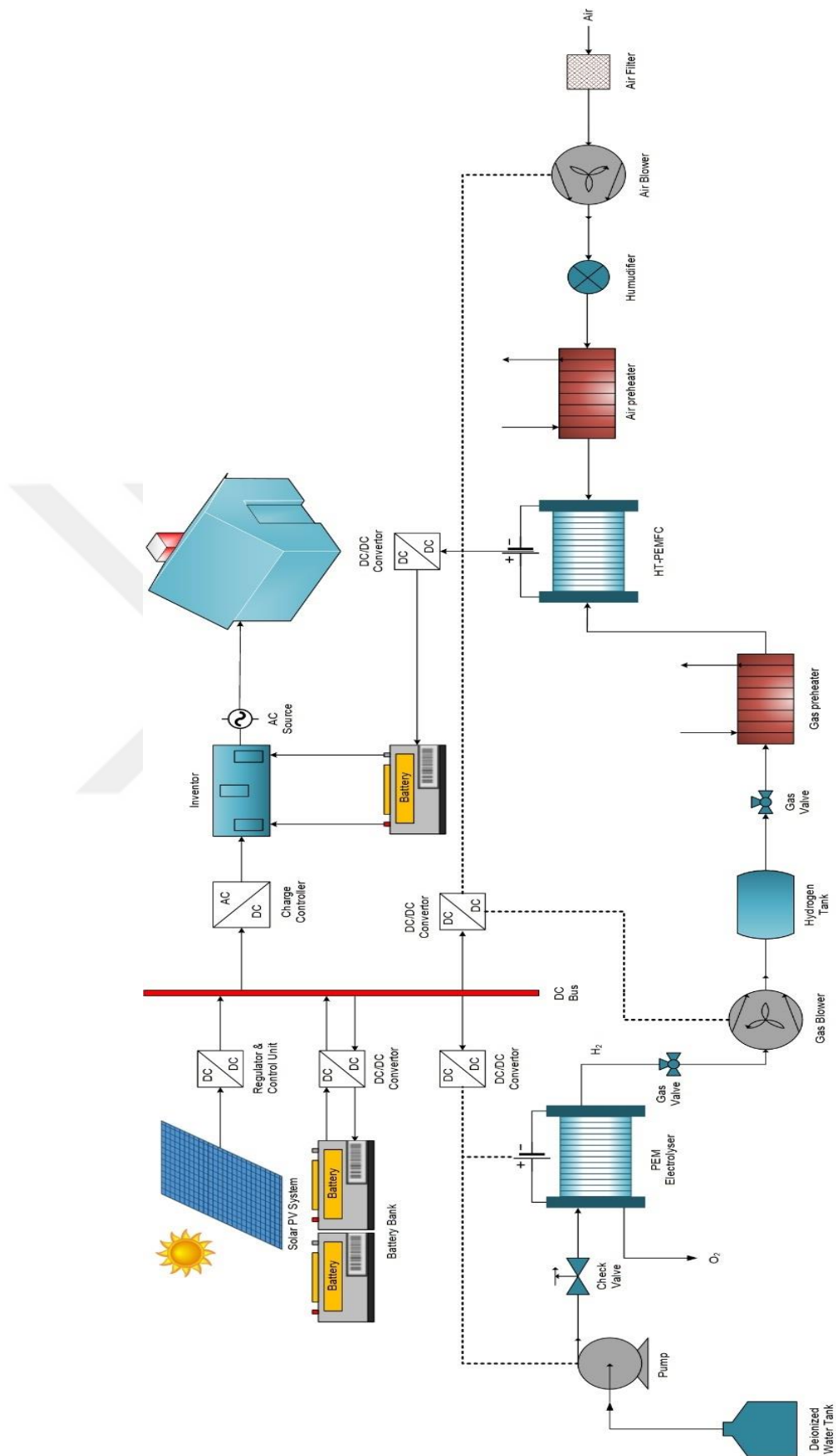


Figure 5.5. The proposed solar-based integrated system.

5.1. SYSTEM COMPONENTS

5.1.1. Solar Power Plant (SPP)

In this section, the technical details of the SPP are presented. The plant was established in the central district of Sakarya province with a total DC installed power of 288 kWp and an AC installed power of 240 kWe. A total of 720 monocrystalline-type modules with a power rate of 400 Wp were used in the power plant. Nominal current/voltage and other significant module characteristics are given in Table 5.2. In addition, the dimensions (mm) of each module are presented in Figure 5.6. All of these technical data were supplied from the Infinite Energy company operating in Sakarya, Türkiye [161]. The aforementioned company is also the one that installed the SPP.

Table 5.2. PV Module characteristics [161].

Module Characteristics	
Cell type	Monocrystalline
Nominal power ($P_{\max}$)	400 W _p
Nominal voltage ($V_{\max}$)	41.70 V
Nominal current ($I_{\max}$)	9.61 A
Short-circuit current (I_{sc})	10.20 A
Open-circuit voltage (V_{oc})	49.80 V
Temperature coefficient for V_{oc}	-0.28%/°C
Temperature coefficient for I_{sc}	0.048%/°C
Temperature coefficient for $P_{\max}$	-0.37%/°C

The application was carried out on the roof of a factory, and some of the power generated is consumed within the factory, but a significant portion is directly transferred to the grid. When developing this kind of roof-mounted power plant project, the static suitability of the roof for the construction placement must come first. The next step is to perform a correct shadow analysis and determine the angular placement slopes of the modules. The other stage is to verify the compatibility of the selected module decided to be used with the inverter data values. In inverter design, the temperature and radiation sensitivity of PV modules should be addressed. This is because the inverter operating range is affected by the temperature of PV modules.

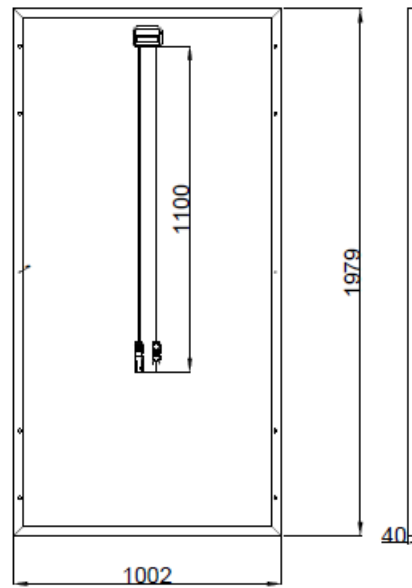


Figure 5.6. The dimensions of the module used in SPP [161].

In addition to the temperature, another situation that must be considered is the high open-circuit voltage when it is switched back on in the case of switching off the inverter due to a mains fault. The open-circuit voltage to prevent damage to the inverter must be less than the maximum DC voltage. Considering all these factors, the maximum number of PV modules in the array that can be connected to an inverter can be determined. Accordingly, in this SPP, four inverters (Huawei Sun2000-60ktl-M0), each with an AC power of 60 kWe and maximum output power of 66 kVA, were used [161]. Other important characteristics of these inverters are given in Table 5.3. In addition, the main tasks of these inverters are given as follows:

- Conversion of DC to AC
- Maximising energy production
- Safe operation of the system
- Integration with the grid or solar battery (solar battery)
- Enabling instantaneous monitoring of power generation

Table 5.3. Inverter characteristics [161].

Inverter Characteristics	
Max DC input voltage	1100 V
Initial voltage	200 V
MPPT voltage interval	200 V – 1000 V
Max input current	6×22 A
Max input short-circuit current	6×30 A
Max output current	95.3 A
Number of MPPT	6
Number of max inputs	12
AC output power	60 kW _e
Max output power	66 kVA
Number of modules in each string	15
Number of strings in each inverter	12

Each inverter has twelve strings, and each string has fifteen PV modules connected in series with one another. Accordingly, each inverter has 180 modules with a nominal power of 400W_p, as depicted in Figure 5.7. Besides, each inverter is accompanied by six Maximum Power Point Trackers (MPPTs) to effectively reduce string misalignment, as illustrated in Figure 5.8. These MPPTs are DC/DC converters that maximise the compatibility between a solar array (PV module) and a battery bank or power grid. Therefore, the efficiency of each MPPT is very high. The maximum efficiency of MPPT is 98.9% at 480 V, whereas it is 98.7% at a voltage interval between 380 V and 400 V. In addition, the weighted European efficiency of the MPPT is 98.7% at 480 V, whereas it is 98.5% at a voltage interval between 380 V and 400 V [161].

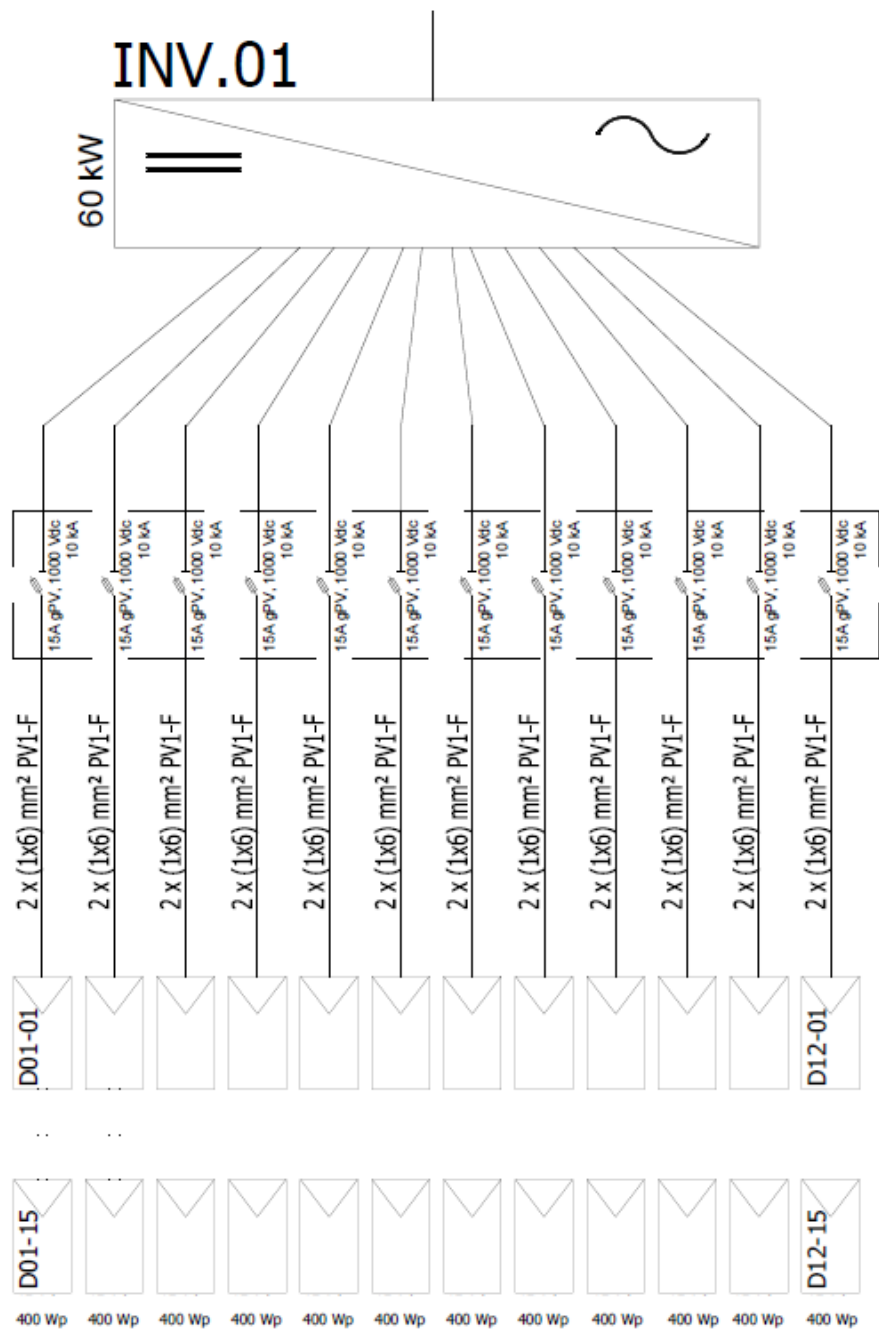


Figure 5.7. The connection of each string to an inverter [161].

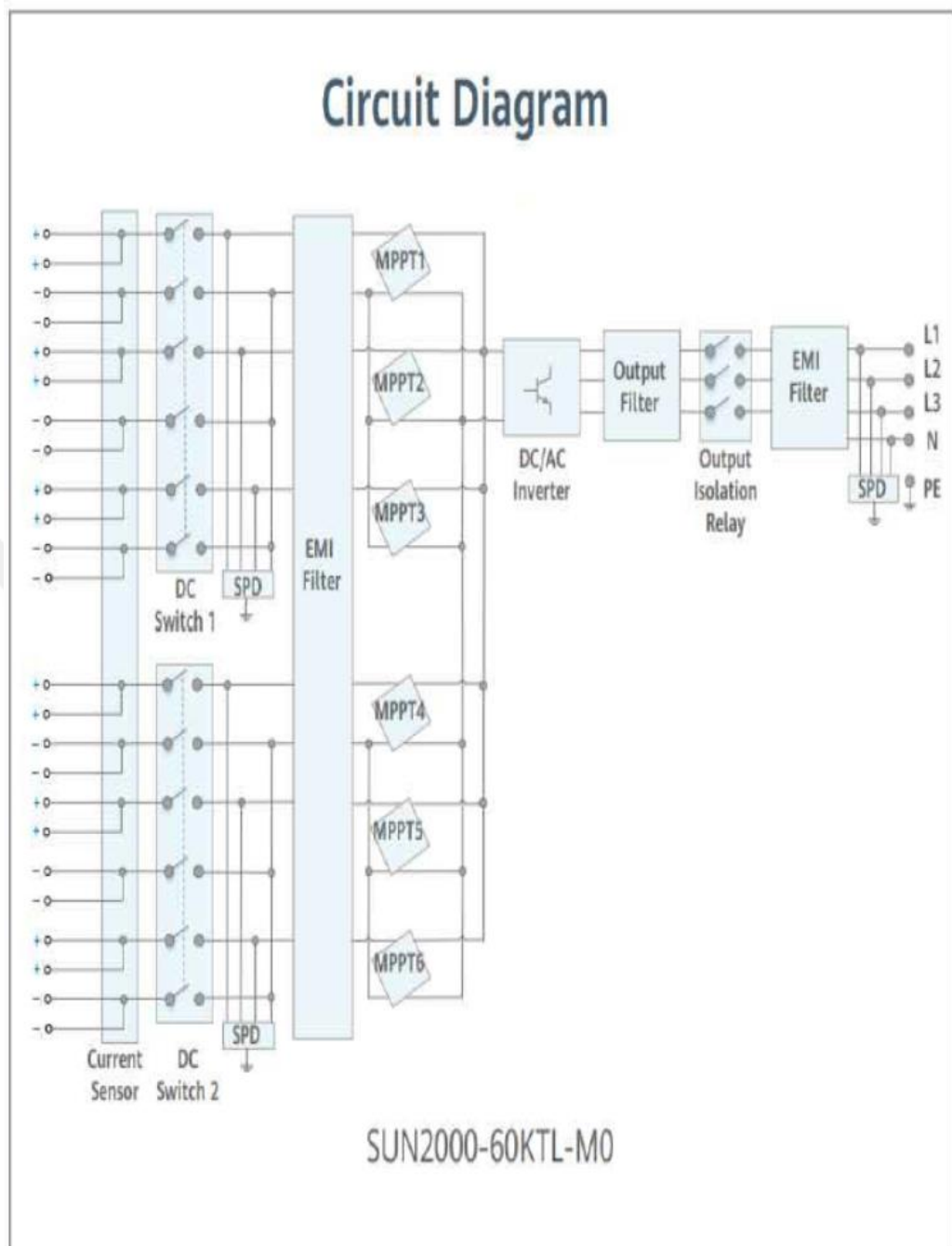


Figure 5.8. The circuit and module connection diagram of each inverter [161].

5.1.2. PEME & HTPMFCE Stack

As demonstrated in the previous chapter, PV modules provide the opportunity to generate electrical energy by converting sunlight into direct current. They continue to generate electricity as long as the solar radiation intensity falling on them is sufficient. Solar energy can be converted into electrical energy with an efficiency of between

10% and 20%, depending on the type and structure of the module. Depending on the power demand, these modules are connected in series or parallel to each other to form strings, and as the number of strings increases, the current value obtained in the inverter also increases. Thus, the power output from a few watts to megawatts becomes possible. However, due to the high cost, one of the most important limitations to using PV systems today is the difficulty of storing the generated electrical energy. Due to this limitation, PV systems are used only in the summer seasons and during sunny hours in regions with low solar energy potential. For a small electrical load, batteries are used for energy storage.

In such systems, the unused part of the energy produced by the PV system during sunny hours is stored in a battery group and used during the hours when the sun is unavailable, e.g., at night. However, the cost of storing large amounts of energy in battery systems is very high, and long-term (seasonal) storage is impossible. In addition, in a system consisting of conventional batteries, for instance, simple cycle batteries used in vehicles, only 20–30% of the stored energy can be extracted, and the battery life is very short. In specially designed extended cycle batteries, the operating life is longer (5 years), and the energy withdrawal rate is higher (about 80%), but the cost increases considerably in this case.

A PV/PEME/HT-PEMFC hybrid system is one of the most promising systems as it largely eliminates these storage drawbacks. In these systems, energy is stored in tanks as hydrogen, employing a PV-PEME unit during the day. At night, the stored hydrogen is used to produce electrical energy by the fuel cell. Therefore, a PEME stack with a power rate of 16.5 kW in the proposed system is utilized to decompose the water and produce the hydrogen. The connection of the PEME stack to the PV system is demonstrated in Figure 5.9. In addition, an HT-PEMFC stack with a power rate of 4 kW is added to the system in order to meet the required electricity during the night.

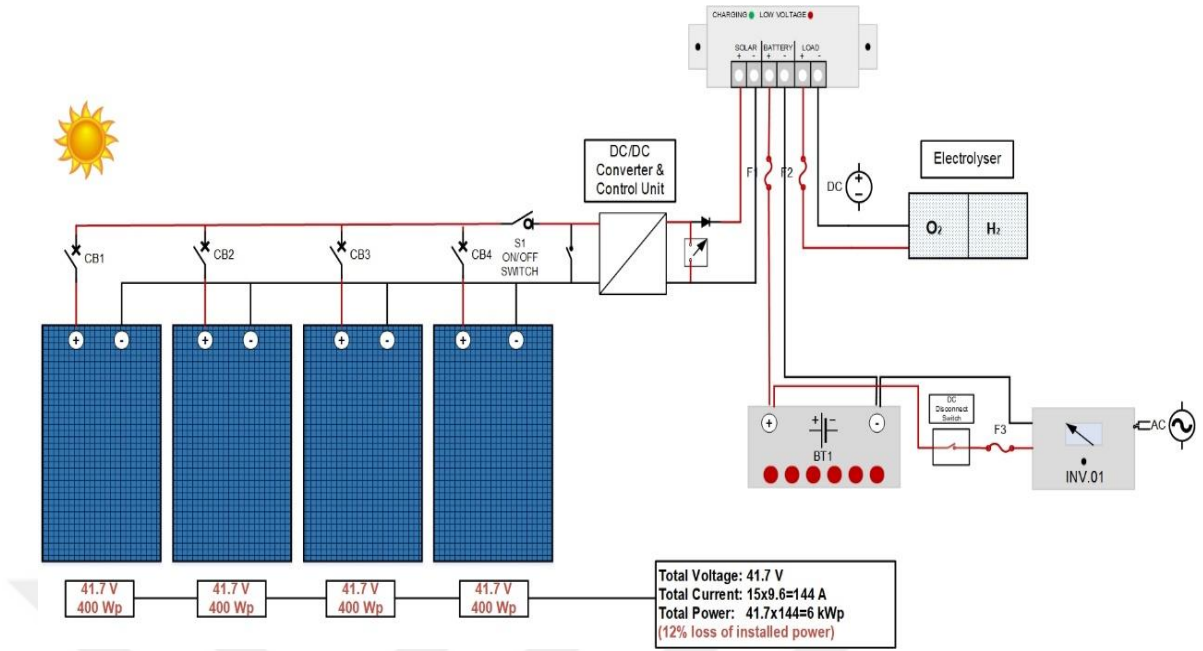


Figure 5.9. The connection of the PEME to a string of the solar PV system.

5.2. PERFORMANCE ANALYSIS OF SOLAR PV SYSTEM

5.2.1. Energy Analysis

The energy analysis of a PV module or array requires the identification of system components. A PV system is naturally formed of solar cells, which are basically configured by a p-n junction. Therefore, solar cells are the building blocks of the PVs, and they ease insight into the system's equivalent circuit model [162].

For an easier insight into the current-voltage (I-V) curve, solar cells are usually represented by the single diode model, which is very simple to apply and suitable for analysing the electrical behaviour of the actual cell. According to this model, the simplest equivalent electric circuit of a solar cell, as given in Figure 5.10, consists of five parameters [163], and it can be defined by considering Kirchhoff's law of current:

$$I = I_l - I_o \left[\exp \left(\frac{V + IR_s}{\frac{\alpha k T_c}{q}} \right) - 1 \right] - \frac{V + IR_s}{R_{sh}} \quad (5.1)$$

where I stand for the output current generated by the solar cell, I_l for the photocurrent, I_o for the reverse saturation current of the diode, V for the output voltage, q for an electron charge rate, k for Boltzmann's constant, T_c for the cell operating temperature, α for the modified ideality factor, R_{sh} for the shunt resistance and R_s for the series resistance of the cell, and finally I_d for the diode current.

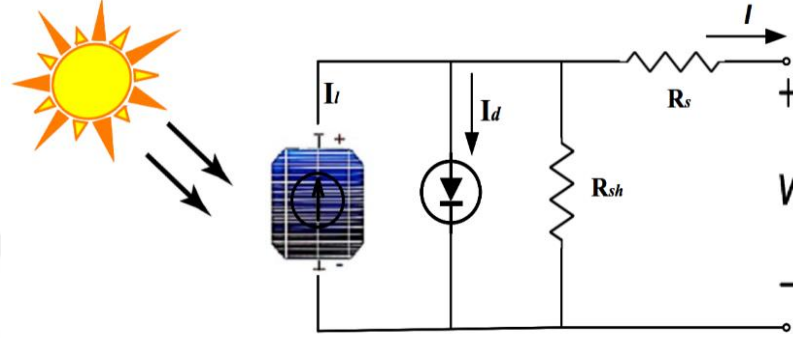


Figure 5.10. The single solar cell diode model.

In a PV module composed of several cells in series (N_s), assuming all cells are identical and under uniform and equal irradiance and temperature, the output current and voltage can be expressed as [162]:

$$I_{\text{mod}} = I_{\text{cell}} \text{ and } V_{\text{mod}} = N_s V_{\text{cell}} \quad (5.2)$$

Thus, Eq. (5.1) can be elaborated to determine the single diode expression for a module, and it can be expanded according to the number of modules connected in series [164]:

$$I_M = I_l - I_o \left[\exp \left(\frac{V_M + I_M N_s R_s}{\frac{\alpha N_s k T_c}{q}} \right) - 1 \right] - \frac{V_M + I_M N_s R_s}{N_s R_{sh}} \quad (5.3)$$

where I_M and V_M stand for the current and the voltage of the module, respectively.

Under ideal conditions, in the case of the shunt resistance of a solar cell is very large ($R_{sh}=\infty$), Eq. (1) can be rewritten as:

$$I = I_l - I_o \left[\exp \left(\frac{V + IR_s}{\frac{\alpha k T_c}{q}} \right) - 1 \right] \quad (5.4)$$

The output characteristic of a solar cell's I-V curve is a nonlinear inclination, giving a clue to the determination of three significant parameters: a short-circuit current (I_{sc}), an open-circuit voltage (V_{oc}), and a maximum power point (P_{max}). These parameters are plotted in Figure 5.11. In order to determine these parameters, some reference conditions given below are needed [165]:

$$\text{For } I_{sc}: I_l = I_{sc,ref} \text{ and } V = 0 \quad (5.5)$$

$$\text{For } V_{oc}: I = 0 \text{ and } V = V_{sc,ref} \quad (5.6)$$

$$\text{For } P_{max}: I_{max} = I_{max,ref} \text{ and } V_{max} = V_{max,ref} \quad (5.7)$$

$$\text{Thus, for } P_{max} \text{ also: } \left[\frac{d(I V_{max})}{d(V_{max})} \right] = 0 \quad (5.8)$$

$$\text{and for } I_{sc}: \left[\frac{dI_{sc}}{dV_{sc}} \right] = - \frac{1}{R_{sh,ref}} \quad (5.9)$$

In addition to the abovementioned conditions, standard test conditions (STC) are also considered for solar cells. In this scope, three parameters can be found by substituting Eqs (5.5–5.9) for Eq. (5.4), as follows [162]:

$$I_{sc} = I + I_o \left[\exp \left(\frac{V + IR_s}{\frac{\alpha k T_c}{q}} \right) - 1 \right] \quad (5.10)$$

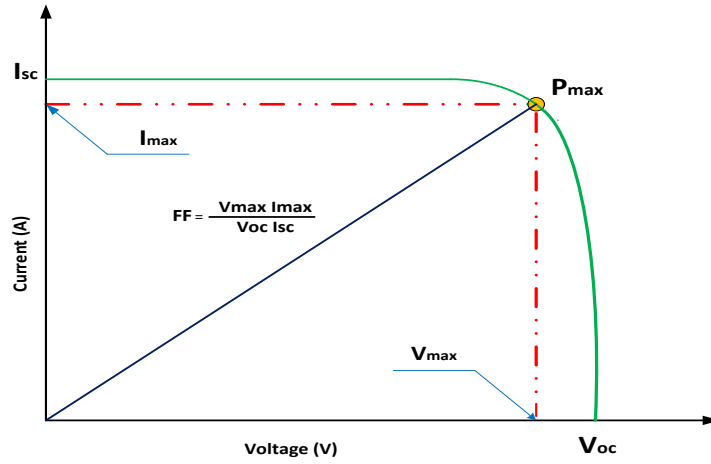


Figure 5.11. The I-V curve of a typical solar cell.

$$V = -IR_s + \frac{\alpha k T_c}{q} \ln \left[\frac{I_{sc} - I + I_o}{I_o} \right] \quad (5.11)$$

Considering Eq (5.6) and (5.11), V_{oc} can be determined as below:

$$V_{oc} = \frac{\alpha k T_c}{q} \ln \left(\frac{I_{sc}}{I_o} + 1 \right) \quad (5.12)$$

As demonstrated in Figure 5.11, P_{max} can be defined as a point where the product of I and V reaches its maximum value. In other words, the P_{max} of a solar cell can also be described graphically as the largest rectangular area that can be fitted under the I - V curve [166]:

$$P_{max} = V_{max} I_{max} \quad (5.13)$$

where V_{max} and I_{max} define the maximum voltage and current, respectively.

Apart from these parameters, fill factor (FF), a measure of cell quality, can also be identified. The FF is the ratio of the maximum power produced by a solar cell to the product of I_{sc} and V_{oc} , given as [167]:

$$FF = \frac{P_{\max}}{V_{oc} I_{sc}} = \frac{V_{\max} I_{\max}}{V_{oc} I_{sc}} \quad (5.14)$$

The energy efficiency of a PV system (η_{en}) is defined as the ratio of the output energy (En_{output}) to the input energy (En_{input}) obtained on the PV surface [168]:

$$\eta_{en} = \frac{En_{output}}{En_{input}} = \frac{V_{oc} I_{sc} + \dot{Q}}{S_T A} \quad (5.15)$$

where S_T , A , and $\dot{Q}$ stand for the hourly measured total solar radiation, the active area of PV surface, and the thermal energy, respectively. Here the $\dot{Q}$ can be defined as:

$$\dot{Q} = h_{ca} A (T_{cell} - T_{amb}) \quad (5.16)$$

where T_{amb} stands for the ambient temperature, and h_{ca} for the convective and radiative heat transfer coefficient between the solar cell and the atmosphere. It is determined by considering of the wind velocity (v), air density and atmospheric conditions, given by [169]:

$$h_{ca} = 5.7 + 3.8 \cdot v \quad (5.17)$$

The power conversion efficiency of a cell (η_{pce}) is the ratio of the maximum actual output power to the incident power [167]:

$$\eta_{pce} = \frac{V_{\max} I_{\max}}{S_T A} \quad (5.18)$$

The power conversion efficiency is also known as the actual electrical efficiency, and it can also be defined through FF as below [167]:

$$\eta_{pce} = \frac{FF V_{oc} I_{sc}}{S_T A} \quad (5.19)$$

The maximum electrical efficiency ($\eta_{max,el}$) is the ratio of the PV's maximum produced electricity to the system's total input energy [170].

$$\eta_{max,el} = \frac{V_{oc} I_{sc}}{S_T A} \quad (5.20)$$

5.2.2. Exergy Analysis

In order to perform exergy analysis, identifying the exergy components of a PV system is important. Physical and chemical exergy expressions for such a system associated with enthalpy, entropy and energy conversion concepts under the Carnot limitations have been clarified in the previous chapter [171]. Therefore, in this thesis, these concepts will not be considered. Instead, two major exergy components, electrical and thermal exergy, will be analysed.

Since the electricity is produced by the photovoltaic effect and can be utilized for useful purposes via the grid, producing electrical energy can be defined as the electrical exergy of the PV. Based on this approach, to calculate the electrical exergy ($\dot{E}x_{el}$) there should be a principal assumption corresponding to the exergy content received by the PV surface and completely usable for generating electricity. Namely, the useful exergy rate is taken as the maximum produced electrical power given by the product of the current and voltage when it operates under the maximum power condition [167]:

$$\dot{E}x_{el} = \dot{W}_{PV} = V_{max} I_{max} \quad (5.21)$$

The other significant exergy component is the thermal exergy, the heat radiated by the solar PV module. In the case of falling solar radiation on the solar cells, the PV modules get heated during electricity production due to the thermal energy in solar irradiance. Since solar cells are manufactured by electronic circuits, they lose their efficiencies because of the heat and internal resistance occurring in the process. Therefore, heat removal on the module surface is necessary for better electrical efficiency [167].

Thermal exergy is not used for useful purposes, including electrical exergy, because it performs only on the PV surface. Therefore, it is called heat loss to the ambient. In this regard, the thermal exergy of the system ($\dot{E}x_{th}$) covers the heat loss from the module surface to the atmosphere [172], and it can be formulated as:

$$\dot{E}x_{th} = \left(1 - \frac{T_{amb}}{T_{cell}}\right) \dot{Q} \quad (5.22)$$

Since the PV systems have only two exergy components and the thermal component wastes heat to the ambient, the total exergy expression of a PV system can be derived considering both electrical and thermal exergy expressions:

$$\dot{E}x_{PV} = \dot{E}x_{el} - \dot{E}x_{th} \quad (5.23)$$

Thereby, it becomes as:

$$\dot{E}x_{PV} = V_{max} I_{max} - \left(1 - \frac{T_{amb}}{T_{cell}}\right) [h_{ca} A (T_{cell} - T_{amb})] \quad (5.24)$$

For evaluating the exergy efficiency, measuring the total solar irradiation is required. The incident solar radiation, with its direct and diffuse components, affects the current and power output of the PV module. Since the magnitude of global solar radiation is not completely converted into electricity in practice, the Carnot limitations and the environmental effects should be mentioned here. In this regard, the exergy of solar irradiation, $\dot{E}x_{solar}$ (also known as $\dot{E}x_{input}$), depends on the intensity of solar irradiance and the area of the PV surface [173]:

$$\dot{E}x_{solar} = \left(1 - \frac{T_{amb}}{T_{sun}}\right) S_T A \quad (5.25)$$

Here, T_{sun} stands for the effective temperature of the Sun, estimated as 5777 K [174].

The exergy efficiency is fundamentally based on the ratio of the output parameter to the input parameter. In this respect, the total exergy rate of the PV system is considered the exergy output. In addition, the exergy input is considered as the exergy of solar radiation formulated as below [167]:

$$\psi_{PV} = \frac{\dot{E} x_{output}}{\dot{E} x_{input}} = \frac{\dot{E} x_{PV}}{\dot{E} x_{solar}} \quad (5.26)$$

After substituting Eqs (5.21-5.24) for Eq. (5.26), the final exergy efficiency expression for a PV system can be obtained as below [167]:

$$\psi_{PV} = \frac{V_{max} I_{max} - \left(1 - \frac{T_{amb}}{T_{cell}}\right) [h_{ca} A (T_{cell} - T_{amb})]}{\left(1 - \frac{T_{amb}}{T_{sun}}\right) S_T A} \quad (5.27)$$

By organizing Eq. (5.26), the exergy efficiency can also be explained through the irreversibility, I' . Since the exergy degradation in PV systems occurs due to both electrical and thermal exergy destruction, whereas it is only the electrical destruction for the PV/T systems, the irreversibility can be shown as [167]:

$$\psi_{PV} = \frac{\dot{E} x_{output}}{\dot{E} x_{input}} = \frac{\dot{E} x_{input} - \sum \dot{E} x_{irr}}{\dot{E} x_{solar}} = 1 - \frac{I'}{\dot{E} x_{solar}} \quad (5.28)$$

If it is continued further, the irreversibility becomes as:

$$I' = (1 - \psi_{PV}) \dot{E} x_{solar} \quad (5.29)$$

If the PV system boundary is considered a control volume, the irreversibility can also be defined in terms of external and internal exergy losses in the control volume [175].

$$\dot{I} = \sum \dot{E}x_{loss} + \sum \dot{E}x_{dest} \quad (5.30)$$

In the above equation, external exergy losses are defined as thermal losses. Internal losses, which mean exergy destructions, include four terms; the first occurred due to the optical losses through the PV surface [165].

$$\dot{E}x_{dest,opt} = S_T A \left(1 - \frac{T_{amb}}{T_{sun}} \right) (1 - (\tau\alpha)) \quad (5.31)$$

Here $(\tau\alpha)$ stands for the effective product of transmittance-absorptance, which cannot be known precisely. However, an approximate estimation of 0.9 is generally adopted without serious error for the PV systems since the term $(1 - (\tau\alpha))$ is smaller compared to unity [176].

The second term is derived from the temperature difference between the PV module surface and the sun temperature:

$$\dot{E}x_{dest,\Delta T_{sun}} = (\tau\alpha) S_T A T_{amb} \left(\frac{1}{T_{cell}} - \frac{1}{T_{sun}} \right) \quad (5.32)$$

The third term is obtained via the temperature variation of the PV module regarding the reference environment given as:

$$\dot{E}x_{dest,\Delta T_{mod}} = \frac{m_{cell} C_p T_{amb}}{\Delta T} \left(\ln \frac{T_{cell}}{T_{amb}} - \frac{(T_{cell} - T_{amb})}{T_{cell}} \right) \quad (5.33)$$

where m_{cell} and ΔT stands for the PV module mass and the time interval, respectively. The time interval can be determined according to the time step of the experiments. C_p is also the specific heat capacity of silicon-based solar cells, and it can be considered as [177]:

$$C_p = 0.844 + 1.18 \cdot 10^{-4} T_{cell} - 1.55 \cdot 10^{-4} (T_{cell})^{-2} \quad (5.34)$$

Finally, the fourth term is the electrical exergy destructions which is the amount where the maximum electrical power output (W_{PV}) is subtracted from the maximum electrical exergy, $W_{\max}$ [178]:

$$\dot{E} x_{dest,el} = \dot{W}_{\max} - \dot{W}_{PV} = V_{oc} I_{sc} - V_{\max} I_{\max} \quad (5.35)$$

5.3. PERFORMANCE ANALYSIS OF HT-PEMFC STACK

This chapter presents the performance analysis of an HT-PEMFC and PEME stack intending to determine energy and exergy efficiency. In this chapter, the HT-PEMFC stack analysis was performed according to the results of the 1-D and semi-empirical cell model.

The hybrid system, whose flowchart is presented in Figure 5.5, is designed to meet the energy requirements of 15 householders. With this configuration, the PV system generates the electricity required by houses when the solar radiation is sufficient during the daytime. Since the power obtained from the PV system is substantially greater than the energy demand, some excess power is fed into the electrolyser unit, providing hydrogen generation. Here, the DC bus provides the energy required by the pump to transport the deionised water to the electrolyser and the energy of other system components, including a compressor or a blower, to store the hydrogen in a rigid tank once it has been produced. Apart from the energy required for the houses and the hydrogen production system, the excess energy is still formed; hence, it is transmitted to the grid to be used in industrial facilities.

During the night, when solar radiation is unavailable, the energy requirements for these houses are met by the HT-PEMFC stack since the PV system cannot produce electricity. In order to determine the minimum stack capacity, the electricity consumption of a family of 4 people (2 adults and 2 children) living in the city centre of Sakarya with an average income was analysed. Based on this analysis, it was found that an average family uses 6 kWh of electricity during the day and 2 kWh during the night, for a total of 8 kWh. Since there are 15 houses in this proposed hybrid system,

the total energy required during the night is determined as 30 kWh per day and 900 kWh per month on average. Therefore, the fuel cell stack should meet this energy rate. Considering that the operating duration of the stack is 8 hours, it is obtained that the net power capacity of the stack should be 4 kW minimum. Apart from the net power, the cell voltage and current density of the fuel cell should be determined as well. According to the results of the 1-D and semi-empirical cell model given in the previous chapter, it is obtained that the average current density and cell voltage are determined as 0.4 A/cm² and 0.6 V at the operating temperature of 453 K. Therefore, these parameters were taken as the basis for the analysis. Other parameters of the fuel cell stack are given in Table 5.4.

The net power of the stack was previously determined as 4 kW considering the energy demand of householders. However, due to the possible losses in the system, the new design power should also be determined, given as:

$$P_{d,power} = P_{net} + P_{net} P_{loss} = P_{net} (1 + P_{loss}) \quad (5.36)$$

where $P_{d,power}$, P_{net} , and P_{loss} express the design power, net power, and parasitic loss, respectively.

The power density of the stack (W/cm²) can be easily calculated as:

$$P_{density} = U_{cell} j_{cell} \quad (5.37)$$

where $P_{density}$, U_{cell} , and j_{cell} denote the power density, cell voltage, and current density, respectively.

The total active area of the stack (A_{active}) is determined by considering the design power and power density, as follows:

$$A_{active} = \frac{P_{d,power}}{P_{density}} \quad (5.38)$$

Table 5.4. The fuel cell stack parameters.

Parameter	Value	Unit
Membrane type	PA-doped PBI	-
Net power	4	kW
Cell voltage	0.6	V
Current density (@ 0.6 V)	0.4	A/cm ²
Cell area	100	cm ²
Number of cells	50	-
Parasitic loss	%20	-
Anode/Cathode stoichiometric ratio	1.2/2.5	-
Anode/Cathode operating pressure	1.2	atm
Anode/Cathode operating temperature	453.15	K
Ambient temperature	298.15	K

The maximum current (I_{max}) can be written as:

$$I_{max} = j_{cell} A_{cell} \quad (5.39)$$

where A_{cell} expresses the cell area given in Table 5.4.

The stack voltage in the design stage ($U_{d,voltage}$) is determined by:

$$U_{d,voltage} = \frac{P_{d,power}}{I_{max}} \quad (5.40)$$

The number of cells in the stack can be determined as a ratio of the design voltage to the cell voltage.

$$N_{cell} = \frac{U_{d,voltage}}{U_{cell}} \quad (5.41)$$

The moles of hydrogen gas entering per cell ($N_{H_2,cell}$) can be calculated by the following equation [179]:

$$N_{H_2,cell} = \frac{I_{max}}{n_e F} \quad (5.42)$$

The total moles of hydrogen required for the fuel cell stack ($N_{H_2,total}$) can be calculated as follows:

$$N_{H_2,total} = N_{cell} \lambda_{H_2} N_{H_2,cell} \quad (5.43)$$

where λ_{H_2} defines the stoichiometric ratio of hydrogen.

In order to determine the total mass amount of hydrogen entering the stack ($\dot{m}_{H_2,react}$), the molecular weight of hydrogen (MW_{H_2}) is used, given as:

$$\dot{m}_{H_2,react} = N_{H_2,total} MW_{H_2} \quad (5.44)$$

In addition, the volume of hydrogen reacted ($V_{H_2,react}$) can be determined by the following equation:

$$V_{H_2,react} = \frac{N_{H_2,total} RT_{anode}}{P_{anode}} \quad (5.45)$$

where T_{anode} denotes the inlet anode temperature. Here, it is worth noting that there is no temperature difference between the inlet and outlet of the anode since the isothermal model is applied. In addition, the anode pressure (P_{anode}) should be converted to the Pascal in order to find the solution as (m^3/s).

In order to find this solution as the standard litres per minute (slpm), the following unit conversion should be applied as:

$$V_{H_2,react(slpm)} = V_{H_2,react} \left(\frac{10^3 L}{1 m^3} \right) \left(\frac{60 s}{1 min} \right) \quad (5.46)$$

The moles of oxygen gas entering per cell ($N_{O_2,cell}$) can be determined as [180]:

$$N_{O_2,cell} = \frac{I_{\max}}{2n_e F} \quad (5.47)$$

The total amount of oxygen moles entering the stack ($N_{O_2,total}$) can be calculated by [180]:

$$N_{O_2,total} = N_{cell} \lambda_{O_2} N_{O_2,cell} \quad (5.48)$$

where λ_{O_2} defines the stoichiometric ratio of oxygen given in Table 5.4.

Total mass amount of oxygen entering the stack can be written as:

$$\dot{m}_{O_2,react} = N_{O_2,total} MW_{O_2} \quad (5.49)$$

where MW_{H_2} stand for the molecular weight of oxygen.

The volume of oxygen entering the stack ($V_{O_2,react}$) is given in both m^3/s and slpm as follows:

$$V_{O_2,react} = \frac{N_{O_2,total} RT_{cathode}}{P_{cathode}} \quad (5.50)$$

$$V_{O_2,react(slp)} = V_{O_2,react} \left(\frac{10^3 L}{1 m^3} \right) \left(\frac{60 s}{1 min} \right) \quad (5.51)$$

where $T_{cathode}$ and $P_{cathode}$ denote the operating temperature and pressure of the cathode.

Total moles of reactants consumed by the system can be determined as follows [180]:

$$N_{H_2,cons} = \frac{I_{\max} N_{cell}}{n_e F} \quad (5.52)$$

$$N_{O_2,cons} = (\lambda_{O_2} - 1) \frac{I_{max} N_{cell}}{2n_e F} \quad (5.53)$$

The total mass amount or the volume of these reactants can be determined using the previous equations.

The output moles of hydrogen ($N_{H_2,output}$) from the system can be calculated as:

$$N_{H_2,output} = N_{H_2,total} - N_{H_2,cons} \quad (5.54)$$

The moles of water produced ($N_{H_2O,pro}$) on the cathode side can be determined as:

$$N_{H_2O,pro} = \frac{N_{cell} I_{max}}{n_e F} \quad (5.55)$$

Here, it should be noted that the produced water is in the gas phase due to the high temperature operation. Therefore, the pressure caused by the released gas must also be calculated, given as [181]:

$$P_{steam} = e^{aT^{-1} + b + cT + dT^2 + eT^3 + f \ln(T)} \quad (5.56)$$

The coefficients used in the above equation are given in Table 5.5.

Table 5.5. The coefficients used for determining the pressure [181].

Parameter	Value
a	-5800.2206
b	1.3914993
c	-0.048640239
d	$0.41764768 \times 10^{-4}$
e	$-0.14452093 \times 10^{-7}$
f	6.5459673

The mass amount of produced water ($\dot{m}_{H_2O,pro}$) in the vapour phase is given by:

$$\dot{m}_{H_2O,pro} = N_{H_2O,pro} MW_{H_2O} \quad (5.57)$$

where MW_{H_2O} signifies the molecular weight of water.

In order to perform energy analysis, the enthalpy of reactants should be determined. The following equation can be used for calculating the enthalpy of input gases [179]:

$$H_{H_2,input} = \dot{m}_{H_2,react} \left[H_{HHV,H_2}^o + (C_{p,H_2} T_{anode}) \right] \quad (5.58)$$

$$H_{O_2,input} = \dot{m}_{O_2,react} C_{p,O_2} T_{cathode} \quad (5.59)$$

where $H_{H_2,input}$, $H_{O_2,input}$, and H_{HHV,H_2}^o stand for the input enthalpy of hydrogen, the input enthalpy of oxygen, and the upper calorific value of hydrogen gas, respectively.

For calculating the output enthalpy of the reactants, the enthalpy of the water should also be considered along with the enthalpy of hydrogen and oxygen, as follows [179]:

$$H_{H_2,output} = \dot{m}_{H_2,output} \left[H_{HHV,H_2}^o + (C_{p,H_2} T_{anode}) \right] \quad (5.60)$$

$$H_{O_2,output} = \dot{m}_{O_2,output} C_{p,O_2} T_{cathode} \quad (5.61)$$

$$H_{H_2O,output} = \dot{m}_{H_2O,output} \left[(C_{p,H_2O} T_{cathode}) + h_{fg} \right] \quad (5.62)$$

where $H_{H_2,output}$ stands for the output enthalpy of hydrogen, $\dot{m}_{H_2,output}$ for the mass flow rate of hydrogen, $H_{O_2,output}$ for the output enthalpy of oxygen, $H_{H_2O,output}$ for the output enthalpy of water, and h_{fg} for the enthalpy difference between the gas and the fluid phase of water.

The total input and output enthalpies of reactants and products can be determined as:

$$\sum H_{input} = H_{H_2,input} + H_{O_2,input} \quad (5.63)$$

$$\sum H_{output} = H_{H_2,output} + H_{O_2,output} + H_{H_2O,output} \quad (5.64)$$

The released heat from the stack can be calculated by the general energy balance, given as [179]:

$$\dot{Q}_{stack} = \sum H_{input} - \sum H_{output} - P_{design} \quad (5.65)$$

Energy and exergy efficiency of an HT-PEMFC has been discussed in the previous chapter. Therefore, Eq. (4.105) and Eq. (4.120) can be used for these analyses.

5.4. PERFORMANCE ANALYSIS OF PEME STACK

5.4.1. Hydrogen Production from Water Electrolysis

The simplest method for hydrogen production is electrolysis method, which is the separation process of water into hydrogen and oxygen, by being used of direct current. In principle, in an electrolysis cell, there are two electrodes, which are usually planar metal or carbon plates, and a conductive liquid called electrolyte into which they are immersed. The current will flow from the positive electrode (anode) to the negative electrode (cathode) in the conductive liquid when the direct current source is connected to these electrodes. As a result, the water in the electrolyte will decompose into the hydrogen released from the cathode, and the oxygen released from the anode. In response to the decomposition of the water here, a substance such as potassium hydroxide is usually added to the electrolyte as conductivity enhancer since the water is not a good conductor.

The efficiency of the electrolysis can be increased by reducing the dissociation voltage for a given current value. The voltage drop process should be also adjusted so that the surface of the electrode accelerates the electrolysis process. One of the methods developed is the coating of fine powdered platinum pieces onto any metal base.

However, other electrode surfaces can also be used due to the fact that platinum is a very expensive metal. Nickel-plated steel electrodes are used in the electrolysis cells used in practice. The effective areas of the electrodes, and therefore the electrolysis process rate is increased by placing porous nickel strips on a wire mesh. The investigations continue on the electrode structures and placement arrangements to obtain higher efficiency from the electrolysis process. In industrial electrolysis cells, two types of electrode arrangement are usually made as the tank type and strainer press. The economics of hydrogen production depends on the efficiency of the method used and can be expressed as the ratio of the output energy in the hydrogen to the input. The efficiency of the hydrogen production via the electrolysis is only 80% when the electricity is considered. However, the heat efficiency of this electricity generation varies from about 34% in light water reactors to 50% in advanced systems and is on the average about 25-40%. Despite their low efficiency, these systems are extremely vital because of the fact that they have no negative impact on the environment and use solar energy.

The water is composed of 11.2% of hydrogen. The purest hydrogen is obtained by this method constituting a significant part of world hydrogen production. This method of the hydrogen production widely used in the 1950s, is now very rarely applied. In the water electrolysis, reactions occur in the opposite direction of the reactions in a fuel cell. Electrolysis are usually classified according to the electrolyte used.

In PEM water electrolysis, gold, platinum, platinum-palladium, and iridium are used as a base material on the anode and cathode electrode, respectively, which are very expensive. Hence, the manufacturing cost of the PEM electrolyser is higher than other electrolysis device. Furthermore, the electrolysis efficiency of the PEM electrolyser is quite low when compared with the other electrolysis processes. Hence alkaline electrolyser is well-known and widely used electrolysis system is since it is capable of overcoming all these problems. This electrolyser works on low temperature (average 80°C). If solution increases in electrolyser, it can work more on high temperatures. Despite being a very new technology compared to alkaline electrolytes, it has the lower efficiency. A third type of electrolyser device has high temperature in which a ceramic ion-conducting electrolyte is used, and its efficiency is very high. High-temperature

electrolyser is the newly developed technology. This kind of electrolyzers are not widely commercialized but have been developed in laboratory scale. Potential advantages are higher temperature, high efficiency, low material cost because temperature, options to working reverse as fuel cell or electrolyser mode [182,183]. PEM devices have begun to be used in small factories where particularly variable productions are done, but PEM electrolyser scaled-up in the recent years and are available up to 2 MW, with alkaline being available for a size of 6 MW [184]. Large businesses prefer alkaline systems. Although hydrogen is obtained by reversing the operation of PEM fuel cells, the conditions of electricity generation and the hydrogen production are greatly different.

5.4.2. Basic Structure and Operating Principle of PEME

The basic structure and operating principle of a PEM-based electrolyser is shown in Figure 5.12. The system consists of polymer membrane allowing only protons to pass, anode catalyst layer in which the water is decomposed by an electrochemical reaction and the oxygen is formed, cathode catalyst layer in which hydrogen is formed, and electrode layers that take on task of the transmission and removal of liquids and gases to the catalyst surfaces at the same time in which the electricity is applied. The water taken into the cell through the anode inlet dissociates into hydrogen ion (H^+ , Proton) and oxygen gas in the anode catalyst layer. While the oxygen gas is given from the anode outlet to outside, the hydrogen ion receives electrons in the cathode catalyst layer by crossing through the Nafion membrane and converts into the hydrogen gas. The reactions occurring in this process are given in the following [185]:



The oxygen is obtained as a result of the above reaction with the effect of the ruthenium, iridium catalyst layer on the membrane surface in the anode region. Hydrogen migrates to the cathode region by giving electrons (H^+), too. Due to the structure of the Nafion membrane, some water migration takes place in this transition.



By the electricity supplied to the cell, the hydrogen ions in the cathode region by taking electrons, hydrogen gas is obtained as the product.

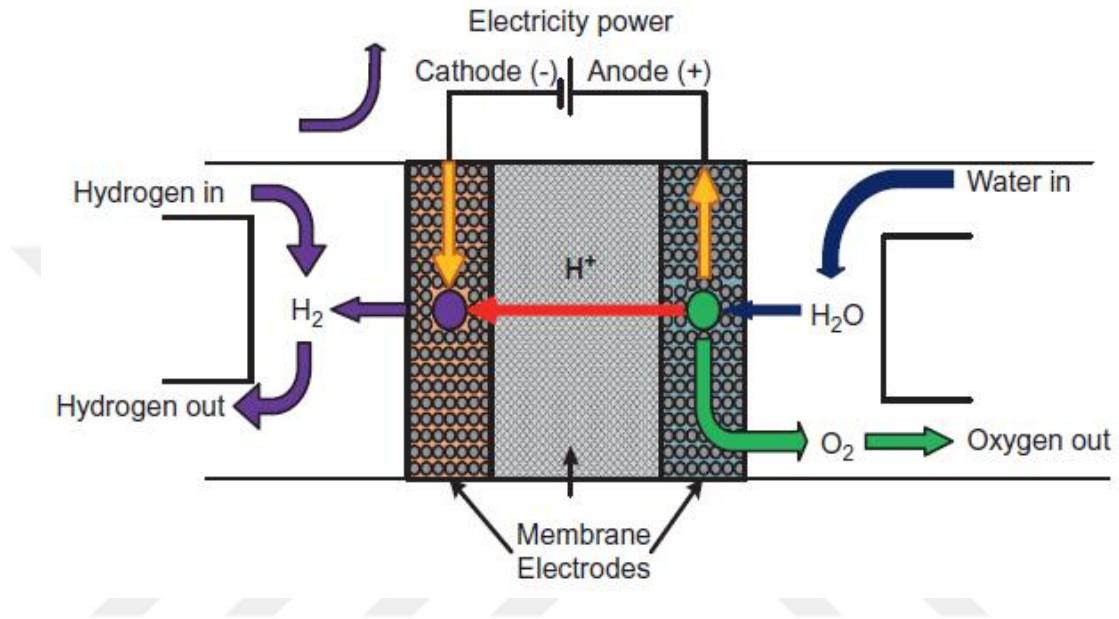
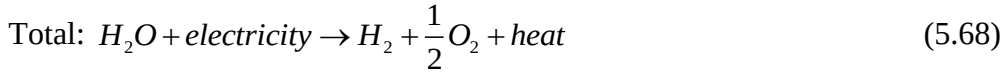


Figure 5.12. The operating principle of a PEME [185].

As a total reaction product in the cell, the oxygen is obtained in the anode region, and hydrogen in the cathode region. Some of the electricity given for the electrolysis is converted into the heat energy due to the ohmic, concentration, and activation losses in the cell, thus the cell temperature rises. As the water circulation occurs in the cell in the PEM electrolyser, the problem of overheating disappears. However, depending on the water flow used for cooling, and the heat transfer conditions, the temperature in the cell increases at a certain level. This increase in the temperature improves reaction kinetics and positively affects the performance. However, as the temperature increases, the corrosion of metallic particles in the cell also accelerates. For this reason, keeping the cell temperature in the range of 40–60°C is suitable for both the performance and life [186].

5.4.3. Modelling of PEME

5.4.3.1. PEME Modelling at Cell Level

Electrochemical reactions in PEM electrolyzers occur on anode and cathode catalyst layers. Under normal conditions, 1.229 V is sufficient to theoretically separate the water into oxygen and hydrogen molecules. However, extra voltage (overvoltage) is required because of the realization of anode and cathode reactions and losses. In a typical PEM electrolyser, most of the overvoltage voltage losses are due to the anode in which the oxygen-induced reaction occurs [187]. For a high-performance PEM electrolyser, the catalysts that keep the overvoltage losses to a minimum are needed to be selected.

In Figure 5.13, the polarization curve of a PEME is given. As it is seen in the figure, no current is drawn when the theoretical voltage (1.48 V) is applied to the system. In order to be able to be drawn of current from the electrolyser (reaction speed), the operating voltage is needed to be greater than the theoretical voltage (voltage loss). The voltage loss is due to the activation, ohmic, and concentration losses depending on the drawn current. The details of these losses are given below. The reaction speed at the electrode surface in the PEME is related to the speed of the current. The electrolysis does not perform at the theoretical voltage, but it is necessary to apply a voltage above the theoretical voltage to the system in order to perform anode and cathode reactions. The applied extra voltage is called the loss of activation.

A very high-voltage drop is observed when the input voltage is applied to the PEM cell. These declines are characterized by reversible decline V_{rev} , activation losses V_{act} , diffusion losses V_{dif} , and ohmic losses V_{ohm} . These losses are influenced by the nonlinear changes of the current. Accordingly, the following equation can be written by the law of electric circuit:

$$U_{elec} = V_{rev} + V_{act} + V_{dif} + V_{ohm} \quad (5.69)$$

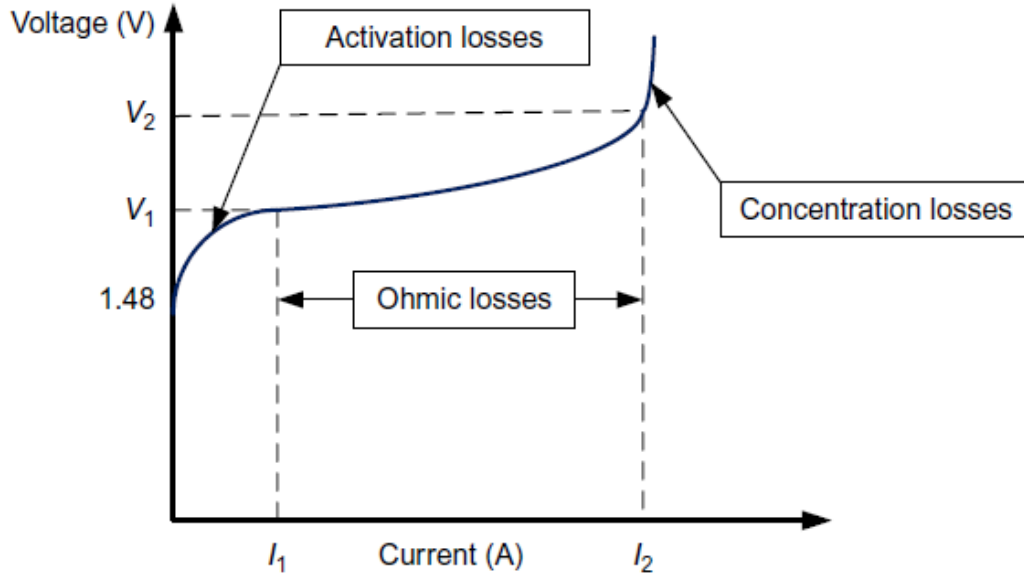


Figure 5.13. The polarization curve of a PEME.

In order to be able to create a steady-state electrical model, each voltage drop must be examined individually.

Reversible voltage

This voltage drops occurring from chemical redox reactions is called also as open circuit voltage. If the current is not drawn ($I=0$), the reversible voltage indicates the cell potential. The reversible voltage, V_{rev} is calculated from Gibbs energy and can be determined by the NERST equation as follows:

$$V_{rev} = V_0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{\alpha_{H_2O}} \right) \quad (5.70)$$

where α_{H_2O} denotes the water activity and equals to 1 for the liquid.

Activation Voltage

Activation voltage losses shown with electrochemical kinetic behaviours are due to proton transfer and chemical reaction rate. Activation voltage losses, V_{act} can be

determined by Butler-Volmer and Tafel's laws. As a function of the current, V_{act} can be written for the electrolyser as follows:

$$V_{act} = \frac{RT}{an_e F} \ln \left(\frac{I}{I_0} \right) \quad (5.71)$$

where I_0 is the variation current

Diffusion Voltage

Fluid (gas and water) concentration near the electrodes and the diffusion affects the existing current values. It affects the present values of close diffusion of electrodes. The diffusion behaviour changes depending on the partial pressure and the chemical reaction rates. This change causes to the diffusion losses, V_{dif} . The diffusion equation, V_{dif} proposed by Fontes for the PEM fuel cells can be given as [185]:

$$V_{dif} = \frac{RT}{\beta n_e F} \ln \left(1 + \frac{I}{I_{lim}} \right) \quad (5.72)$$

where β and I_{lim} are the constant coefficient and the limit of the diffusion current, respectively.

Ohmic Voltage

The main reason for ohmic losses is the selective polymer membrane, R_{mem} . The resistance value is usually given by empirical equations proposed by Springer et al. As it is given in the equation, the selective membrane, R_{mem} is a function of area A_m (cm²), membrane thickness, l_m (cm), hydration rate l_m (if $l_m=7$ dry, if $l_m=14$ good hydration, if $l_m=22$ wet), and the temperature T is given below:

$$R_{mem} = \frac{I_m}{A_m (0.005139\lambda_m + 0.00326) \exp \left(1267 \left(\frac{1}{303} - \frac{1}{T} \right) \right)} \quad (5.73)$$

Ohmic losses can be given as follows:

$$V_{ohm} = R_{mem} I = R_{mem} = \frac{I_m}{A_m (0.005139 \lambda_m + 0.00326) \exp \left(1267 \left(\frac{1}{303} - \frac{1}{T} \right) \right)} I \quad (5.74)$$

Accordingly, the electrical model can be written by putting the voltage losses in its place in the equation, as follows:

$$U_{elec} = V_0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{\alpha_{H_2O}} \right) + \frac{RT}{an_e F} \ln \left(\frac{I}{I_0} \right) + \frac{RT}{\beta n_e F} \ln \left(1 + \frac{I}{I_{lim}} \right) + R_{mem} I \quad (5.75)$$

If the hydrogen flow is given as (mol/s):

$$F_{H_2} = \frac{I}{2F} \quad (5.76)$$

5.4.3.2. PEME Modelling at Stack Level

The formula for calculating the amount of water consumption was previously indicated in Eq. (5.68). Thanks to this formula, it is observed that the mole of hydrogen produced is equal to the mole of water consumed. Therefore, the moles of hydrogen from Eq. (5.43) will be taken as the basis for the following calculations.

The operating current of the electrolyser, I_{elec} , can be calculated, given as:

$$I_{elec} = j_{elec} A_{elec} \quad (5.77)$$

where j_{elec} is the current density taken as 1 A/cm², and A_{elec} is the active area of the electrolyser considered as 100 cm². Accordingly, the number of cells ($N_{cell,elec}$) in the electrolyser stack can be determined as [186]:

$$N_{cell,elec} = \frac{N_w n_e F}{I_{elec}} \left(\frac{1}{\eta_{elec}} \right) \quad (5.78)$$

where N_w and η_{elec} denotes the moles of water consumed and the efficiency of electrolyser stack, respectively.

In addition, the operating voltage of the electrolyser stack (V_{elec}) can be given by [186]:

$$V_{elec} = U_{elec} N_{cell,elec} \quad (5.79)$$

Here, the cell voltage (U_{elec}) is considered as 1.50 V. Thus, the power required for the electrolyser can be written as:

$$P_{elec} = V_{elec} I_{elec} \quad (5.80)$$

This result obtained in the above equation is in kW. Considering that the electrolyser will operate for 8 hours to produce the hydrogen required for the fuel cell, the power of the electrolyser will be easily found in kWh through the following equation.

$$P_{elec,kWh} = P_{elec} t_h \quad (5.81)$$

where t_h denotes the operating duration in hours.

CHAPTER 6

RESULTS AND DISCUSSION

6.1. PERFORMANCE RESULTS OF HT-PEMFC AT CELL LEVEL

6.1.1. Results of 0-D & Isothermal Model

This section introduces the results and discussion of the proposed 0-D and isothermal model of the HT-PEMFC. The general performance analysis results using the operational and design parameters given in Table 4.3 are presented as the base case.

6.1.1.1. Comparison of Experimental and Numerical Findings

Based on a set of electrochemical analyses from Section 4.2.1, the polarization curve ($U-j$) of the HT-PEMFC is plotted in Figure 6.1. To certify the validity of the presented model, the analysis results were compared with two experimental data sets from Ref [188]-[189]. In this validation process, the net output voltage was determined and compared separately according to the operating temperatures of 423 K and 433 K at a constant pressure of 1 atm. Here, the doping and relative humidity levels were considered 5.6 and 3.8%, respectively, while air and hydrogen acted as reactants.

In order to prove the strengths of the proposed model, each numerical or experimental data was subjected to statistical analyses using equations presented in Section 4.2.3. First of all, different statistical methods, including the mean, median, standard deviation, variance, coefficient of variance, skewness, and kurtosis, were applied in the validation process. These methods were primarily used to present the statistical results of each experimental or numerical data in itself. Accordingly, at the operating temperature of 423 K, the standard deviation was determined to be 0.223 and 0.192 for experimental and numerical data, respectively. In contrast, at 433 K, it was

calculated as 0.097 for experimental and 0.083 for numerical data. In addition, at 423 K, the coefficient of variance was calculated to be 0.404 and 0.363 for experimental and numerical data, respectively, whereas, at 433 K, it was computed as 0.181 for experimental and 0.157 for numerical data. The results of these series regarding each analysis are given in Table 6.1.

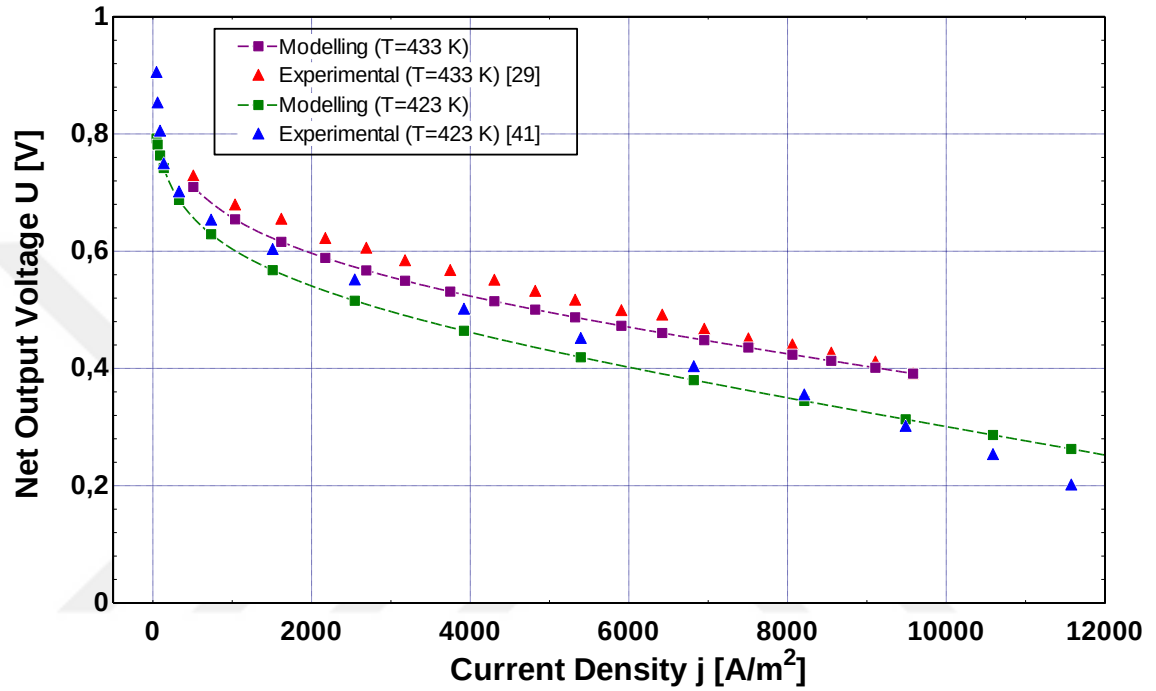


Figure 6.1. The comparison of polarization curves between modelling and experimental results for different operating temperatures of 423 K and 433 K.

Apart from the analysis of each series, experimental and numerical results were evaluated integrally, and model performance analyses were performed to find the best fit. In these performance analyses, multiple highly reliable indicators, including the ratio of means (ϵ^-), the mean absolute error (*MAE*), the mean fractional error (*MFE*), the mean square error (*MSE*), the root mean square error (*RMSE*), the R-squared (R^2), the normalised mean bias (*NMB*), the normalised mean error (*NME*), the mean fractional bias (*FBIAS*), the mean fractional error (*FERR*), the standard error of the mean (*SEM*), and uncertainty values, were used to assess and compare the experimental and numerical results. Accordingly, *RMSE* was determined to be 0.046 and 0.028, whereas R^2 is computed as 0.986 and 0.991 for the operating temperature of 423 K and 433 K, respectively, as presented in Table 6.2. In addition, the

distribution of the R^2 correlation between numerical and experimental data is illustrated in Figure 6.2. Accordingly, a good agreement between the two data sets (423 K and 433 K) is achieved; hence, the proposed modelling is highly validated in almost the entire current density region.

Table 6.1. Summary series statistics for experimental and numerical results.

Summary Series Statistics	Experimental (423 K)	Model (423 K)	Experimental (433 K)	Model (433 K)
Minimum	0.201900	0.262500	0.391500	0.423500
Maximum	0.905800	0.792400	0.729200	0.709500
Mean	0.553187	0.529933	0.534911	0.530600
Median	0.551900	0.515500	0.524800	0.514600
Standard Deviation	0.223990	0.192605	0.097308	0.083776
Variance	0.050172	0.037097	0.009469	0.007018
Coefficient of Variation	0.404909	0.363452	0.181914	0.157890
Skewness	0.006889	0.070292	0.388716	0.728282
Kurtosis	-1.185928	-1.599114	-0.706576	-0.147220
Number of Observations	15	15	18	18

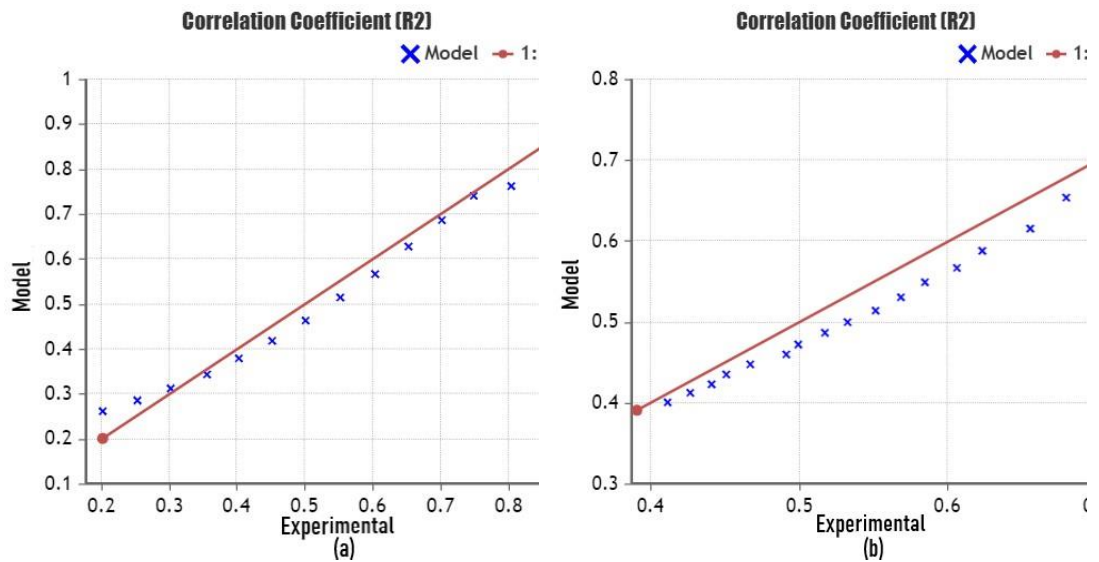


Figure 6.2. The distribution of R^2 correlation for (a) 423 K and (b) 433 K.

Table 6.2. The model performance comparison between two data sets.

Model Performance	Exp. vs Model (423 K)	Exp. vs Model (433 K)
Mean Error (ϵ^-)	0.023	0.027
Ratio of Means (Rat)	14.770	17.154
The Mean Absolute Error (MAE)	0.037	0.026
Mean Fractional Error (MFE)	0.020264	0.048299
Mean Square Error (MSE)	0.0020932	0.0007819
Root Mean Square Error (RMSE)	0.046	0.028
R-squared (R^2)	0.986	0.991
Normalized Mean Bias (NMB)(%)	4.2035	5.099
Normalized Mean Error (NME)(%)	6.72	4.82
Mean Fractional Bias (FBIAS)(%)	2.03	4.83
Absolute Mean Fractional Error (FERR) (%)	7.60	4.83
Standard Deviation (differ.)	0.039	0.011
Standard Error of Mean (SEM)	0.010	0.003
Uncertainty (95% of confidence interval)	7.946	2.043

6.1.1.2. Generic Performance Analysis Results

The variation of internal resistance, reversible voltage, net output voltage, and overpotentials, including the activation, concentration, and ohmic, according to current density, is demonstrated in Figure 6.3. As demonstrated in the figure, the activation, concentration, and ohmic voltage increase, whereas the reversible voltage is constant, and the net output voltage decreases with the current density. This increase in the activation, concentration, and ohmic voltage is hyperbolic, logarithmic, and linear, respectively. Therefore, the activation voltage rapidly rises in the low current density region, whereas the concentration voltage gradually increases in the high current density region. Besides, the internal resistance density (R_I^*) sharply decreases at first, then almost remains constant, approaching zero with increasing current density values, where R_I^* equals $R_I A$.

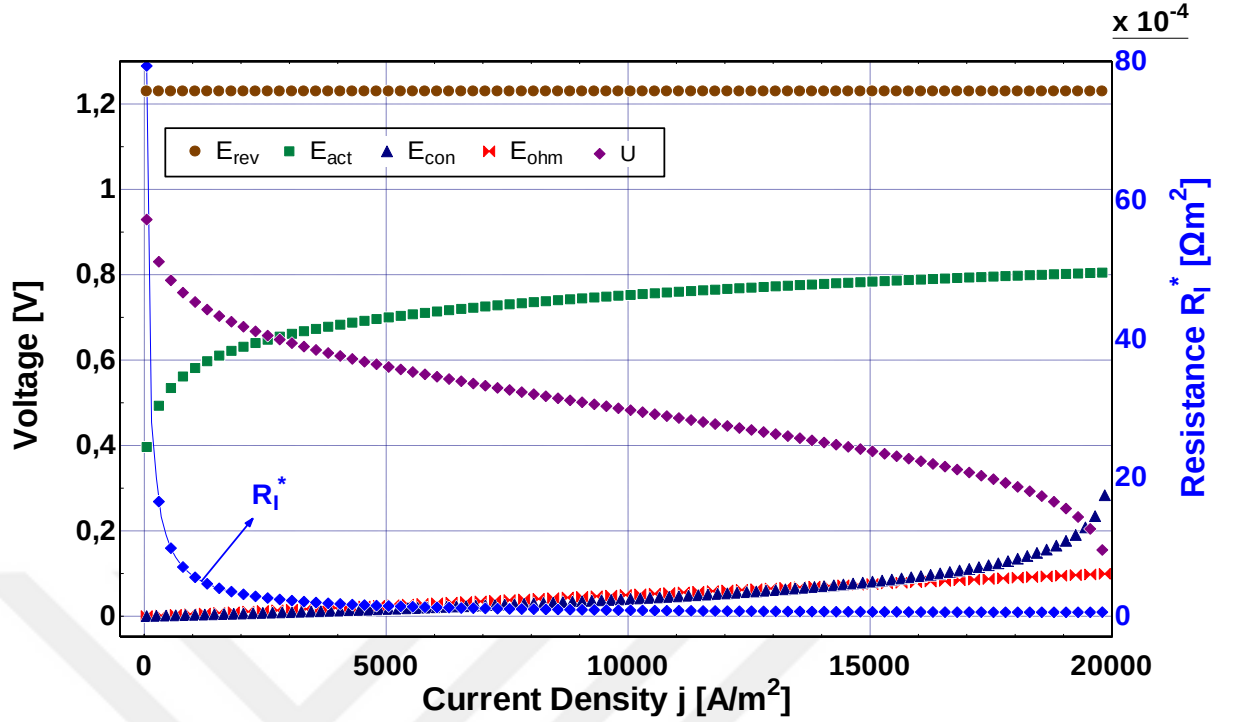


Figure 6.3. The comparison of curves versus current density, including reversible voltage, net output voltage, overpotentials, and internal resistance.

Figure 6.4 presents the variation of power density (P^*) and energy and exergy analysis results for current density. Accordingly, energy and exergy efficiencies gradually decrease with the current density, such that energy efficiency is slightly higher than exergy efficiency at constant temperature and pressure. Besides, the power density first increases until the peak level, $P^*=P^*_{max}$ at 5831 Wm^{-2} , then decreases during the high current density region, where $P^*=P/A$. Correspondingly, the current density becomes the optimum (j_p) at 15650 Am^{-2} in a case where $P^*=P^*_{max}$. The maximum energy and exergy efficiencies are determined as 63.75% and 59.02% at the initial state, whereas the optimum energy and exergy efficiencies are computed as 25.56% and 23.56%, respectively, where $P^*=P^*_{max}$ and $j=j_p$.

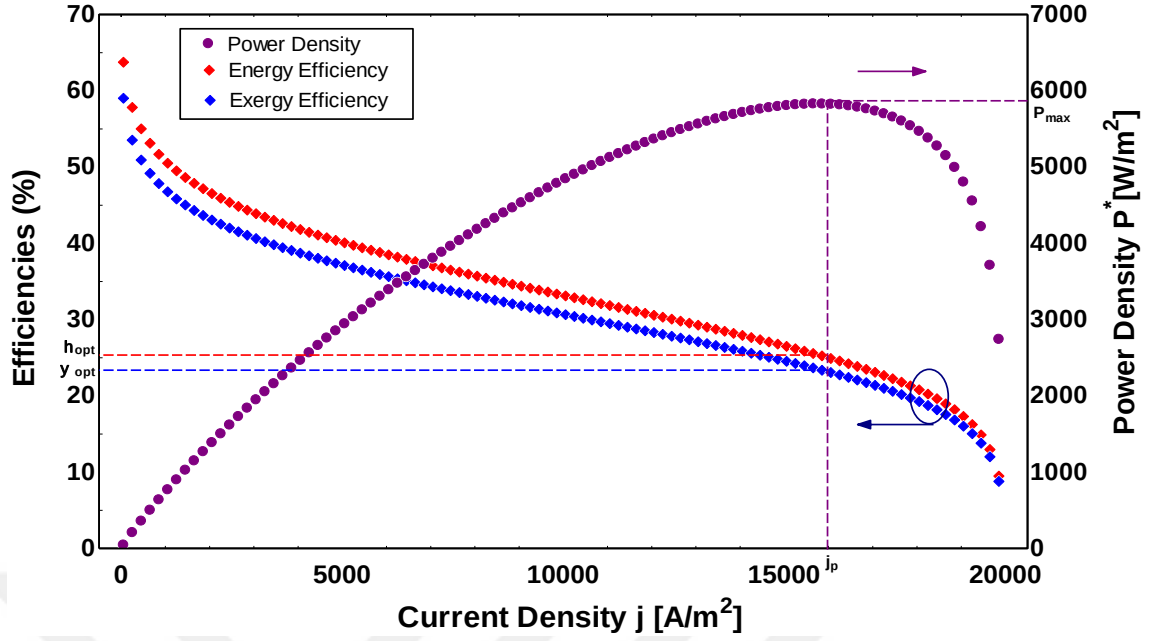


Figure 6.4. The variation of energy, exergy efficiency and power density versus current density.

Figure 6.5 represents the variation of energy/exergy efficiency, irreversible voltage, and entropy production density (δ^*), where $\delta^* = \dot{\delta}/A$. According to the figure, the entropy production density and irreversible voltage increase, whereas energy and exergy efficiencies decrease with the current density. A logarithmic increase is obtained in irreversible voltage, starting from 0.4 V to 1.18 V, whereas an almost linear increase is obtained in the entropy production density, reaching its maximum at 61.6 $\text{Wm}^{-2}\text{K}^{-1}$ at the high current density region. Based on Eq. (4.34), the term $(-\Delta\dot{H})$ rises with increasing the current density. However, this increment is greater than the power output. This situation reduces both efficiencies and raises the entropy production density in the whole region of the current density.

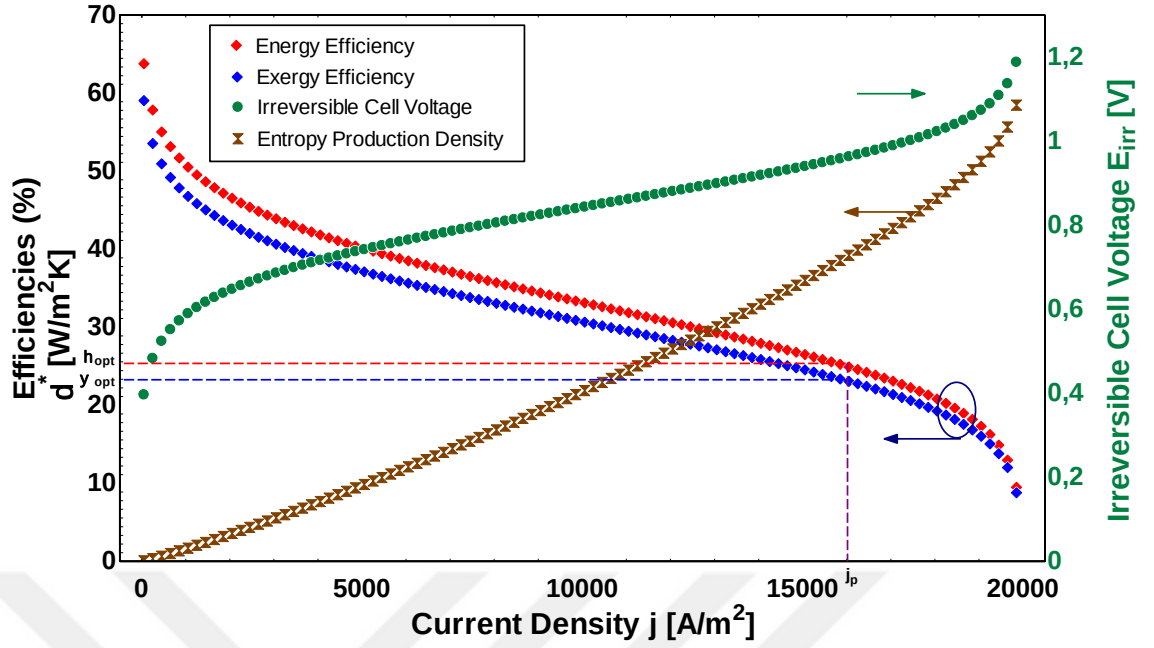


Figure 6.5. The variation of efficiencies, irreversible cell voltage and entropy production density versus current density.

The variation of exergy efficiency and exergy destruction density ($\dot{E}x_D^*$) to the current density is given in Figure 6.6. Accordingly, there is an inverse correlation between exergy efficiency and exergy destruction density, where $\dot{E}x_D^* = \dot{E}x_D / A$ as is often encountered in the literature. The main reason is that the exergy destruction density is directly related to the difference between input and output exergy and the work, as given in Eq. (4.44). Since $\dot{E}x_{heat}$ increases considerably and $\dot{E}x_{work}$ decreases in the high current density region, the exergy destruction density rises, reaching its maximum at 37185 Wm^{-2} . As a result, exergy efficiency decreases with increasing the current density.

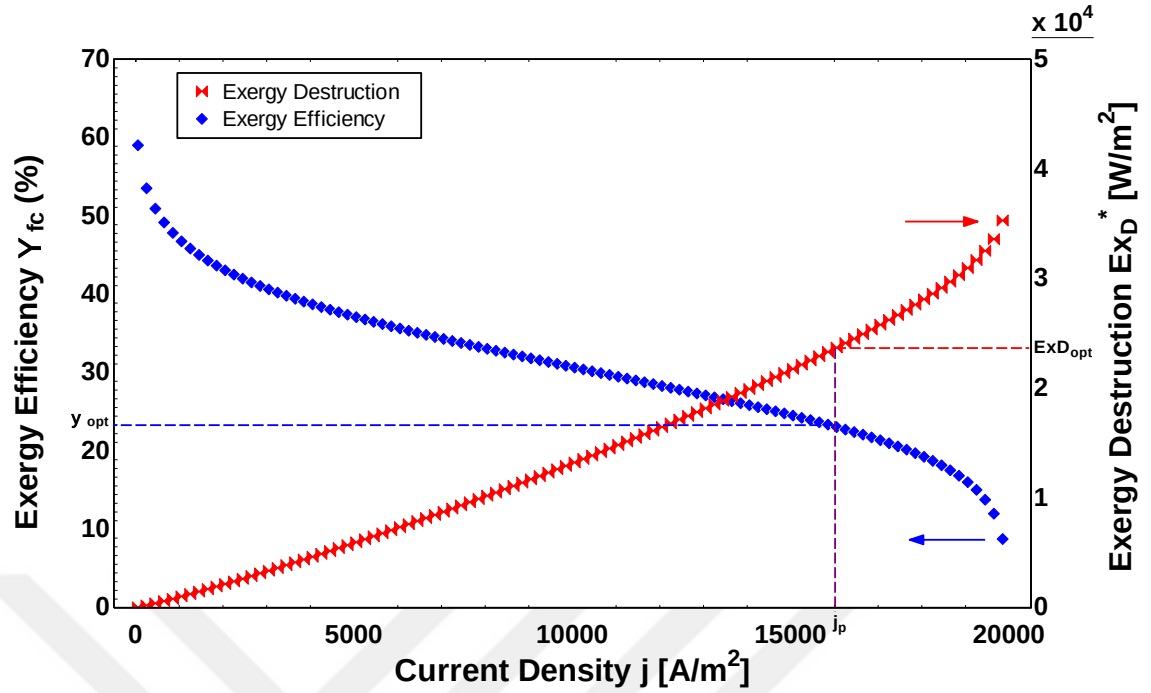


Figure 6.6. The variation of exergy efficiency and exergy destruction rate versus current density.

6.1.1.3. Parametric Study Results

In this section, significant parametric studies have been conducted to discover how different operating (temperature and pressure) and design (relative humidity and membrane thickness) parameters affect the performance of the HT-PEMFC, and the findings have been comprehensively discussed.

Effects of Operating Temperature

Since higher operating temperatures increase the concentration and activation voltage while decreasing the ohmic and reversible voltage, the net output voltage and power density rise as the operating temperature rises, as depicted in Figure 6.7. As illustrated in the figure, a broad range of the temperature scale from 373 K to 473 K is used. Consequently, the power density is calculated to be 4169, 6377, and 9006 Wm^{-2} over the temperature range of 433 K to 473 K with a 20 K interval, respectively. Thus, increasing the temperature to 453 K and 473 K enhances the maximum power density by 9.36% and 54.45%, respectively, compared to the base case. Although the cell

performance could enhance with increasing temperature, Zhang et al. [190] obtained that the degradation occurs around 453 K and might be serious at 473 K from their experimental study conducted for durability. Therefore, maintaining the operating temperature in an acceptable range is critical.

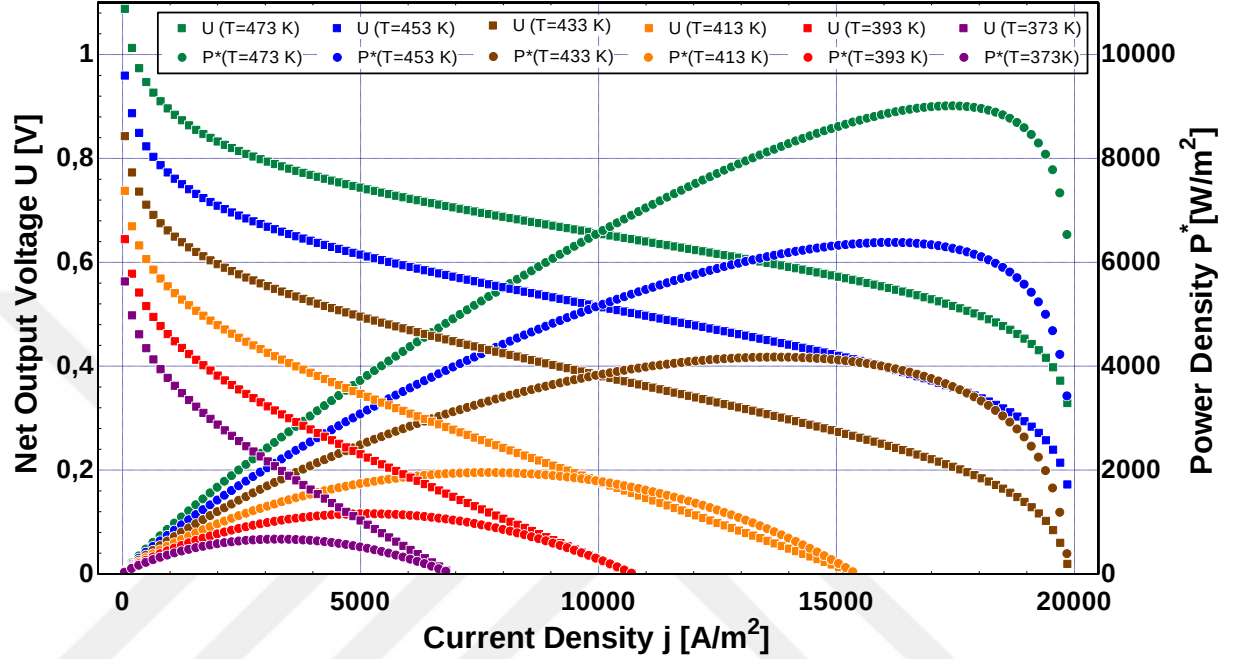


Figure 6.7. The variation of net output voltage and power density versus current density at different operating temperatures.

As plotted in Figure 6.8, since energy efficiency is a ratio of power output, an increase in the operating temperature leads to a significant increase in efficiency. At operating temperatures between 433 K and 473 K with a 20 K interval, the optimum energy efficiency is calculated to be 20.99%, 27.27%, and 35.71%, respectively, where $j=j_p$ and $P^*=P^*_{max}$. Additionally, the energy efficiency is improved by 6.7% and 39.71% over the base case when the temperature is raised to 453 K and 473 K, respectively. Along with increasing energy efficiency, a gradual decrease in the entropy production density is achieved, where the maximum point is observed in the high current density region. To summarise, the maximum entropy production densities are computed as 87.5, 102.7, and 119 $\text{Wm}^{-2}\text{K}^{-1}$ for the same temperature interval.

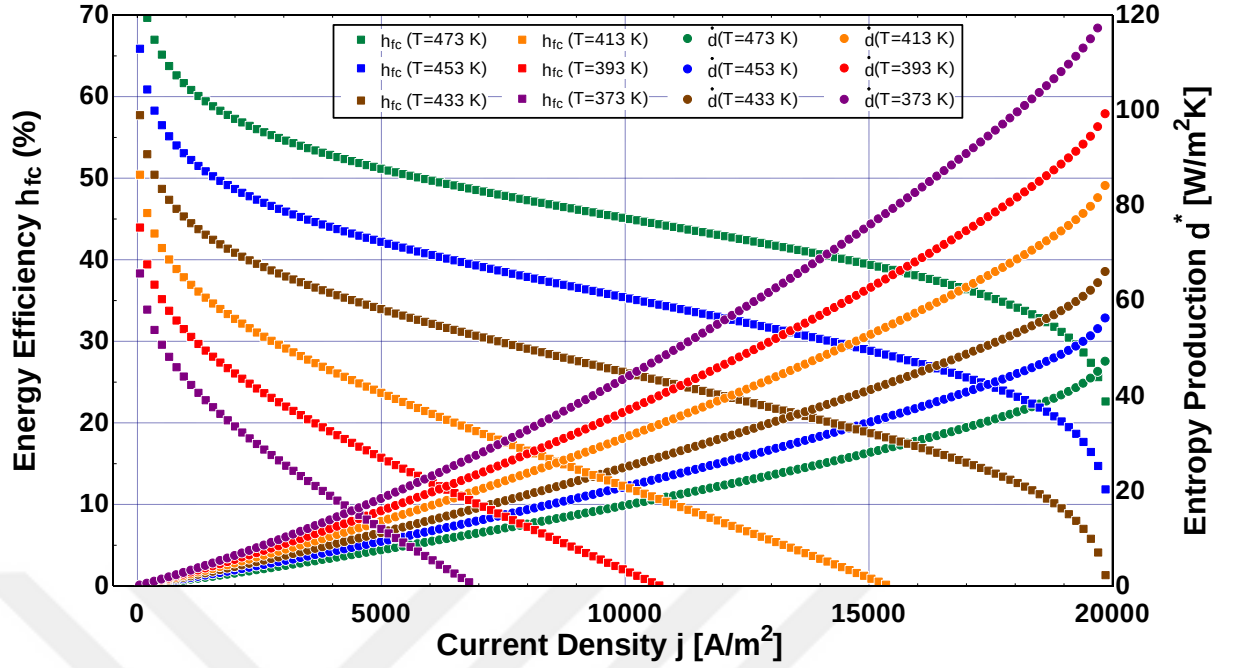


Figure 6.8. The variation of energy efficiency and entropy production density versus current density under different operating temperatures.

The variation of exergy efficiency and exergy destruction density under different operating temperatures is illustrated in Figure 6.9. At operating temperatures between 433 K and 473 K with a 20 K interval, the optimum exergy efficiency is calculated to be 19.57%, 25.19%, and 32.67%, respectively, where $j=j_p$ and $P^*=P_{max}^*$. Thus, raising the temperature to 453 K and 473 K improves exergy efficiency by 6.92% and 38.67%, respectively, compared to the base case. In addition, the maximum exergy destruction density is computed as 34658, 38210, and 41960 Wm^{-2} for the same temperature interval, respectively. Although the maximum exergy efficiency is achieved at 473 K, the minimum exergy destruction density is determined at 393 K. Therefore, it can be stated that increasing the temperature does not linearly increase the exergy destruction density.

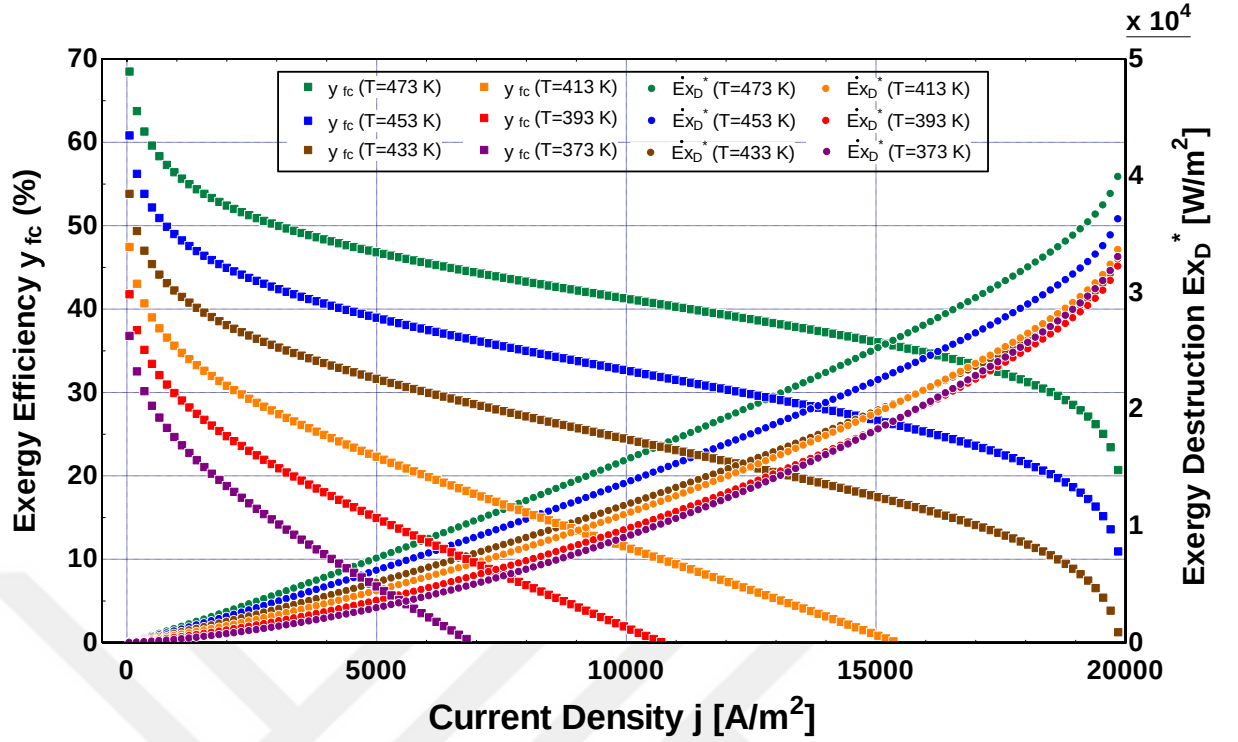


Figure 6.9. The variation of exergy efficiency and exergy destruction versus current density at different operating temperatures.

Effects of Operating Pressure

The operating pressure is also another factor influencing the performance of the HT-PEMFC. Since increasing the pressure increases the reversible voltage, as discussed in Eq. (4.5), the net output voltage and power density rise slightly, as depicted in Figure 6.10. In this parametric study, both anode and cathode pressures increased from 1 to 4 atm. Accordingly, increasing the pressure causes a slight rise in the net output voltage and power density values such that the maximum power density is determined as 5831, 5937, 5999, and 6043 Wm^{-2} for the pressures of 1, 2, 3, and 4 atm, respectively. Thus, increasing the pressure to 4 atm leads to only a 3.64% enhancement in the maximum power density compared to the base case.

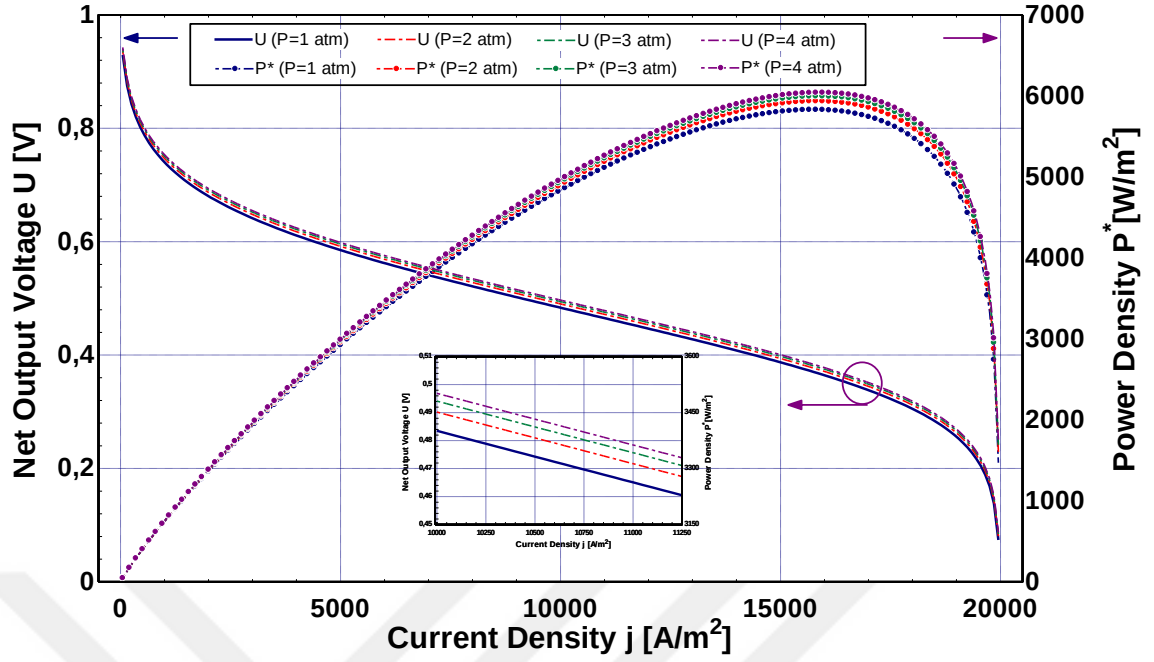


Figure 6.10. The variation of net output voltage and power density versus current density at different operating pressures.

The variation of energy efficiency and entropy production density for the current density under different operating pressures is given in Figure 6.11. According to the figure, there is a slight rise in energy efficiency and an imperceptible decline in the entropy production density with increasing pressure. In the case where $j=j_p$ and $P^*=P^*_{max}$, the optimum energy efficiency is calculated as 25.56%, 25.86%, 26.04%, and 26.24% for pressures of 1, 2, 3, and 4 atm, respectively. As a result, increasing the pressure to 4 atm only improves energy efficiency by 2.66% over the base case. In addition, the maximum entropy production densities are determined as 61.61, 61.31, 61.14, and 61.02 $\text{Wm}^{-2}\text{K}^{-1}$ for the same pressure scale, respectively.

The variation of exergy efficiency and exergy destruction density to the current density is shown in Figure 6.12. Accordingly, increasing the pressure causes a decrease in the exergy destruction density, hence a slight rise in exergy efficiency. The optimum exergy efficiency is determined as 23.66%, 23.94%, 24.11%, and 24.29% for pressures of 1, 2, 3, and 4 atm, respectively, in the case that $j=j_p$ and $P^*=P^*_{max}$. The enhancement in exergy efficiency is the same as energy efficiency, despite the increasing pressure. In addition, the maximum exergy destruction densities are calculated as 37185, 37007, 36903, and 36829 Wm^{-2} for the same pressure scale, respectively.

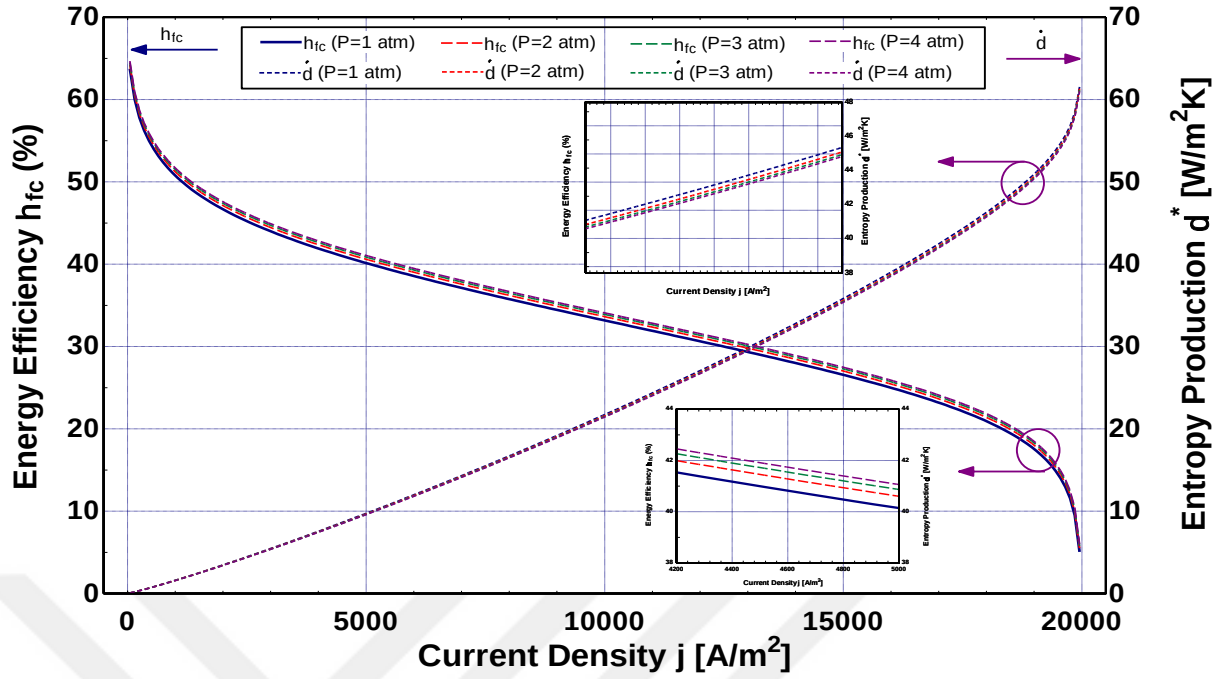


Figure 6.11. The variation of energy efficiency and entropy production density versus current density at different operating pressures.

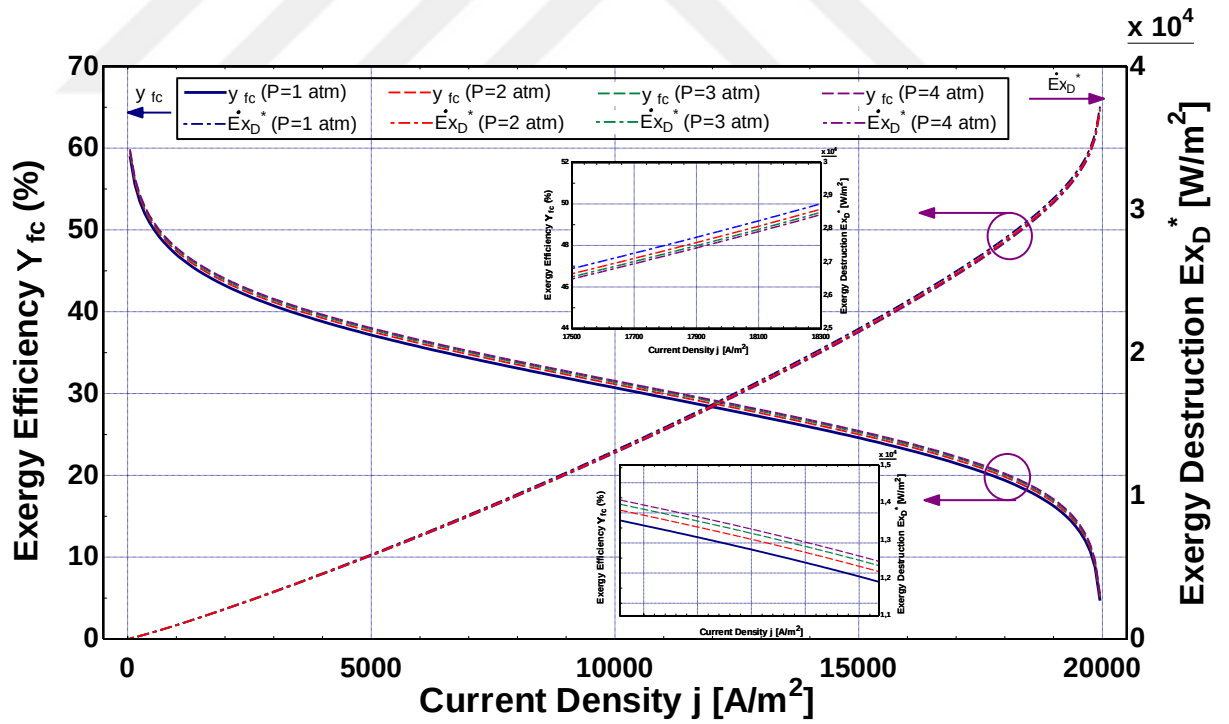


Figure 6.12. The variation of exergy efficiency and exergy destruction density versus current density at different operating pressures.

Effects of Relative Humidity

According to Eqs. (4.10–4.13), increasing the relative humidity increases the coefficient of B_0 ; hence, the proton conductivity of the PBI membrane rises. This situation causes the ohmic voltage to decrease significantly, the net output voltage to rise noticeably, and the power density to increase significantly, as plotted in Figure 6.13. According to the figure, increasing the relative humidity has a negligible impact on the maximum net output voltage at the low-current density region. On the other hand, the slope of the net output voltage and power density varies with the current density. Namely, a rapid decrease in the net output voltage is observed with increasing the current density in a case without humidity. In this case, power density values are considerably lower. Although not as fast as the previous trend, a linear decrease in the net output voltage values is observed in the case of 1% humidity ($RH=1$), too. This situation can be clarified by the fact that the conductivity of the fuel cell is adversely influenced in a condition with insufficient humidity. After the level of 1%, both net output voltage and power density values gradually increase with increasing the relative humidity up to 7.6%. Apart from this, an increase in relative humidity does not cause a noticeable increase in the net output voltage and power density values due to saturation after 11.4%. In summary, the maximum power densities are calculated to be 808.7, 5831, 6471, and 6702 Wm^{-2} , respectively, for the relative humidity ranging from 0 to 11.4% with a 3.8% interval. Thus, increasing the relative humidity to 11.4% leads to an enhancement of the maximum power density by 14.94%.

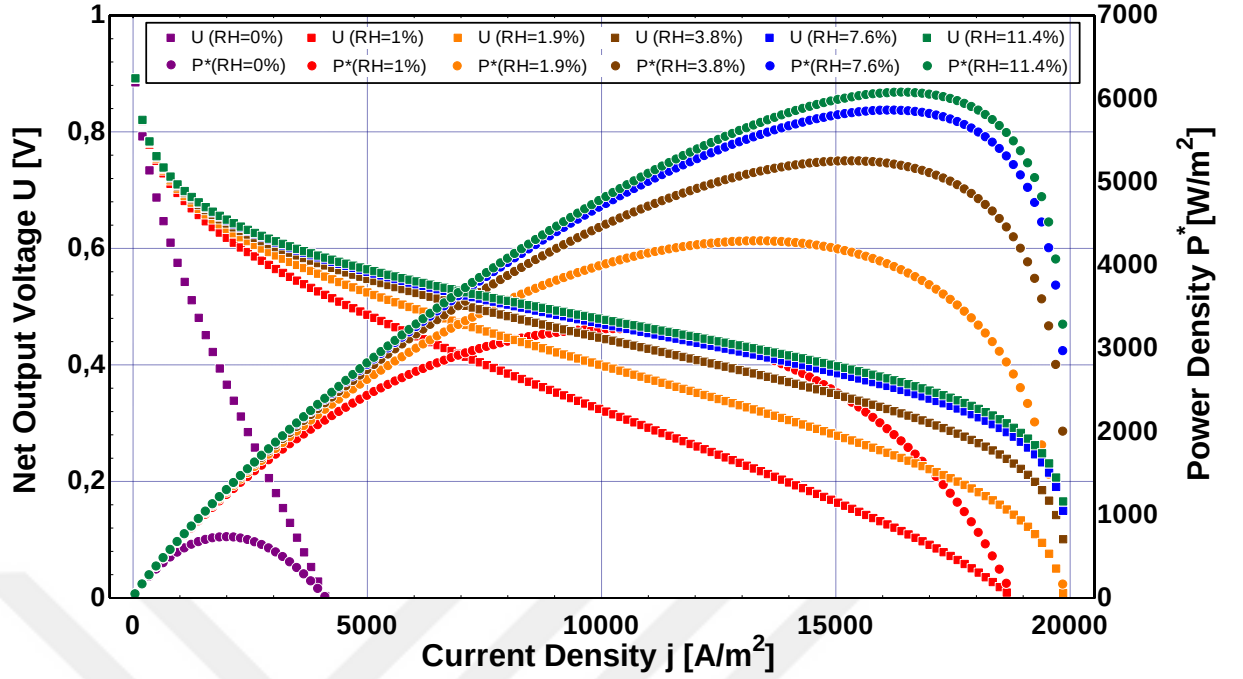


Figure 6.13. The variation of net output voltage and power density versus current density at different relative humidity levels.

The same situation applies to the variation of energy efficiency and entropy production density, as given in Figure 6.14. Accordingly, a rapid decrease in energy efficiency and a dramatic increase in the entropy production density are obtained in a case with no humidity. The maximum entropy production densities are determined as 184.6, 72.6, 65.8, and 58.7 $\text{Wm}^{-2}\text{K}^{-1}$. Besides, the optimum energy efficiencies are calculated to be 26.42%, 25.56%, 26.98%, and 27.61%, respectively, for the relative humidity ranging from 0 to 11.4% with a 3.8% range, where $P^* = P^*_{max}$ and $j = j_p$. Thus, increasing the relative humidity to 11.4% enhances energy efficiency by 8.02%.

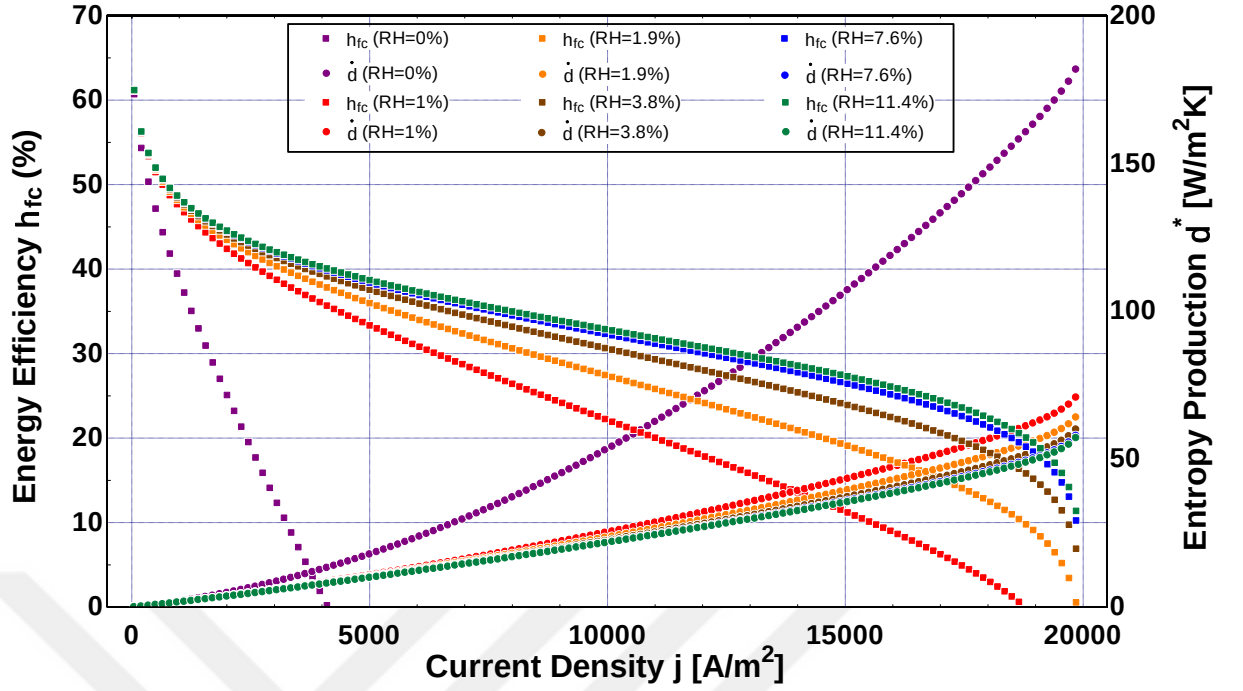


Figure 6.14. The variation of energy efficiency and entropy production density versus current density at different relative humidity levels.

The variation of exergy efficiency and exergy destruction density for the current density under different pressure levels is indicated in Figure 6.15. According to the figure, the exergy destruction density decreases with increasing relative humidity. Depending on this situation, the overall efficiency trend is positively affected from the %1 relative humidity level to 7.6%, and exergy efficiency values gradually increase. After the level of 7.6%, the increase in relative humidity does not affect the exergy efficiency. To summarize the data, the maximum exergy destruction densities are obtained as 110723, 37185, 35880, and 35435 Wm^{-2} . Besides, optimum exergy efficiencies are determined as 24.46%, 23.66%, 24.98%, and 25.56%, respectively, for relative humidity ranging from 0 to 11.4% with a 3.8% interval, where $P^*=P^*_{max}$ and $j=j_p$. Thus, increasing the relative humidity up to 11.4% causes an enhancement of 8.03% in exergy efficiency values compared to the base case.

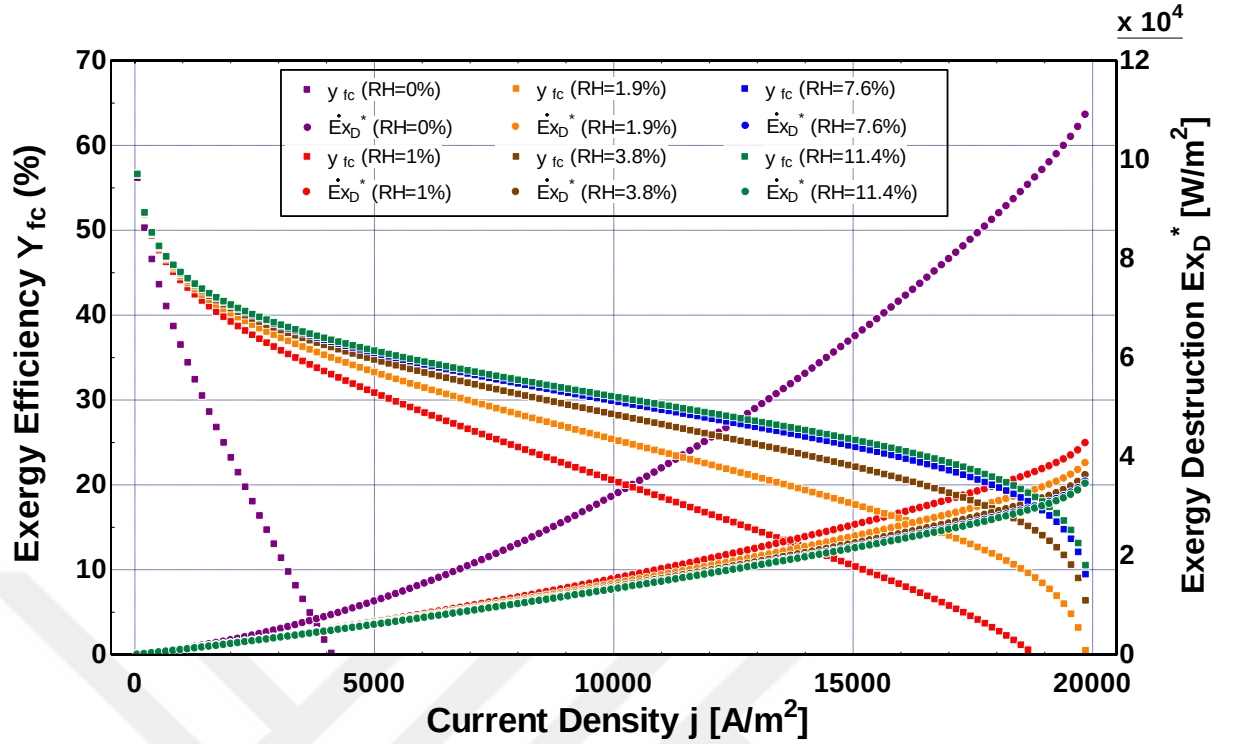


Figure 6.15. The variation of exergy efficiency and exergy destruction density versus current density at different relative humidity levels.

Effects of Membrane Thickness

Based on Eq. (4.10), the membrane thickness directly affects the ohmic and net output voltage, as depicted in Figure 6.16. Since the thinner membrane leads to greater proton permeability in a fuel cell, resulting in increased output voltage, it should be selected as thin as possible in the design stage. Accordingly, increasing the membrane thickness from 0.01 cm to 0.15 cm causes a decrease in the net output voltage and power density. However, the effect of the variation in the membrane thickness on the net output voltage and power density is much more pronounced than the variation in the relative humidity. To elaborate, maximum power densities are obtained as 6902, 5831, 4734, and 3921 Wm^{-2} for the membrane thicknesses of 0.01, 0.05, 0.1, and 0.15 cm, respectively. Thus, reducing the membrane thickness to 0.01 cm enhances the power density by 18.37% compared to the base case.

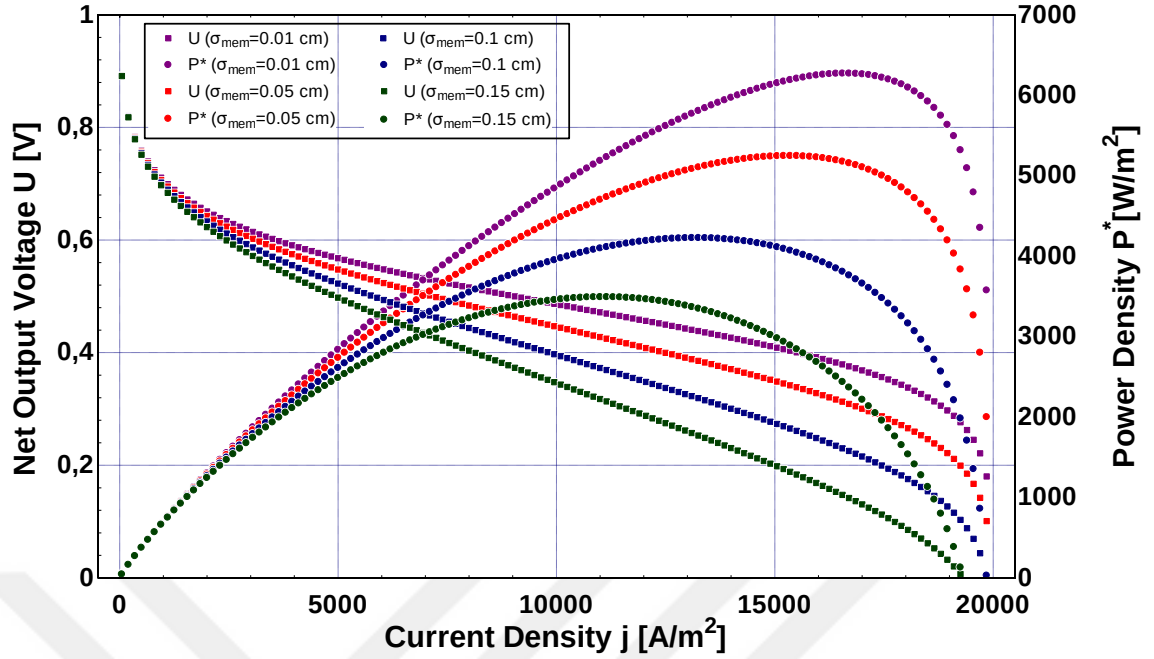


Figure 6.16. The variation of net output voltage and power density versus current density at different membrane thicknesses.

The variation of energy efficiency and entropy production density according to the current density under different membrane thicknesses is given in Figure 6.17. Accordingly, along with considerably increasing maximum power density, energy efficiency remarkably increases, whereas the entropy production density noticeably decreases with decreasing the membrane thickness. In the case that $P^* = P^*_{max}$ and $j = j_p$, the maximum entropy production densities are obtained as 70.5, 66.1, 61.6, and 58.1 $\text{Wm}^{-2}\text{K}^{-1}$. Besides, optimum energy efficiencies are determined as 23.09%, 23.70%, 25.56%, and 28.10% for the membrane thicknesses of 0.15, 0.1, 0.05, and 0.01 cm, respectively. Thus, reducing the membrane thickness increases energy efficiency by 9.94% compared to the base case.

The variation of exergy efficiency and exergy destruction density under different membrane thicknesses is indicated in Figure 6.18. Similarly, reducing the membrane thickness leads to higher exergy efficiency; hence, exergy destruction density noticeably decreases. In the case that $P^* = P^*_{max}$ and $j = j_p$, the maximum exergy destruction densities are obtained as 39981, 39841, 37185, and 35060 Wm^{-2} . Besides, optimum exergy efficiencies are determined as 21.37%, 21.94%, 23.66%, and 26.01% for the membrane thicknesses of 0.15 cm, 0.1 cm, 0.05 cm, and 0.01 cm, respectively.

Thus, decreasing the membrane thickness to 0.01cm enhances exergy efficiency by 9.93%.

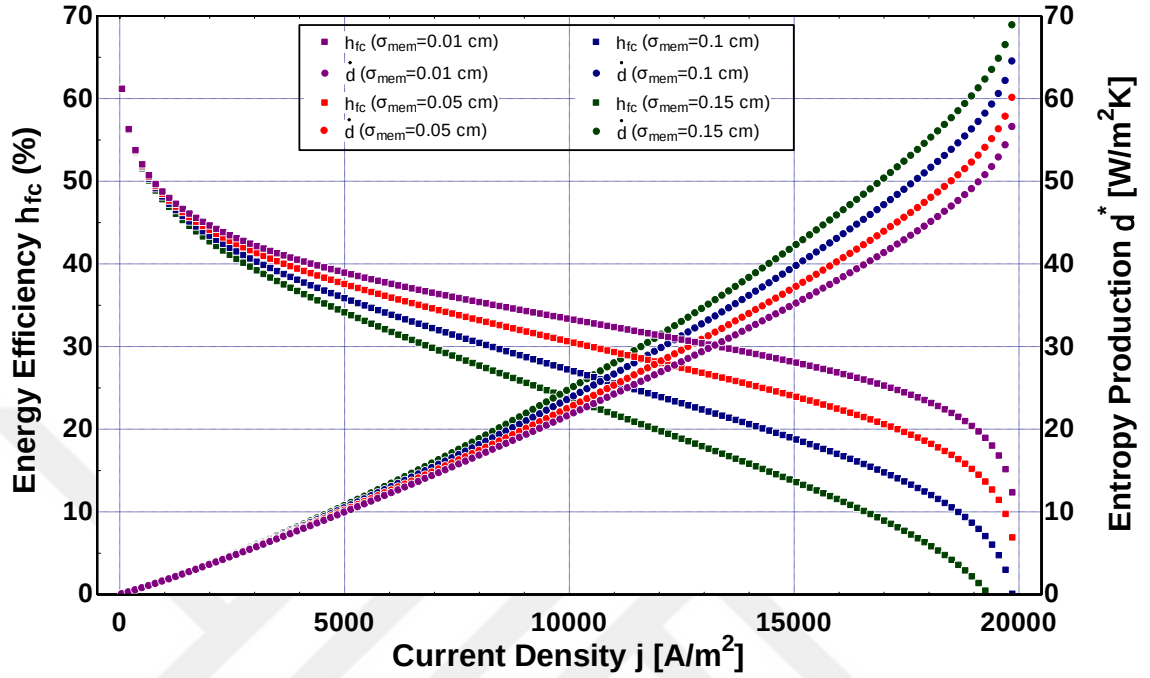


Figure 6.17. The variation of energy efficiency and entropy production density versus current density at different membrane thicknesses.

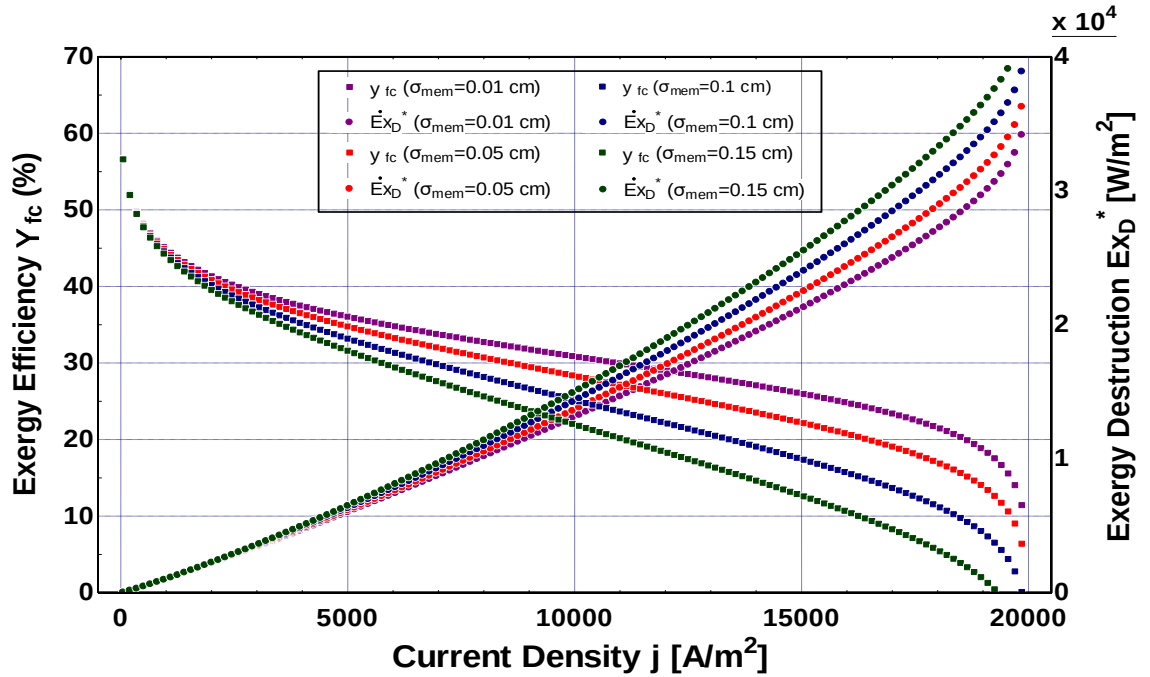


Figure 6.18. The variation of exergy efficiency and exergy destruction density versus current density at different membrane thicknesses.

6.1.2. Results of 1-D & Semi-empirical Model

This section presents the results of a 1-D and semi-empirical model of the HT-PEMFC. Based on the proposed modelling performed utilizing some parameters given in Table 6.3, the generic performance analysis results are reported as the base case.

6.1.2.1. Comparison of Experimental and Numerical Findings

The polarization curve of the HT-PEMFC as a result of the electrochemical analysis presented in Section 4.3.1 is depicted in Figure 6.19. In this figure, four experimental data sets that belong to the different operating temperatures of 393 K (from Ref [191]), 413 K (Ref [192]), 433 K (Ref [193]), and 453 K (Ref [193]) were used to the verification of the proposed model. In addition, the experimental data and modelling results for each temperature of the net output voltage were subjected to different statistical analyses to prove how close the data were to each other.

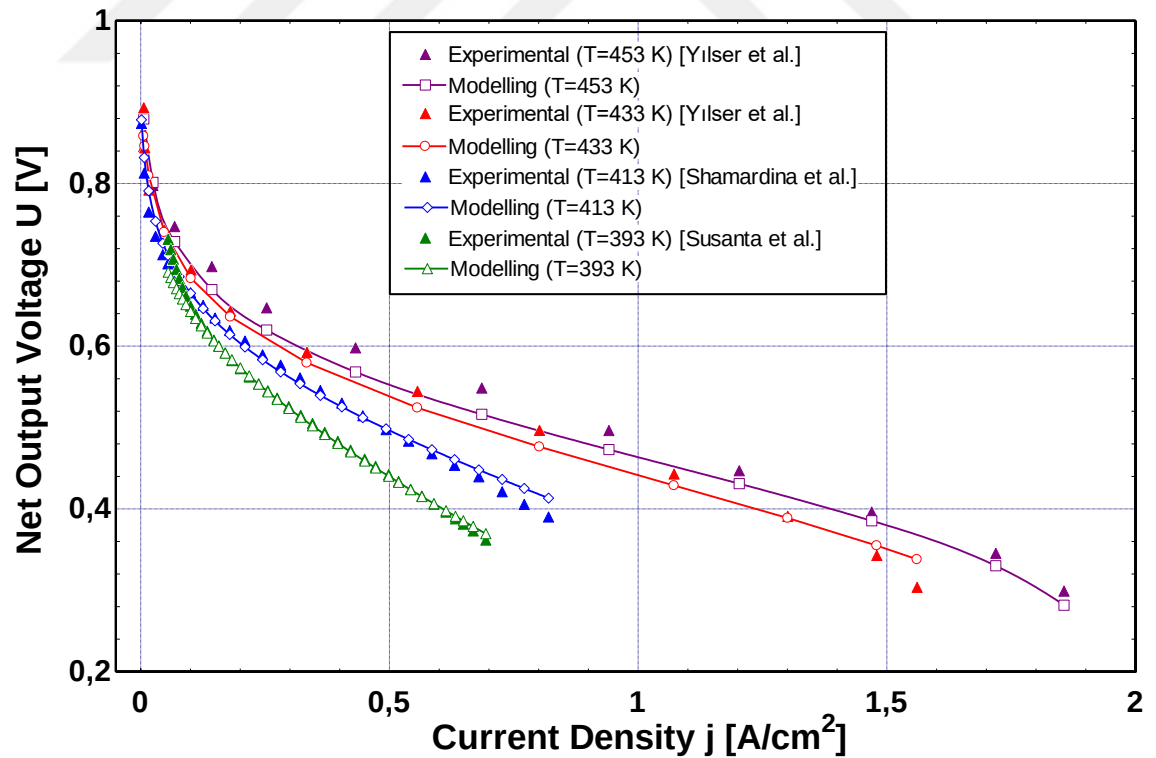


Figure 6.19. The comparison of polarization curves according to different operating temperatures.

The numerical and experimental results in Figure 6.19 were compared using different statistical methods, including the standard deviation (S), R^2 , and adjusted R^2 (R^2_{adj}). Among them, the R^2 correlation distribution of two data sets (experimental and modelling) and residual plots for the operating temperature of 393 K are given in Figure 6.20. In contrast, the same plots for 413 K, 433 K, and 453 K are depicted in Figures 6.21, 6.22, and 6.23, respectively. Accordingly, it is obtained that the modelling findings are in excellent agreement with these experimental data. In addition, the results of these statistical methods used to prove that the regression model is highly reliable and self-consistent are also summarized in Table 6.4. Accordingly, the maximum R^2 and adjusted- R^2 values are determined at 393 K, whereas the minimum R^2 and adjusted- R^2 values are found at 433 K. The minimum R^2 and adjusted- R^2 values are determined as 99.75% and 99.67%, whereas the maximum values are the same and computed as 99.97%. In addition, the minimum S value is computed at 393 K, whereas the maximum is calculated at 433 K.

Table 6.3. Operating and design parameters used in the modelling.

Parameters	Value	Unit
Universal gas constant, R	8.314	J. mol ⁻¹ K ⁻¹
Faraday constant, F	96,485	C.mol ⁻¹
Reference temperature, T_0	298.15	K
Operating temperature, T_{fc}	433.15	K
Anode/Cathode pressure	1:1	atm
Leak current density, j_{leak}	$5.10^{(-3)}$	Acm ⁻²
Limiting current density, j_l	2	Acm ⁻²
Relative humidity, RH	3.8	%
Cathode stoichiometry, λ	2	-
Number of electrons, n	2	-
Doping level, DL	6.2	-
Charge transfer coefficient, α	0.5	-

Table 6.4. Regression analysis results for different temperatures.

Model			
Summary	S	R^2	$R^2 (adj)$
T=393 K	0.0019555	99.97%	99.97%
T=413 K	0.0030977	99.95%	99.94%
T=433 K	0.0110634	99.75%	99.67%
T=453 K	0.0037966	99.97%	99.96%

Apart from these regression analyses, the R^2 correlation distributions between the numerical and experimental data are presented in the following figures. The R^2 distribution and residual plots for the operating temperature of 393 K, 413 K, 433 K, and 433 K are presented in Figures 6.20, 6.21, 6.22, and 6.23, respectively. In these residual plots, the normal probability, the versus fit, histogram graph, and versus graphs are plotted to examine the distribution of numerical residuals and their closeness to each experimental data.

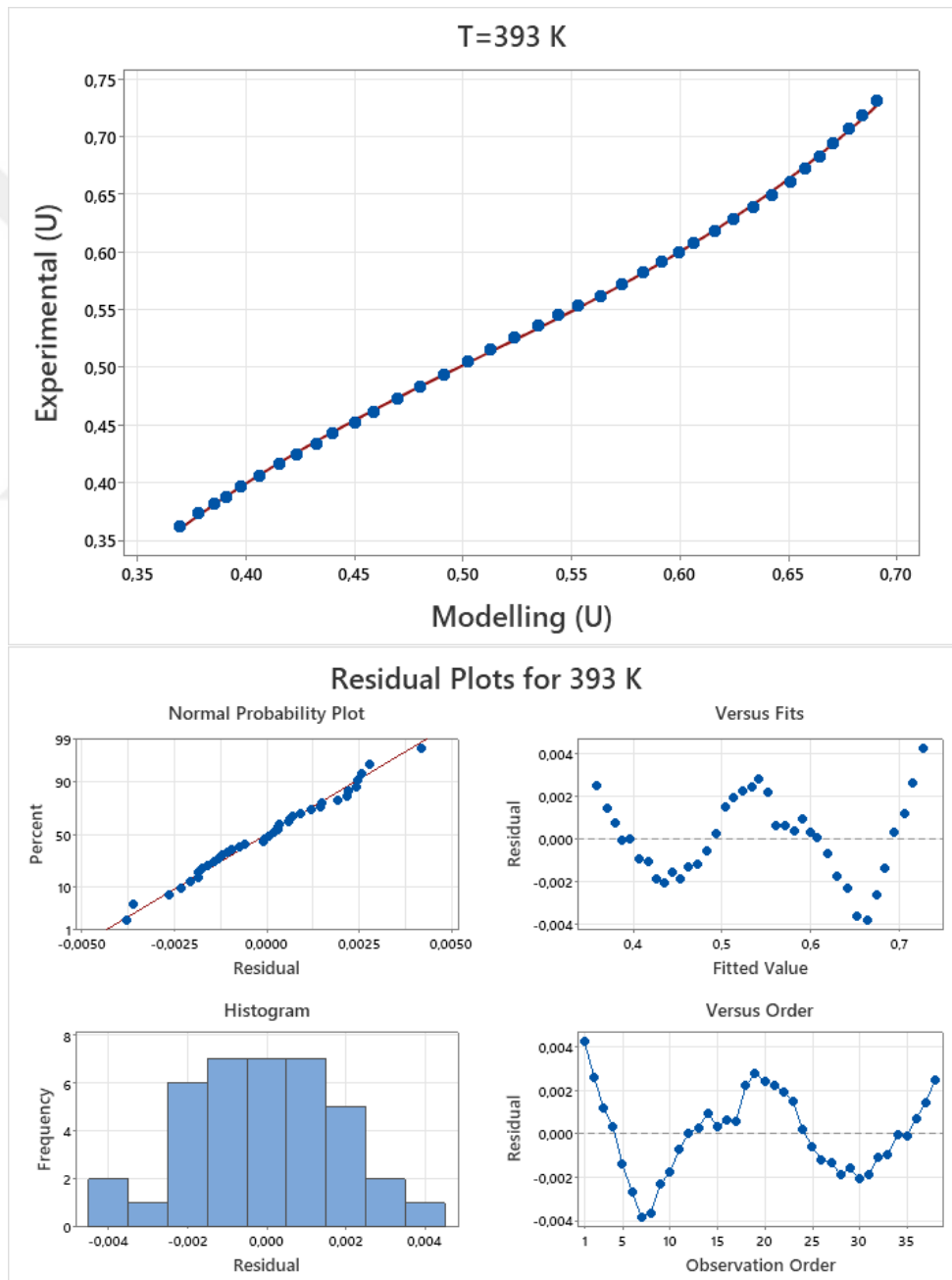


Figure 6.20. Regression model and residual plots for 393 K.

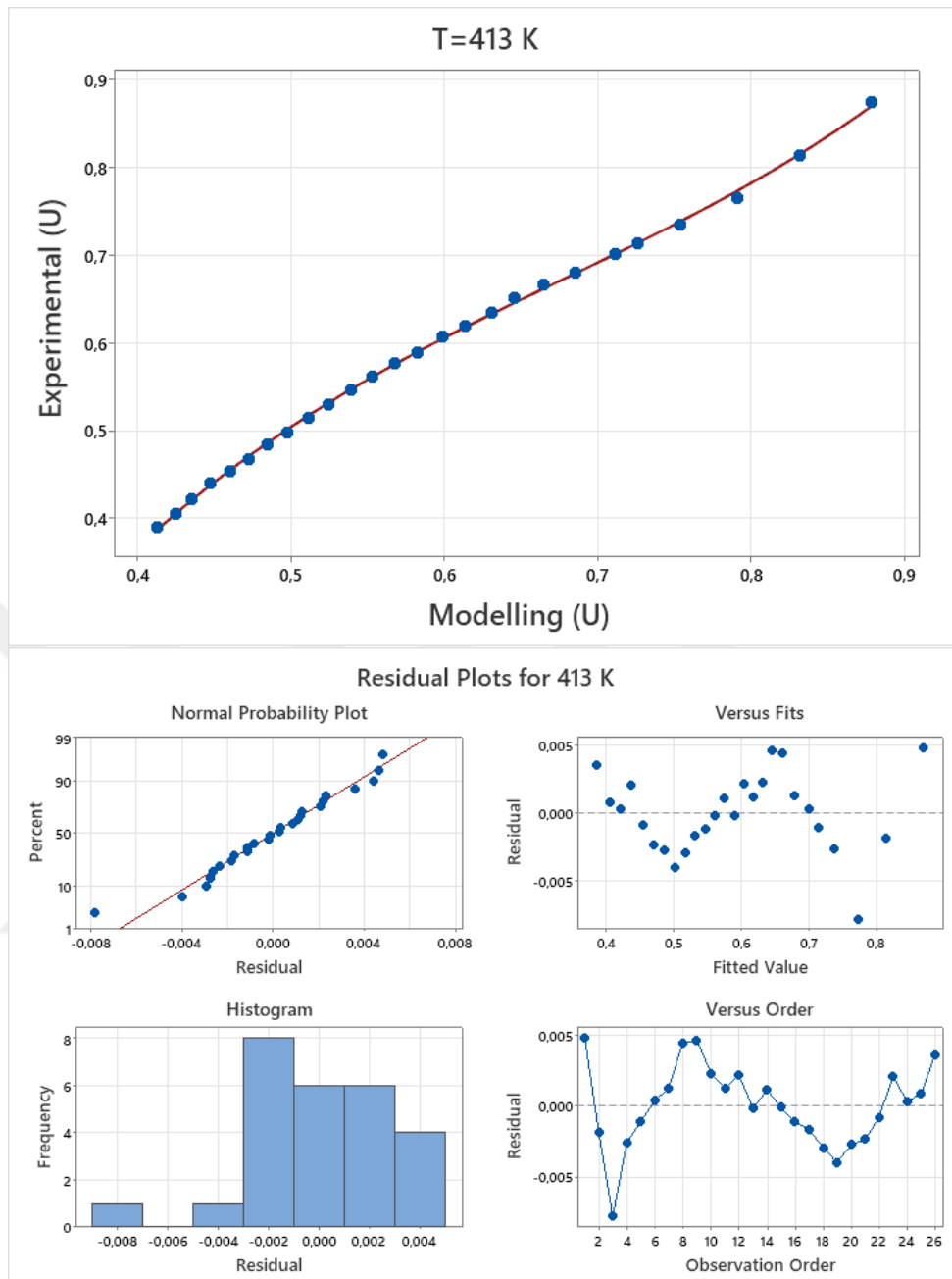


Figure 6.21. Regression model and residual plots for 413 K.

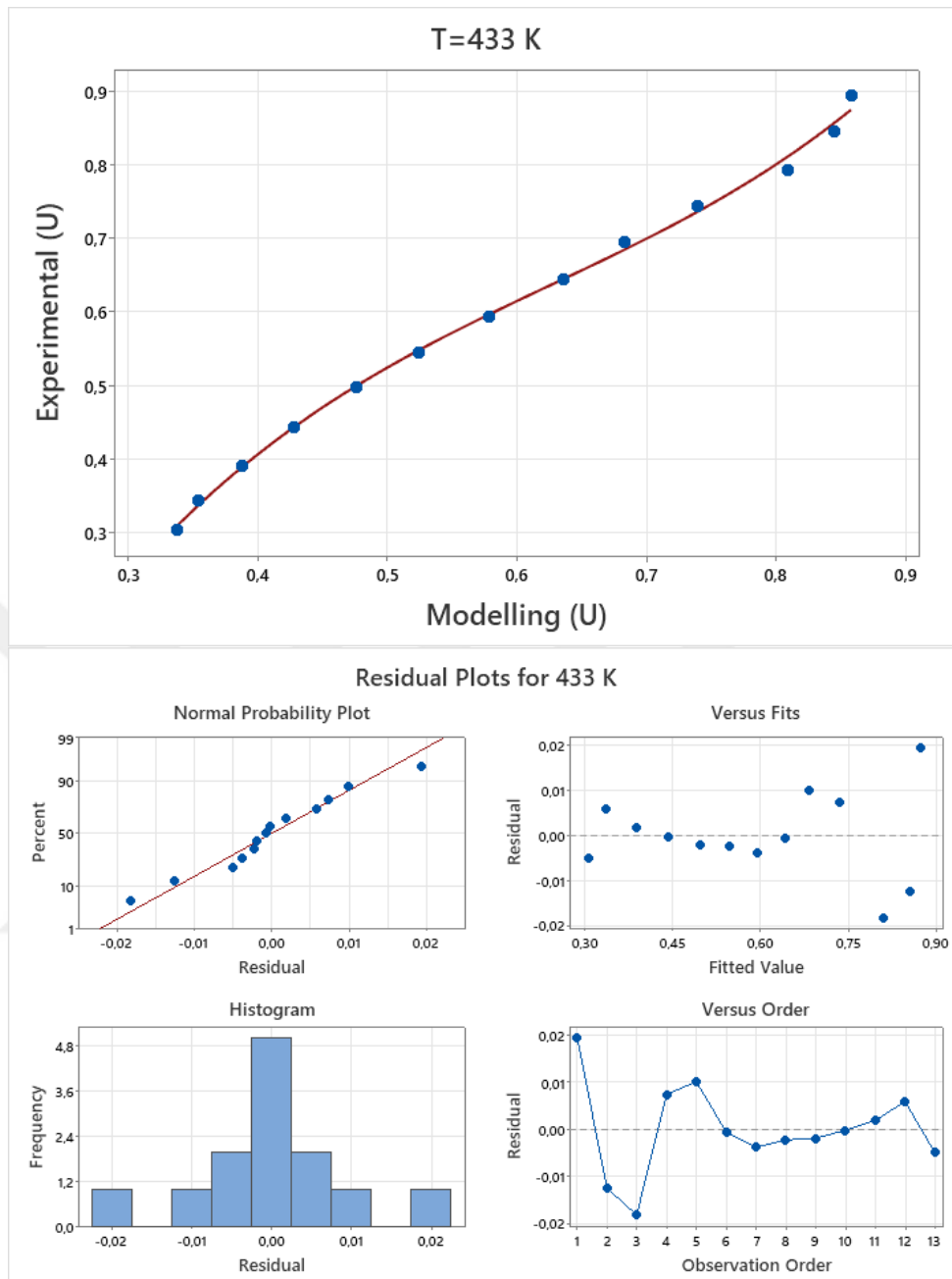


Figure 6.22. Regression model and residual plots for 433 K.

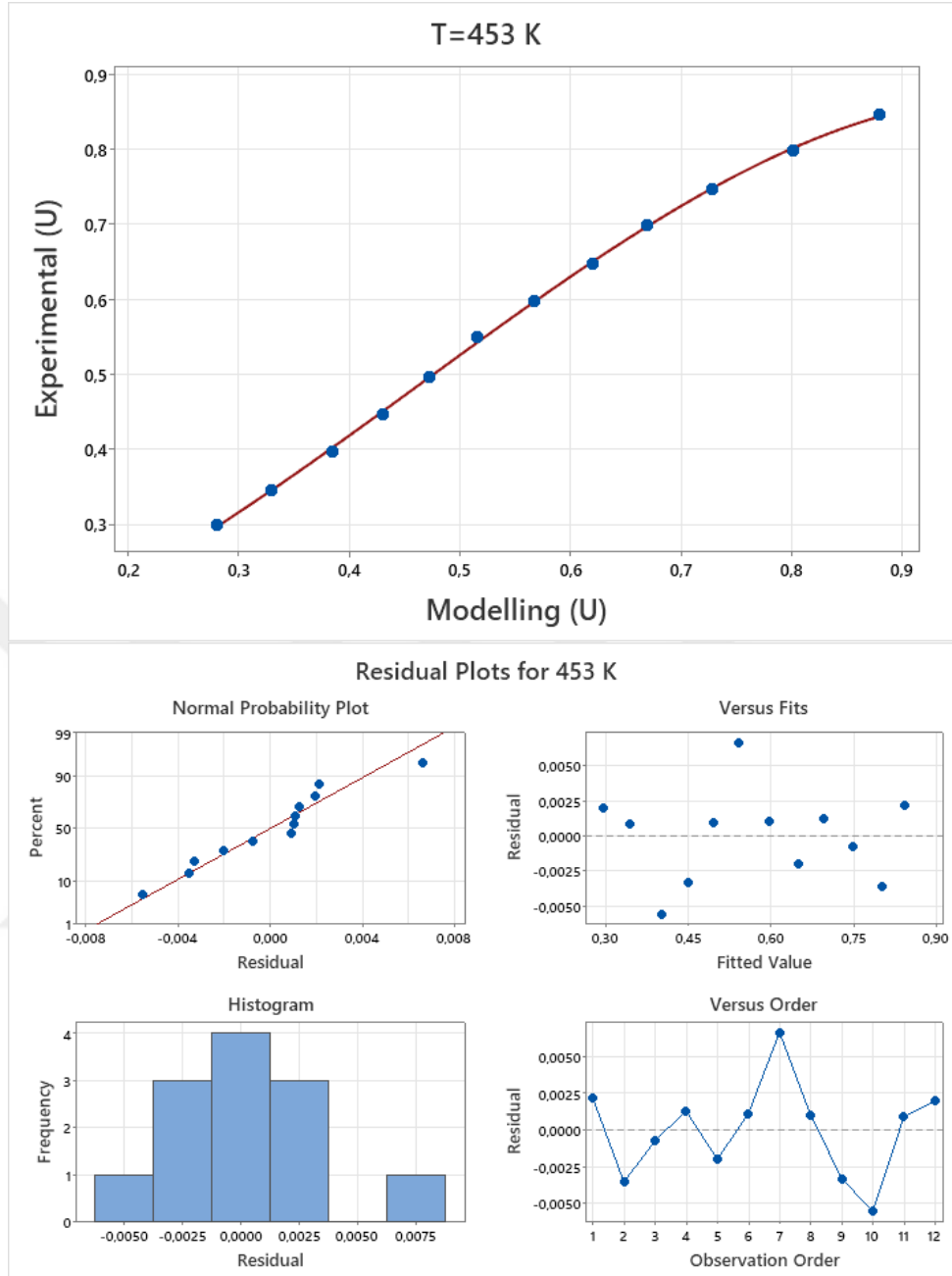


Figure 6.23. Regression model and residual plots for 453 K.

6.1.2.2. Parametric Study Results

Effects of Leak Current Density

The effects of different leak current densities on the net output voltage and power density variation are presented in Figure 6.24, where $P^* = P/A$. Accordingly, increasing the leak current density from 0.005 to 0.5 Acm^{-2} causes a remarkable reduction in the

net output voltage and power density. In the base case, the maximum power density (P^*_{max}) and optimum net output voltage (U_{opt}) values are determined as 0.52 Wcm^{-2} and 0.34 V , where the leak current density is considered 0.005 Acm^{-2} . In addition, the minimum power density and optimum net output voltage values are computed as 0.49 Wcm^{-2} and 0.32 V , respectively, which are 5.77% and 5.88% lower than the base case. This situation is due to the fact that increasing the leak current density enhances the activation overpotential and reduces the net output voltage values.

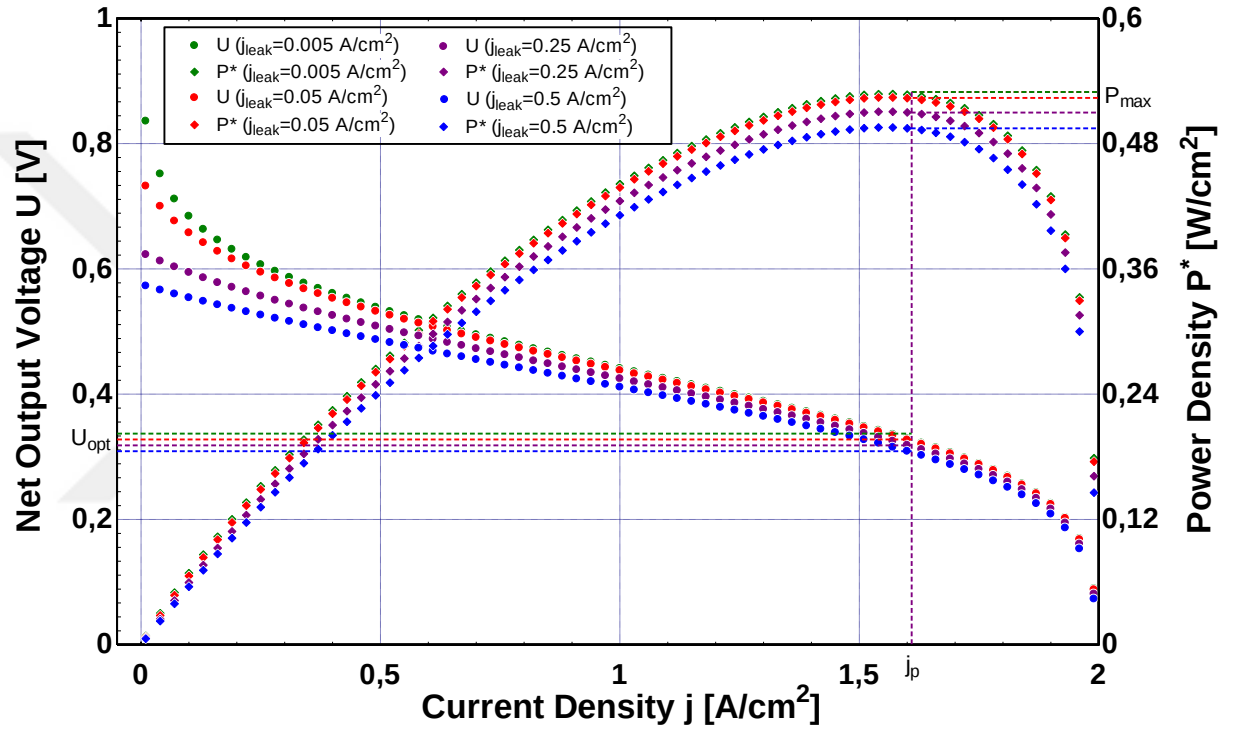


Figure 6.24. The variation of net output voltage and power density versus current density at different leak current densities.

The effects of leak current density on the variation of energy efficiency and entropy production density are presented in Figure 6.25, where $\delta^* = \dot{\delta}/A$. According to the figure, increasing the leak current density from 0.005 to 0.5 Acm^{-2} leads to a slight rise in the entropy production density and a notable drop in energy efficiency. The optimum energy efficiency is determined as 26.99% , and correspondingly, the entropy production density is computed as $0.0033 \text{ Wcm}^{-2}\text{K}^{-1}$, where $P^*=P_{max}$, $U=U_{opt}$, $j=j_p$, and $j_{leak}=0.005 \text{ Acm}^{-2}$. In contrast, the optimum energy efficiency decreases by 5.44% and

drops to 25.52% when the leak current density increases to 0.5 A/cm^2 , compared to the base case.

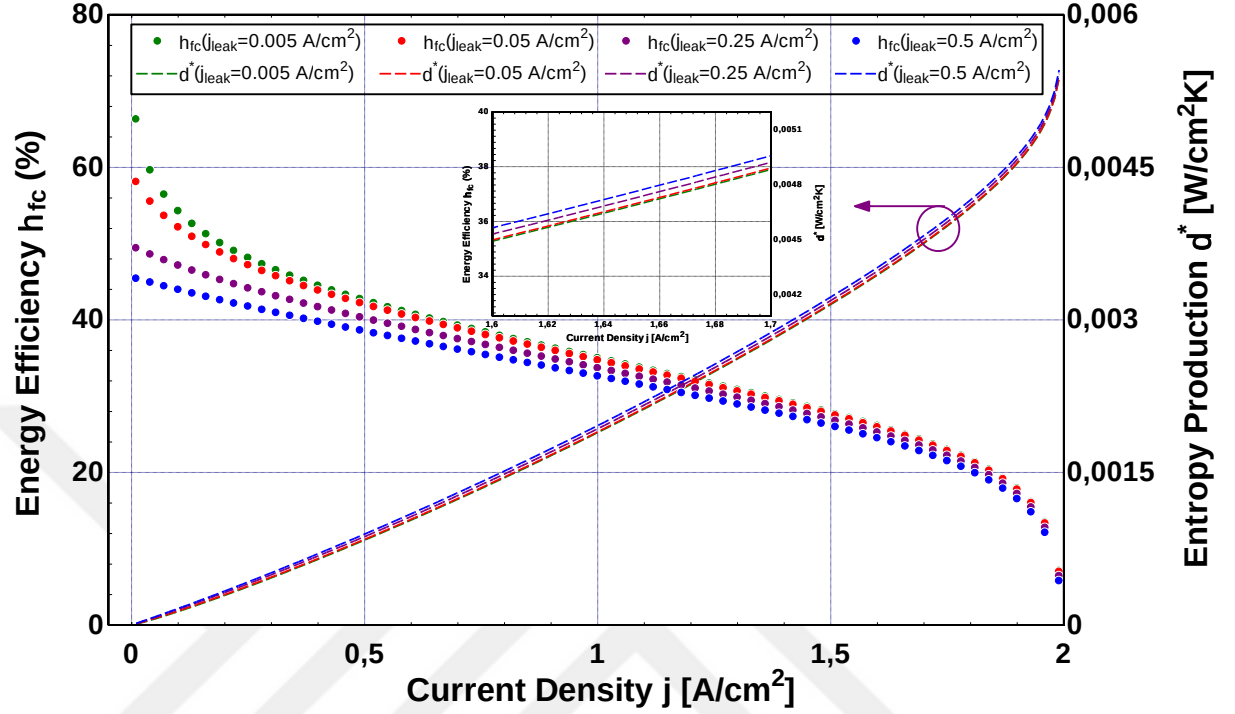


Figure 6.25. The variation of energy efficiency and entropy production density versus current density at different leak current densities.

The effects of leak current density on exergy efficiency and exergy destruction density variation are plotted in Figure 6.26, where $\dot{E}x_D^* = \dot{E}x_D / A$. Accordingly, the inverse correlation between exergy efficiency and exergy destruction density is obtained, as is frequently observed in the literature [194]. The primary reason for this is that exergy destruction density is directly proportional to the difference between $\dot{E}x_{in}$ and $\dot{E}x_{out}$, as well as the useful work stated in Eq (4.93). In the base case, the optimum exergy efficiency and exergy destruction density rates are calculated as 29.01% and 0.707 Wcm^{-2} , respectively. However, the optimum exergy efficiency declines by 5.48% and reduces to 27.42%, whereas the exergy destruction density increases by 1.58% and reaches 0.718 Wcm^{-2} , where $P^* = P_{max}$, $U = U_{opt}$, and $j_{leak} = 0.5 \text{ Acm}^{-2}$.

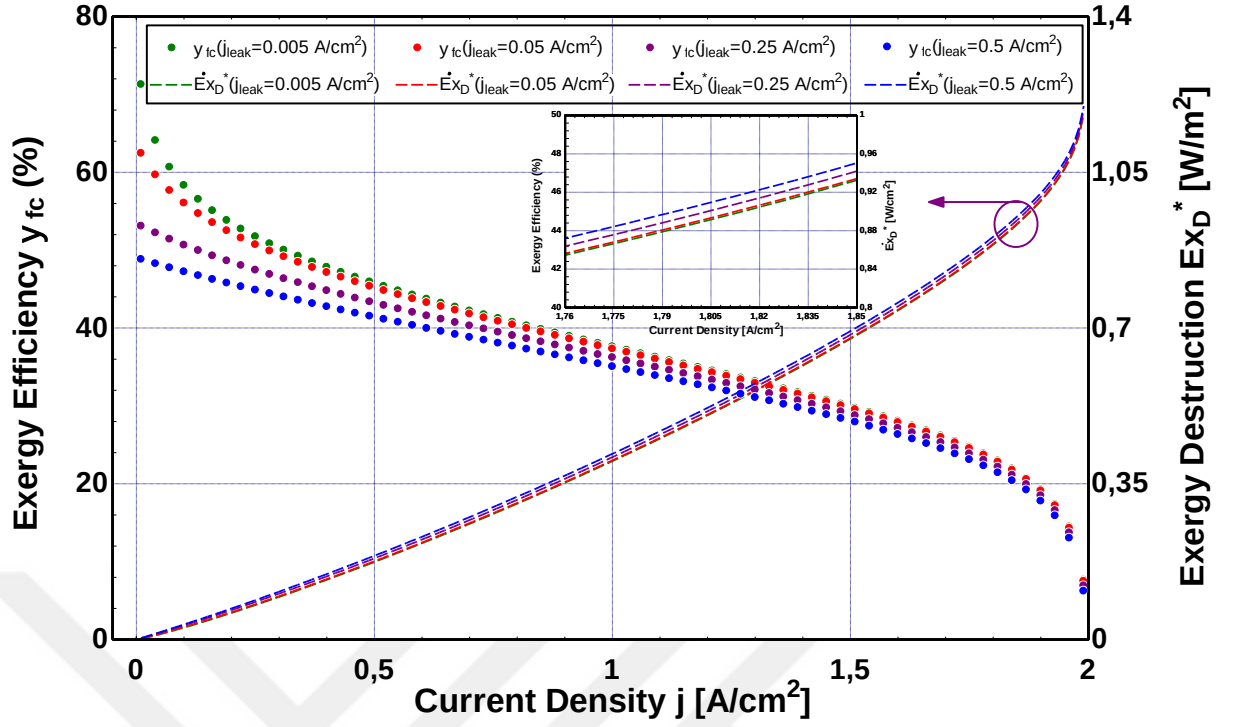


Figure 6.26. The variation of exergy efficiency and exergy destruction density versus current density at different leak current densities.

The effects of the leak current density on the variation of ecological function (E_f) and improvement potential (IP) according to the power output are presented in Figure 6.27. Accordingly, in the base case, E_f first increases in parallel with the increase of power output, starting from almost 0 to 75.6 W, which is the peak level where E_f becomes the maximum ($E_{f,max}$). Along with increasing the leak current density, E_f drops from the peak to 75.3, 74.9, and 68.4 W, respectively, where leak current densities are considered 0.05, 0.25, and 0.5 Acm⁻². The decrease in $E_{f,max}$ values can be explained by the power output decreases, and the entropy production density increases with the leak current density rising. Considering Eq. (4.102), the power is lost due to increasing the entropy generation; hence, $E_{f,max}$ decreases at a constant operating temperature. Similarly, the underlying reason for the rapid decrease in E_f values and the obtaining of negative values after the peak point is that entropy production continues to increase exponentially, whereas the power output values drop slightly. In addition, the IP increases along with power output, although the power output started to decline after a peak, where $P_{fc}=P_{fc,max}$. This can be explained by the fact that IP values are not directly related to power output values, but indirectly. Going further in details, exergy efficiency always decreases with increasing the current density, as presented in

previous figures. Correspondingly, the IP constantly increases since the decrease in exergy efficiency always creates a theoretical potential for keeping the efficiency at its maximum. Finally, increasing the leak current density from 0.005 to 0.5 Acm^{-2} does not significantly alter the maximum improvement potential rate, where $IP=IP_{max}$. However, the optimum IP values increased from 83.4 to 83.5, 83.7, and 86.1 for leak current densities of 0.005, 0.05, 0.25, and 0.5 Acm^{-2} , respectively, where $P_{fc}=P_{fc,max}$, and $j=j_p$.

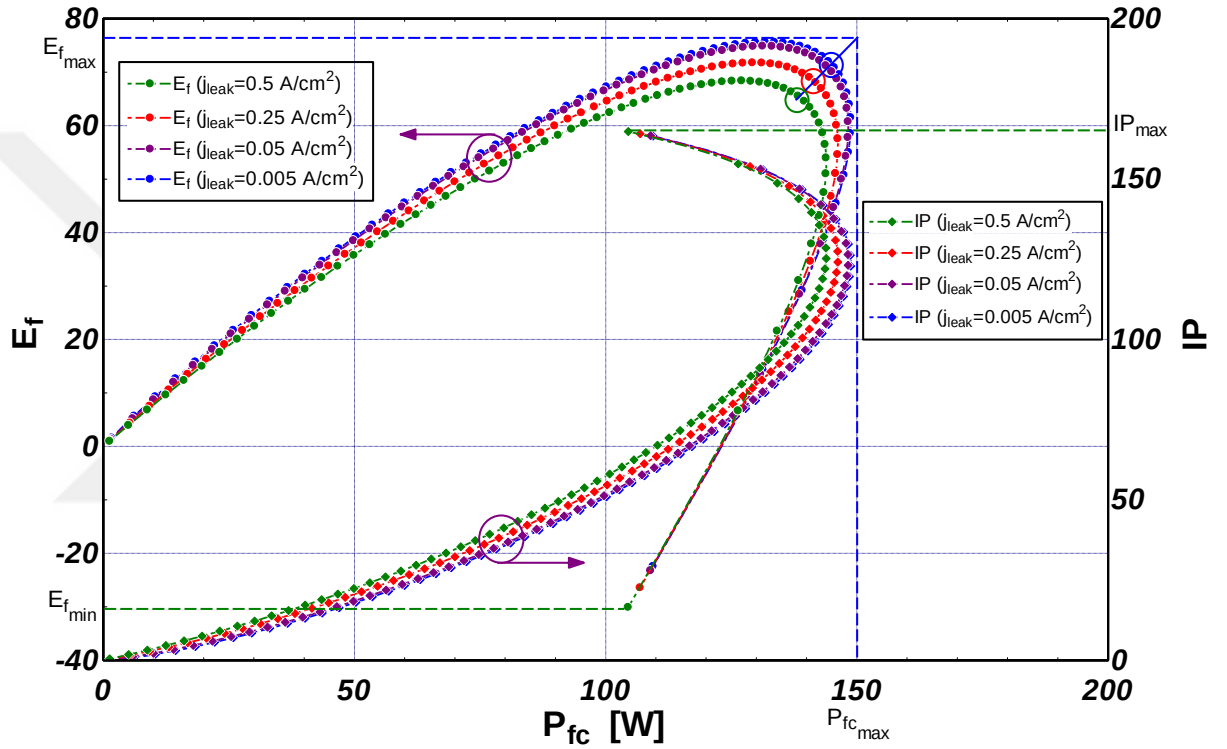


Figure 6.27. The variation of E_f and IP versus power output at different leak current densities.

The effects of leak current density on the variation of ecological coefficient of performance ($ECOP$) and ecological function (EOF) according to the power output are plotted in Figure 6.28. Accordingly, $ECOP$ continually decreases along with the power output, although the power output first increases from 0 to the peak, then decreases with the current density. This is because $ECOP$ is a ratio of the power output to the entropy generation, and the entropy production density is sharply increasing compared to the power output along with increasing the current density. The maximum $ECOP$ ($ECOP_{max}$) values are determined as 10.9, 7.2, 5.8, and 3.0 for leak current

densities of 0.05, 0.25, and 0.5 Acm^{-2} , respectively. In addition, the effect of leak current density is negligible on the minimum $ECOP$ values ($ECOP_{min}$). Furthermore, the variation of EOF concerning the power output is relatively similar to that of the E_f . The main difference is that EOF focuses on the $\dot{E}_{x_D}$; hence, it also depends on the input and output exergy rate. Accordingly, EOF_{max} values are obtained as 52.0, 51.6, 51.2, and 44.3 for leak current densities of 0.05, 0.25, and 0.5 Acm^{-2} , respectively.

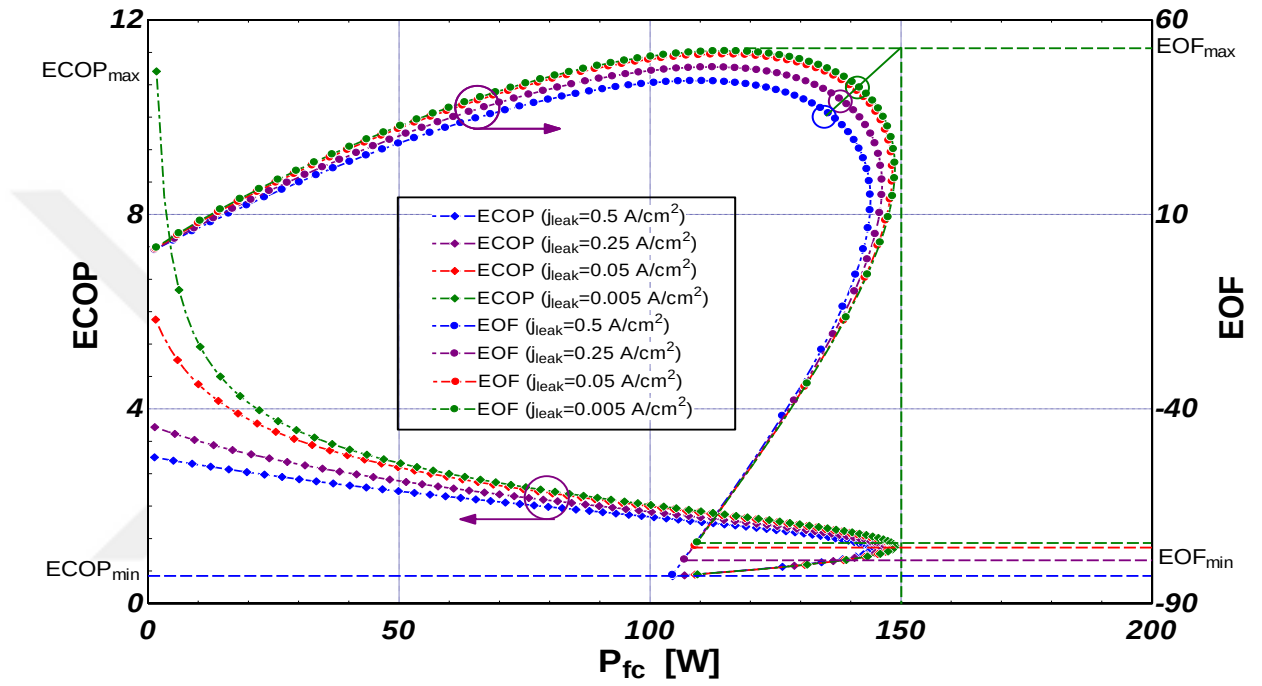


Figure 6.28. The variation of $ECOP$ and EOF versus power output at different leak current densities.

Effects of Doping Level

The doping level is also a critical parameter affecting the performance of the HT- PEMFC and is specified as the number of PA molecules per PBI. Since the increase in the doping level drops the required activation energy of the membrane (E_a), and thus, decreases the ohmic voltage (E_{ohm}), the optimum net output voltage and, correspondingly, power density increase, as indicated in Figure 6.29. Accordingly, a slight increase in the optimum net output voltage (U_{opt}) values and a considerable rise in the power density is obtained by raising the doping level from 6.2 to 30. To briefly describe, the maximum power density (P_{max}^*) values are calculated as 0.52, 0.57, 0.62,

and 0.64 Wcm^{-2} and, correspondingly, U_{opt} values are computed as 0.34, 0.35, 0.37, and 0.38 V, whereas the optimum current densities are determined as 1.55, 1.62, 1.67, and 1.68 Acm^{-2} for doping levels of 6.2, 10, 20, and 30, respectively. Thus, P_{max}^* values increase by 9.62%, 19.23%, and 23.07, whereas U_{opt} values rise by 2.94%, 8.82%, and 11.76%, compared to the base case. Here, it is worth noting that the increase in the doping level is no longer significant after the level of 30. This is because the E_a decreases with increasing the doping level, but the pre-exponential coefficient for the doping level (A_0) significantly increases; hence the proton conductivity (κ_{mem}) becomes nearly the same. Therefore, the E_{ohm} does not considerably alter, and the U_{opt} and P_{max}^* values become almost constant.

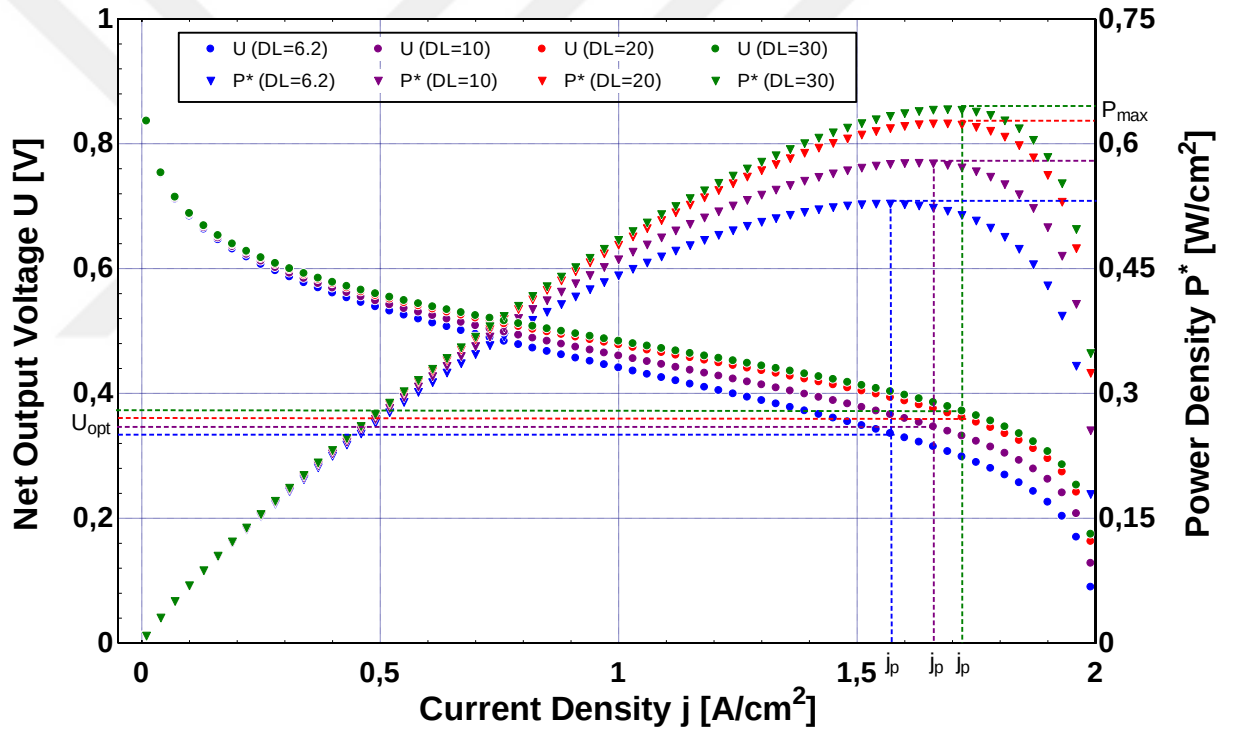


Figure 6.29. The variation of net output voltage and power density versus current density for different doping levels.

The effects of different doping levels on the variation of energy efficiency and entropy production density are plotted in Figure 6.30. Accordingly, the maximum energy efficiency does not display a remarkable change in the low-current density region. However, energy efficiency noticeably rises as a general trend, whereas the entropy production density drops slightly with the doping level. The optimum entropy production density values are computed as 0.0032, 0.0033, 0.0034, and 0.0034

$\text{Wcm}^{-2}\text{K}^{-1}$, whereas the optimum energy efficiency values are found to be 26.99%, 28.23%, 29.63%, and 30.25% for the doping levels of 6.2, 10, 20, and 30, respectively, where $P^*=P_{max}^*$ and $j=j_p$. Thus, the contribution of doping level to the energy efficiency enhancement is computed as 4.59%, 9.78%, and 12.07%, compared to the base case.

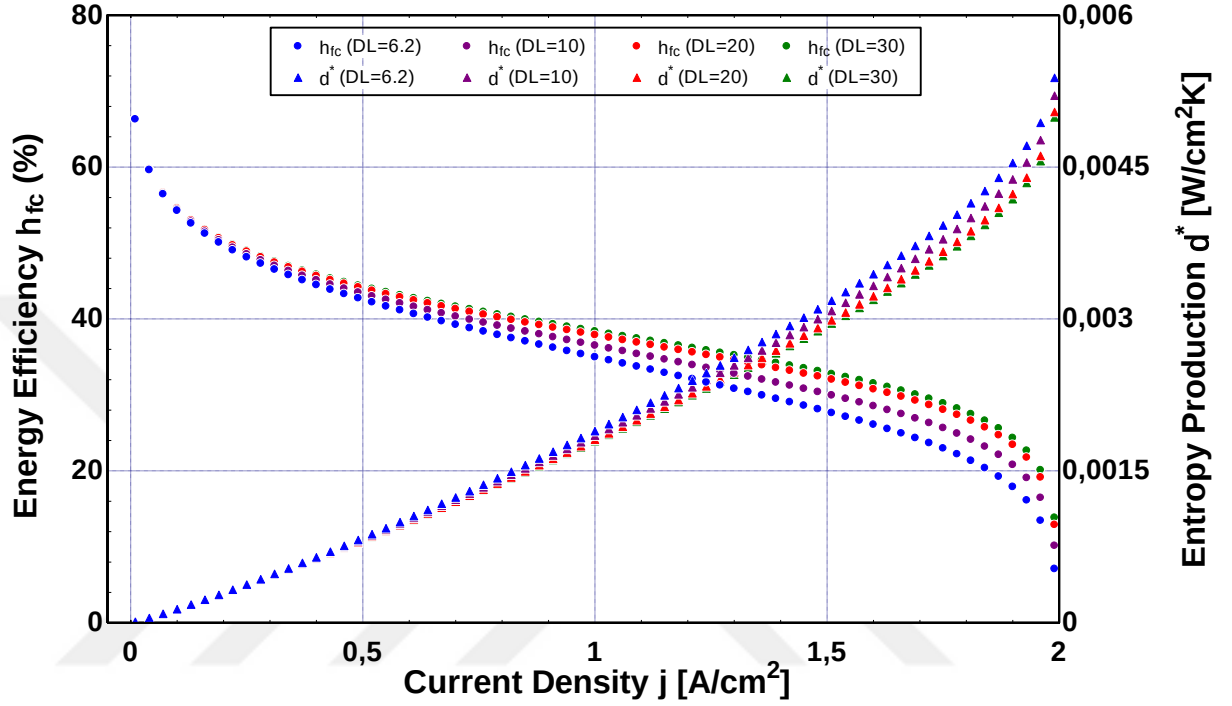


Figure 6.30. The variation of energy efficiency and entropy production density versus current density for different doping levels.

The effects of doping level on the variation of exergy efficiency and exergy destruction density are depicted in Figure 6.31. Accordingly, although the maximum exergy efficiency in the low-current density region is almost the same, exergy efficiency gradually rises with increasing the doping level from 6.2 to 30. In addition, exergy destruction density values also rise with growing doping levels; however, this increase is more limited compared to the exergy efficiency. The optimum exergy destruction density values are determined as 0.707, 0.725, 0.731, and 0.728 Wcm^{-2} , whereas the optimum exergy efficiency values are obtained as 29.01%, 30.34%, 31.85%, and 32.52% for the doping levels of 6.2, 10, 20, and 30, respectively, where $P^*=P_{max}^*$ and $j=j_p$. Thus, exergy efficiency is boosted by 4.58%, 9.78%, and 12.09%, whereas the increase in the optimum exergy destruction density values is realized by 2.54%, 3.39%, and 2.97%, compared to the base case.

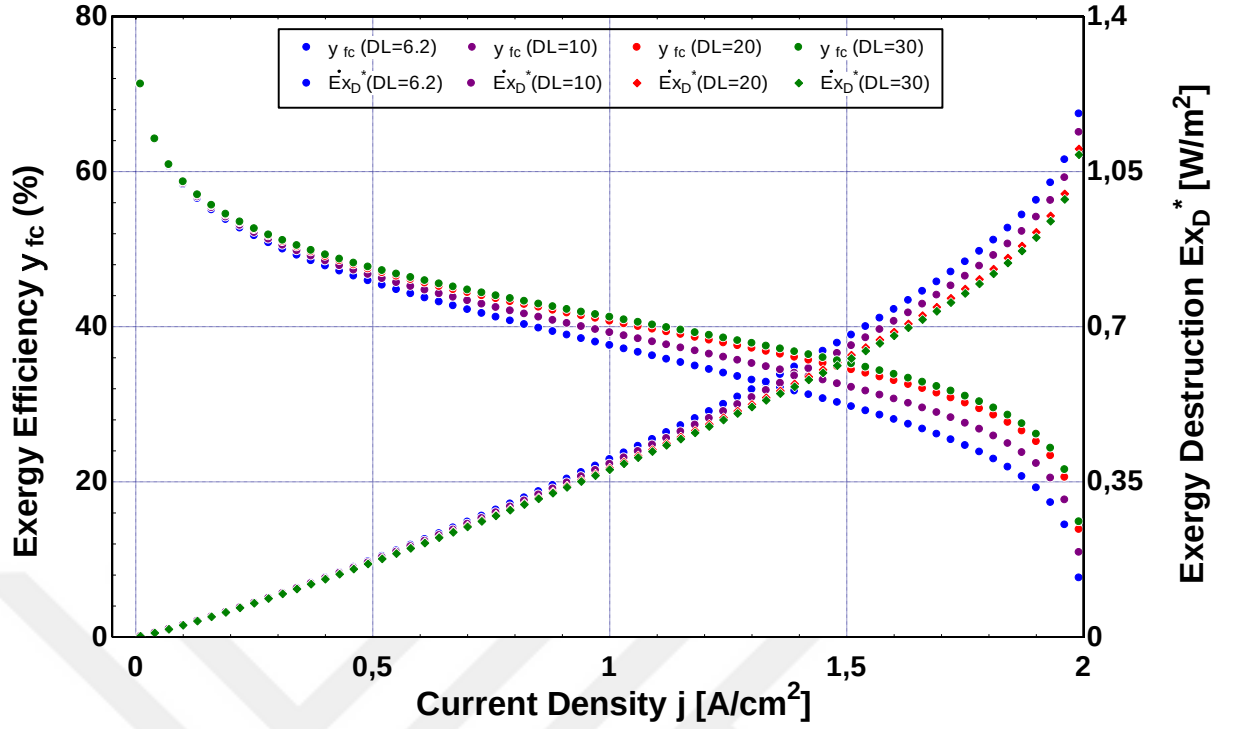


Figure 6.31. The variation of exergy efficiency and exergy destruction density versus current density for different doping levels.

The effects of doping level on the variation of E_f and IP to the power output are represented in Figure 6.32. According to the figure, the maximum E_f ($E_{f,max}$) values increase with rising doping levels, whereas the maximum IP (IP_{max}) values decrease with the power output. $E_{f,max}$ values are obtained as 75.6, 84.3, 93.2, and 96.5, whereas IP_{max} values are determined as 163.4, 159.7, 156.0, and 154.7 for doping levels of 6.2, 10, 20, 30, respectively. Thus, it is proven that increasing the doping level increases exergy efficiency and E_f and decreases the IP .

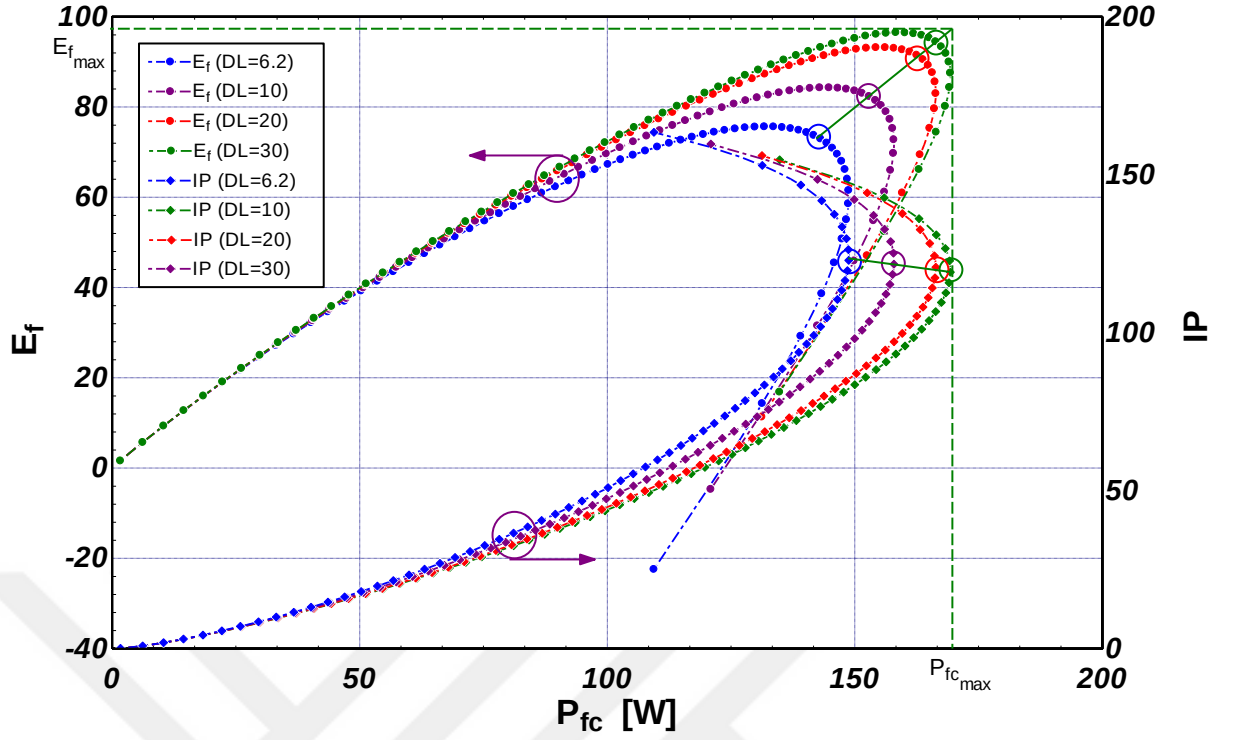


Figure 6.32. The variation of E_f and IP versus power output for different doping levels.

The effects of doping level on the variation of $ECOP$ and EOF to the power output are indicated in Figure 6.33. Accordingly, the contribution of doping level to the enhancement of $ECOP_{max}$ values is negligible. However, $ECOP_{min}$ values increase from 0.59 to 0.81 when the doping level increases from 6.2 to 30, respectively. In addition, increasing the doping level increases EOF_{max} values, which are determined as 52.0, 58.5, 65.7, and 68.5 in doping levels of 6.2, 10, 20, and 30, respectively. Thus, it is obtained that EOF values increase with the maximum power point, $P_{fc,max}$, whereas $ECOP$ continually decreases along with the power output.

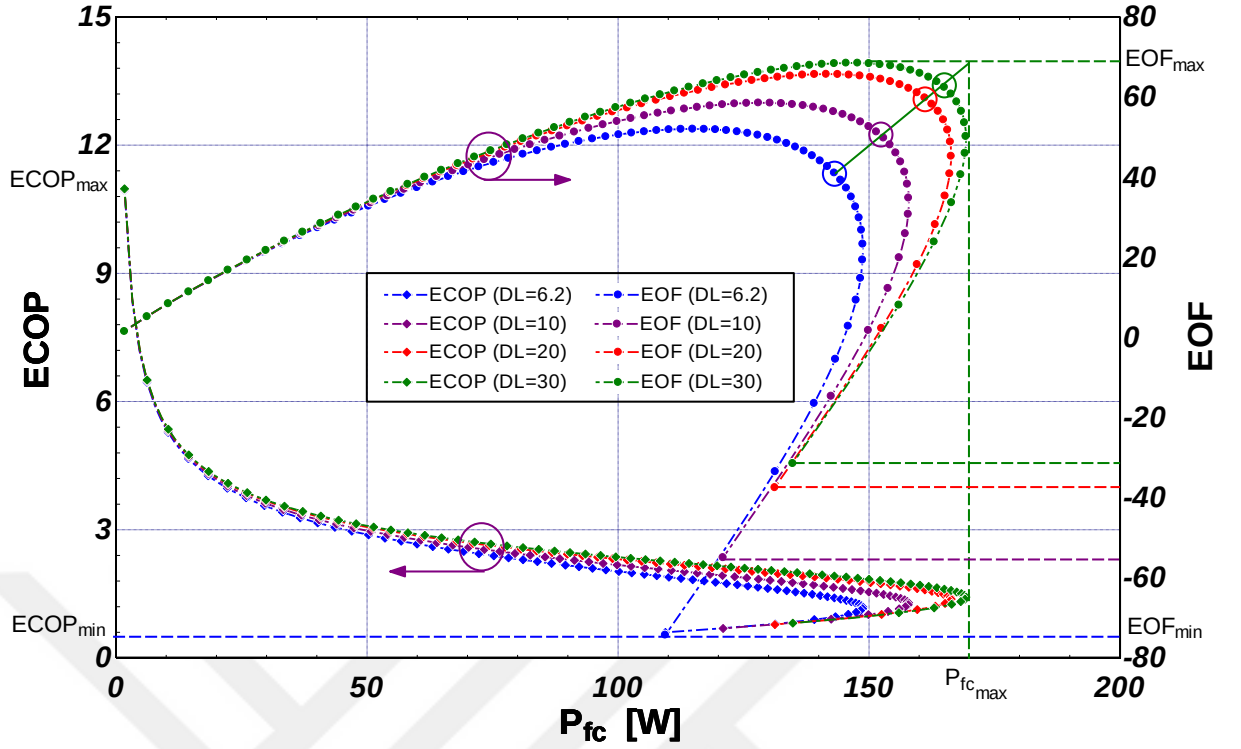


Figure 6.33. The variation of $ECOP$ and EOF versus power output for different doping levels.

6.2. PERFORMANCE RESULTS OF HYBRID SYSTEM

This section presents the results and discussion of the proposed hybrid system. First of all, the performance of a grid connected SPP installed in Sakarya, Turkey, and commissioned last year will be discussed. The fixed solar PV system with the optimal annual tilt angle, whose design phases were described in detail in Section 5.1.1, was analysed and discussed. As mentioned earlier, 4 inverters, each with 60 kW_e AC power and 66 kVA maximum output power, were used in the plant, and the data of these inverters were monitored through the SCADA system. The data were received at 15-minute intervals for 24 hours and processed into the system. The monthly amount of energy produced by these inverters is demonstrated in Figure 6.34. Accordingly, the minimum energy production was performed as 1488.75 kWh in January in the red-coloured inverter. In contrast, the maximum energy production was performed as 12155.19 kWh in July in the yellow-coloured inverter.

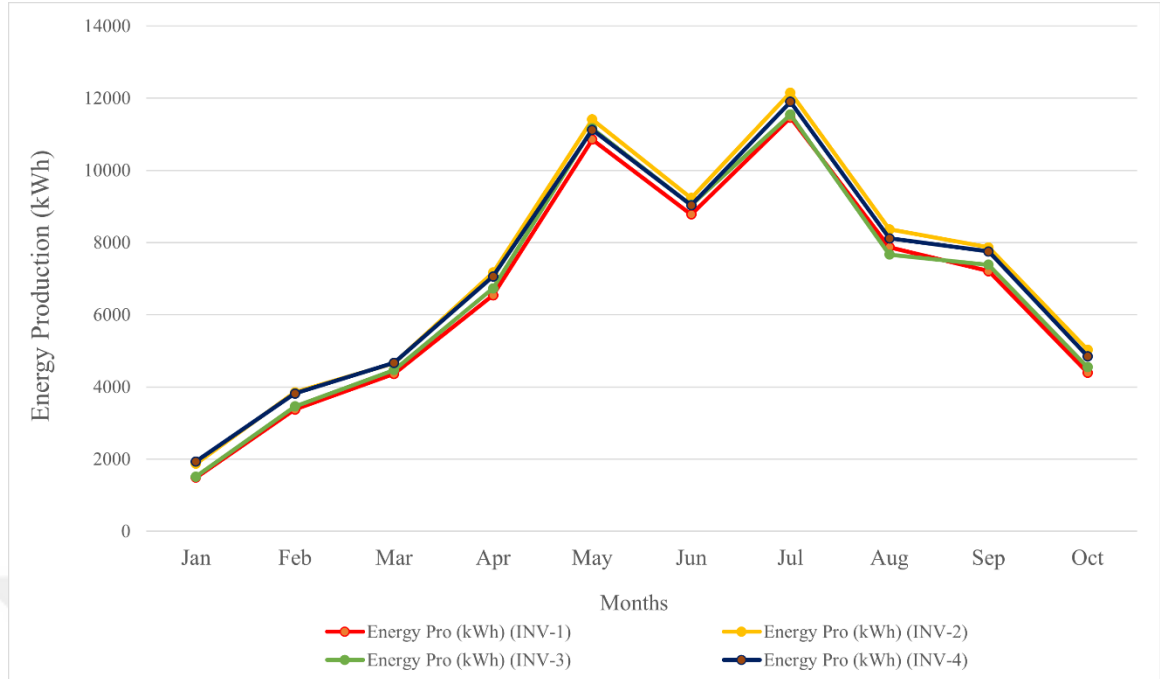


Figure 6.34. Monthly energy generated by each inverter in kWh.

The monthly energy production considering all inverters is presented in Figure 6.35. Accordingly, it is observed that energy production increases from January to July along with increasing global solar radiation, except in June. After July, the peak level for both energy production and solar radiation, the energy generation decreases with decreasing the radiation. During the year, the minimum energy production was obtained as 6813.71 kWh in January, whereas the maximum energy production was obtained as 47065.72 kWh in July. Apart from the summer months, a very high rate of energy production was also realised in May with 44552.13 kWh. Finally, as depicted in the figure, the statistics belonging to November and December are not yet available since this plant is newly established.

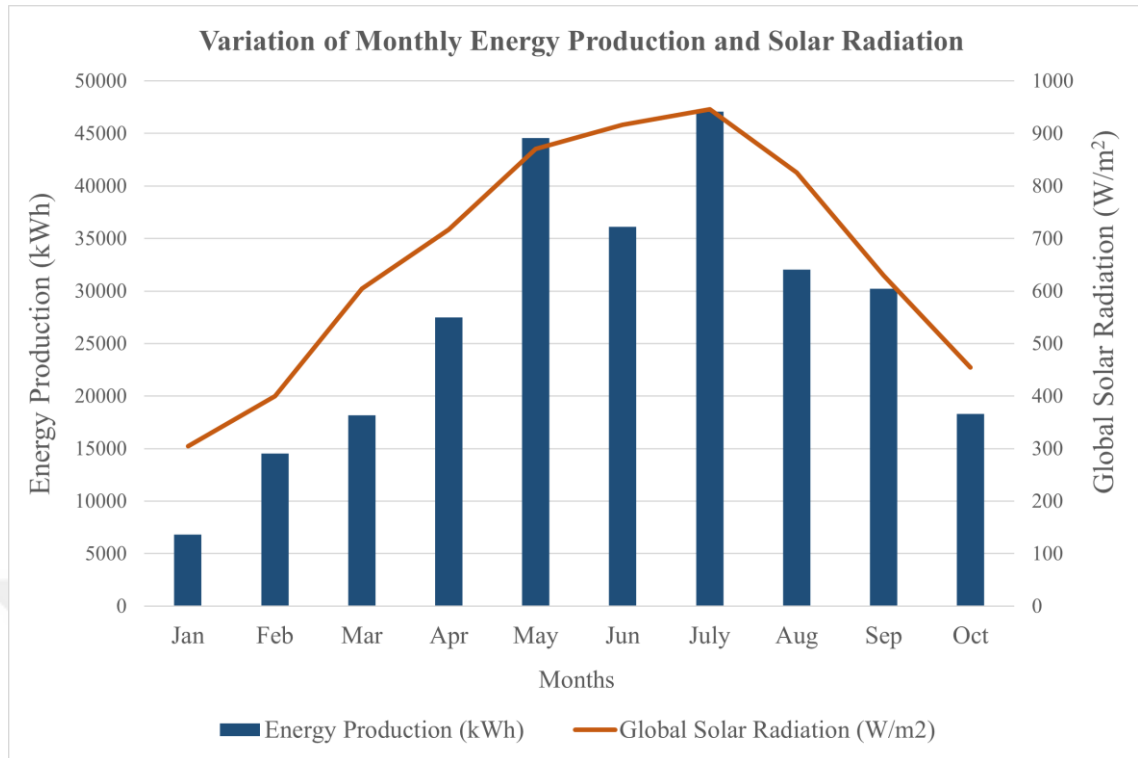


Figure 6.35. Total monthly energy production of the PV system in kWh.

In order to demonstrate the fluctuation of solar energy more clearly, the daily energy production for a sample month, September, is presented in Figure 6.36. According to the figure, it is possible to notice that the energy production from the solar PV system is highly affected by weather conditions. It is obtained that energy generation is at the maximum level on clear and sunny days, whereas it decreases considerably on days where the weather is overcast, cloudy, or rainy. In addition, the minimum energy generation was 363.27 kWh on 28 September, whereas the maximum energy production was 1385.50 kWh on 8th September.

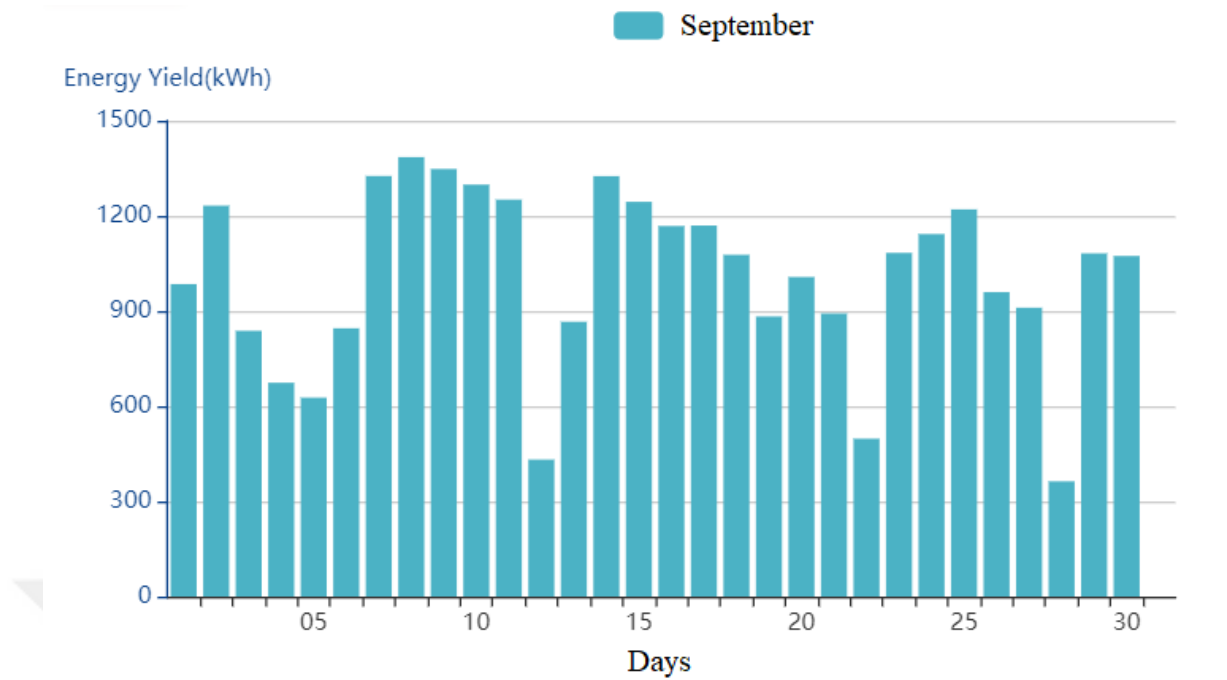


Figure 6.36. Daily energy production in kWh during September.

The variation of input power (DC) and inverter cabinet temperature on 8th September is depicted in Figure 6.37. According to the figure, it is observed that energy production takes place effectively from 7 am to 7 pm, along with the sun's rays falling on the PV modules. Depending on the increase in air temperature, it is obtained that the inverter cabinet temperature increases from 7 am to 3 pm and decreases until 8 pm with the decrease in the ambient temperature. Although the ambient temperature continues to decrease from 8 pm to midnight, the cabin temperature does not alter. This situation can be explained as follows. The maximum operating and standby ambient temperatures of solar inverters are generally provided on their datasheets. These values specify where the inverter should be installed and in which areas it may be utilised. In solar-exposed installations during the summer, the inverter temperature might reach 80 to 90 °C. Therefore, inverters are installed in sheltered places that are not directly exposed to the sun. Hence, the inverter temperature remains constant in the evening unless there is a significant drop in the ambient temperature. Furthermore, the maximum input power was performed as 49.5 kW in inverter-4 at 1.30 pm, whereas the cabinet temperature reached 65.5 °C in the same inverter at that time. In addition, the maximum cabinet temperature was observed as 67.5 °C in inverter-4 at 3.00 pm, whereas the minimum temperature was 41.2 °C in inverter-3 at 06.30 am.

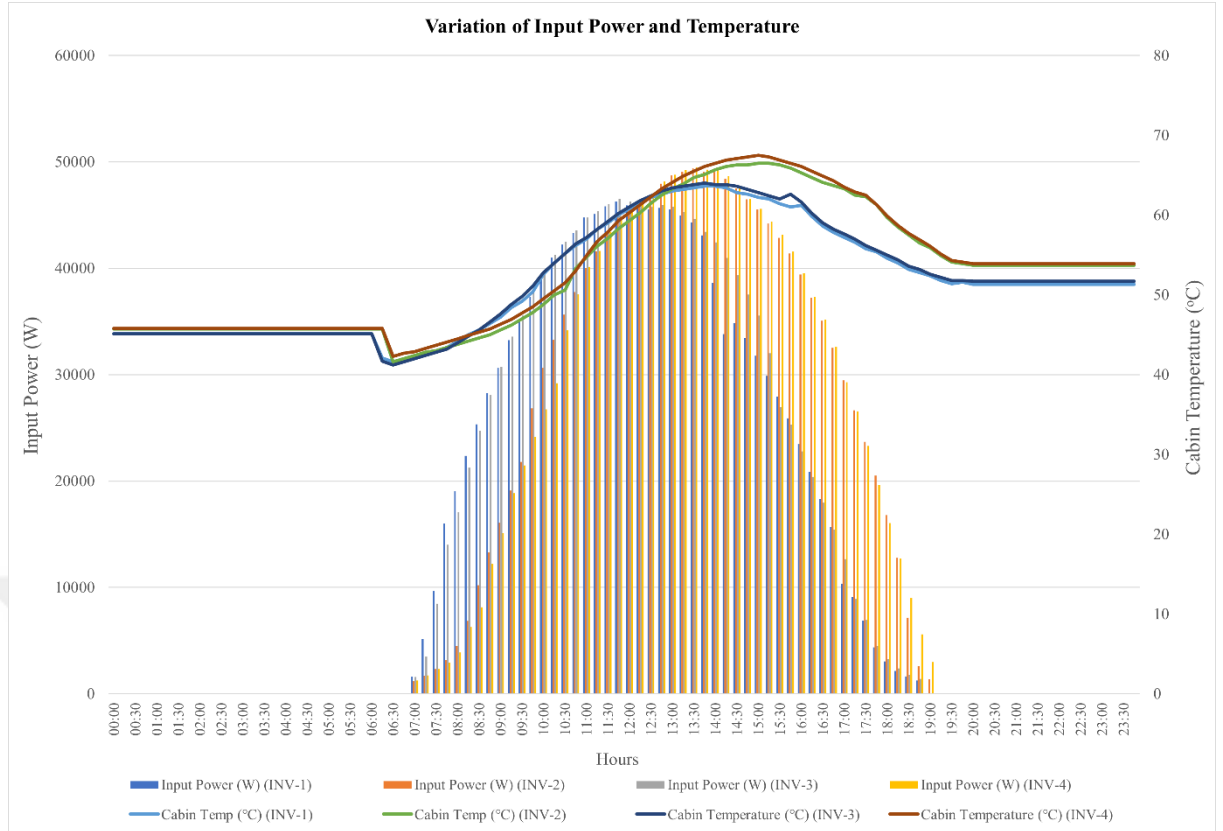


Figure 6.37. The variation of input power and inverter cabin temperature on 8th September.

The variation of active power (AC) and the inverter efficiency on 8th September is illustrated in Figure 6.38. As it is known, the power consumed or utilised in an AC circuit refers to the true, real, or active power. It is measured in kilowatts (kW) or MW. It is the actual outcomes of the electrical system which runs the electric circuits or load. Therefore, the DC power generated by PV modules must be converted to AC before it can be utilised for residential or industrial purposes by being sent to the grid. This transformation is performed by DC/AC inverters. Inverters typically accomplish this conversion process with high efficiency, although this efficiency might vary slightly depending on the intensity of solar radiation and, therefore, the DC power generated. Accordingly, the minimum inverter efficiency was found to be 75.48, 72.47, 75.28 and 74.86% for inverter-1, 2, 3 and 4, respectively, at 06.30 am. From this moment, the inverter efficiency increases rapidly and reaches slightly over 98% during the noon. The maximum efficiency was obtained as 98.60% at inverter-4 between 5:30 and 6:15 pm. In addition, the active power graph is similar to the input

power, as expected. Furthermore, the maximum active power was determined as 48.5 kW in the inverter-4 at 01:30 pm, and it is zero in the absence of radiation.

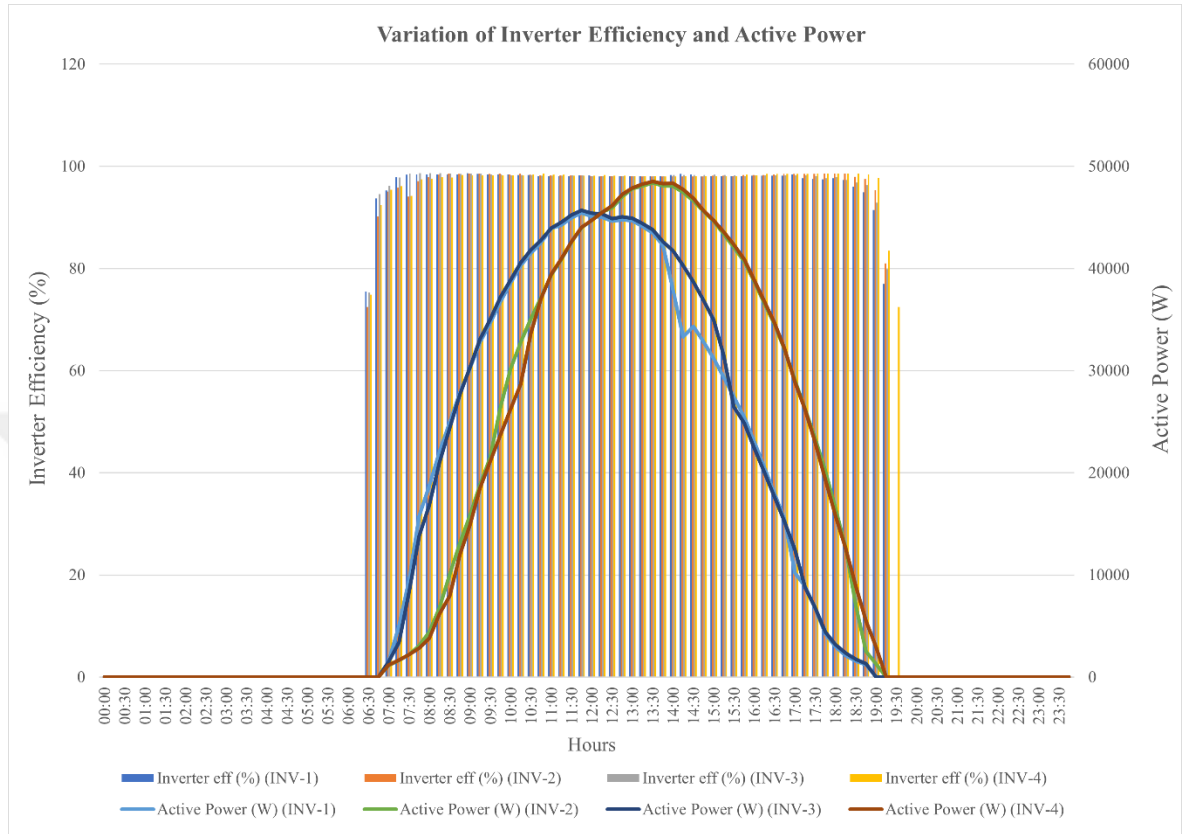


Figure 6.38. The variation in active power and inverter efficiency on 8th September.

As discussed in Section 5.3, the electricity consumption of one residency, where a family of 4 people (2 adults and 2 children) is living, is analysed. Based on this analysis, it was found that an average family uses 6 kWh of electricity during the day from 06.00 am to 09.00 pm and 2 kWh during the night, from 09.00 pm to 06.00 am. Here, it is worth noting that the electricity consumed by families is assumed the constant during the night; however, there are some fluctuations in the electricity demand during the specified daytime hours. These fluctuations are determined according to the load profiles of the families. For instance, small household appliances or power-consuming machines are usually operated during the daytime hours. Accordingly, a householder's monthly minimum and maximum energy consumption for the daytime hours are calculated as 164 kWh in June and 203 kWh in January, respectively. In addition, the energy consumption during the night hours is constant

and 60 kWh. The energy consumption for during the day and night hours for other months is presented in Figure 6.39.

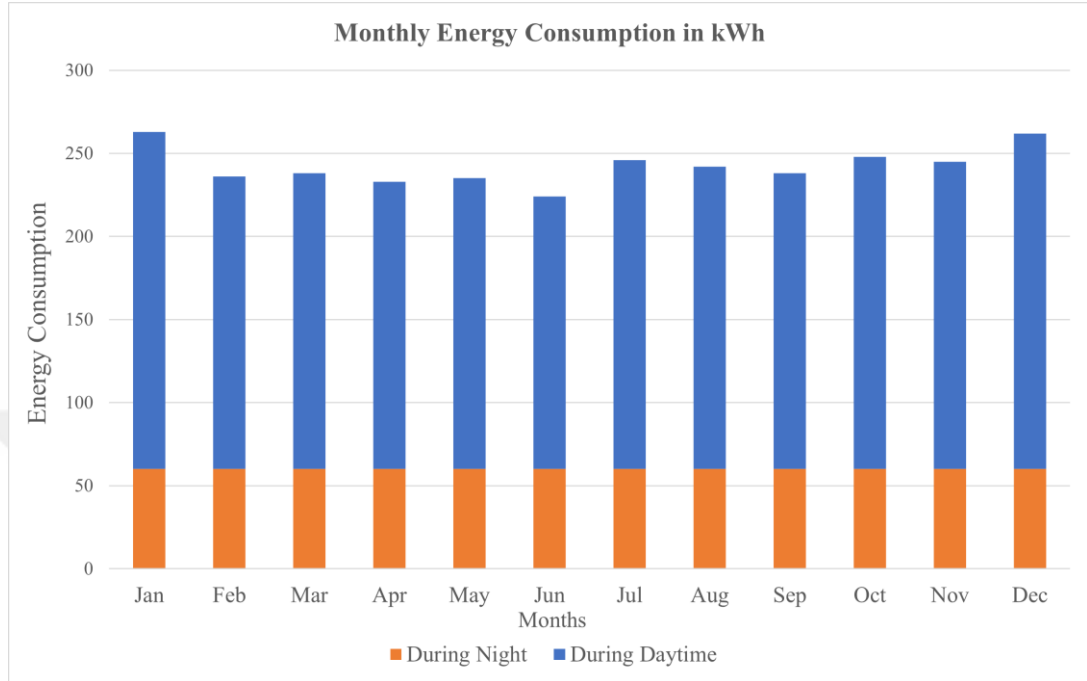


Figure 6.39. Monthly energy consumption of a householder in kWh.

Considering that this solar power plant meets the required energy of a residential site containing 15 households, it is necessary to multiply the monthly consumption given in Figure 6.39 by this number of households. Thus, the monthly energy consumption of the site can be determined. Considering Figure 5.5., it is evident that the monthly energy consumption of a pump operating 8 hours a day with a power output of 1 kW would be 240 kWh. In addition, it is determined that the monthly energy consumption of 2 blowers with a power output of each 1 kW is 480 kWh. Since the energy produced by the SPP is very high (far higher than the energy required by the site), a part of the energy produced during the day is supplied to the electrolyser stack. Thus, a portion of the energy generated during the day is stored as hydrogen and reused to meet the residential site's energy needs at night when there is no solar radiation. Using the formulations provided in Section 5.4, the power output of the electrolyser stack (PEME) is calculated to be 16.5 kW and considering that it operates 8 hours per day, the monthly energy consumption of the PEME would be 3960 kWh. Considering the energy consumption of the integrated system components proposed in Chapter 5 as the

constant, the monthly energy consumption of all these components is illustrated in Figure 6.40.

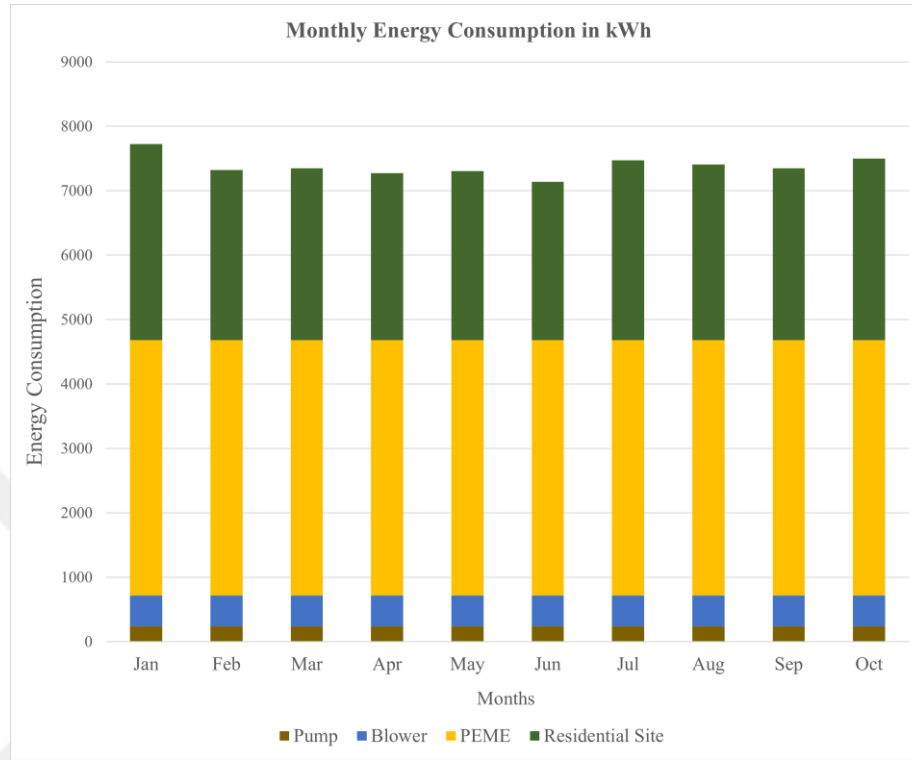


Figure 6.40. Monthly energy consumption of all system components during the day.

The monthly energy production and energy transmitted to the grid are depicted in Figure 6.41. According to the figure, the energy transmission increases with increasing the produced energy by SPP from January to July. As mentioned earlier, only two components produce useful energy for the residential areas in the integrated system. These are the HT-PEMFC stack meeting the required energy of these residencies during the night, and the SPP, which has the largest share in energy production and generates income by transmitting excess energy to the grid. Considering parasitic losses, the monthly minimum and maximum energy production in the HT-PEMFC stack is determined as 900 and 1152 kWh and assumed to be constant throughout the year. However, the energy produced in the SPP varies primarily depending on the global solar radiation, climatic conditions, weather status (clear, cloudy, rainy, etc.) and other environmental factors. In addition, the minimum and maximum energy transmission to the grid is determined as 240 in January and 40747 kWh in July, respectively.

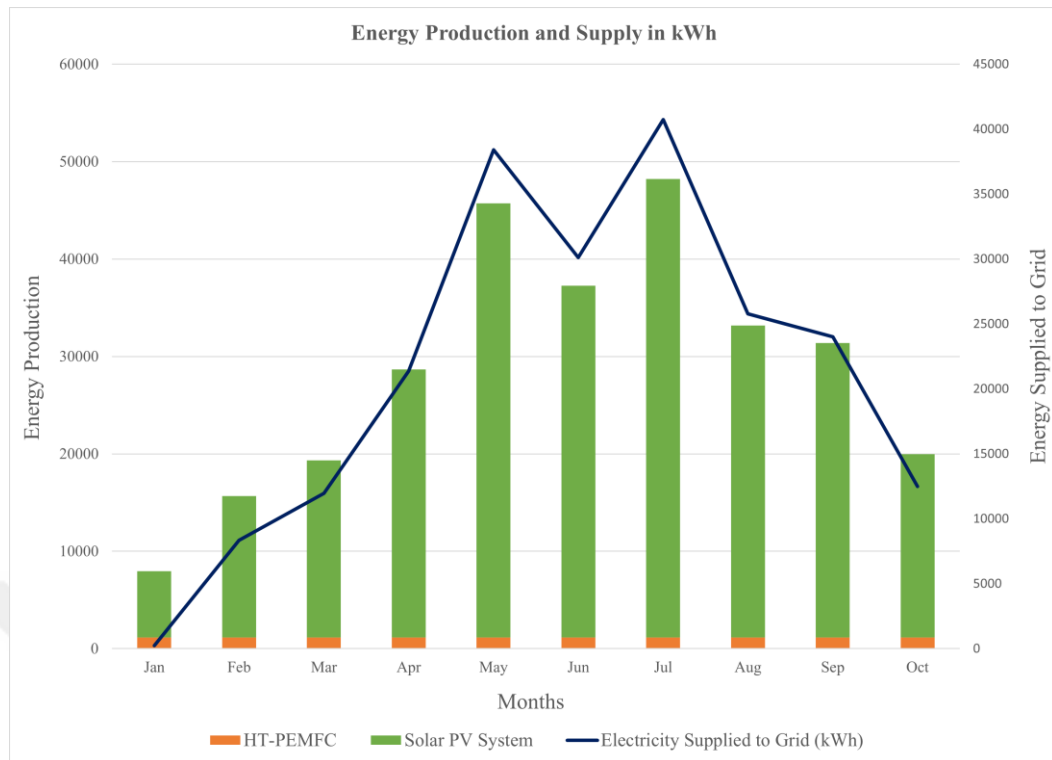


Figure 6.41. Monthly energy production and energy transmitted to the grid in kWh.

The monthly energy efficiency of all system components, including HT-PEMFC stack, PEME stack, and solar PV system, along with the overall integrated system, is given in Figure 6.42. According to the figure, the PEME stack efficiency firstly increases from January to July and then decreases each month. The underlying reason for this situation is that as the amount of energy produced in solar PVs increases, the DC electricity fed to the electrolysis stack also rises, allowing more water to be separated. The minimum and maximum PEME efficiency is determined as 20.43% and 89.02%, respectively. The energy efficiency of the PEME was previously calculated as 87.27% at the design stage. As can be observed, there are substantial differences in efficiency values according to specified months. The HT-PEMFC stack, unlike the PEME stack, is much less sensitive to the amount of energy produced by the PV system. The efficiency of the HT-PEMFC stack increases from January to Jun and then decreases to October. The minimum and maximum energy efficiency is calculated as 37.83% in January and 46.83% in May, respectively. As noticed from the 0-D or 1-D cell modelling, the stack efficiency of HT-PEMFC is lower than the cell size efficiency. The energy efficiency of the solar PV system firstly decreases from the winter months to the summer months and then increases from August. It is well-known that the

efficiency of PV modules declines during the summer months when solar radiation is high and rises during the fall and winter months when the air temperature drops dramatically compared to the summer months. Therefore, along with the energy production, the global solar radiation intensity and other environmental factors are mostly effective in the efficiency. Accordingly, the minimum and maximum energy efficiency of the solar PV system is determined as 9.46% in June and 20.02% in February, respectively. Furthermore, the minimum and maximum overall system efficiency is computed as 24.87% in January and 48.97% in May, respectively.

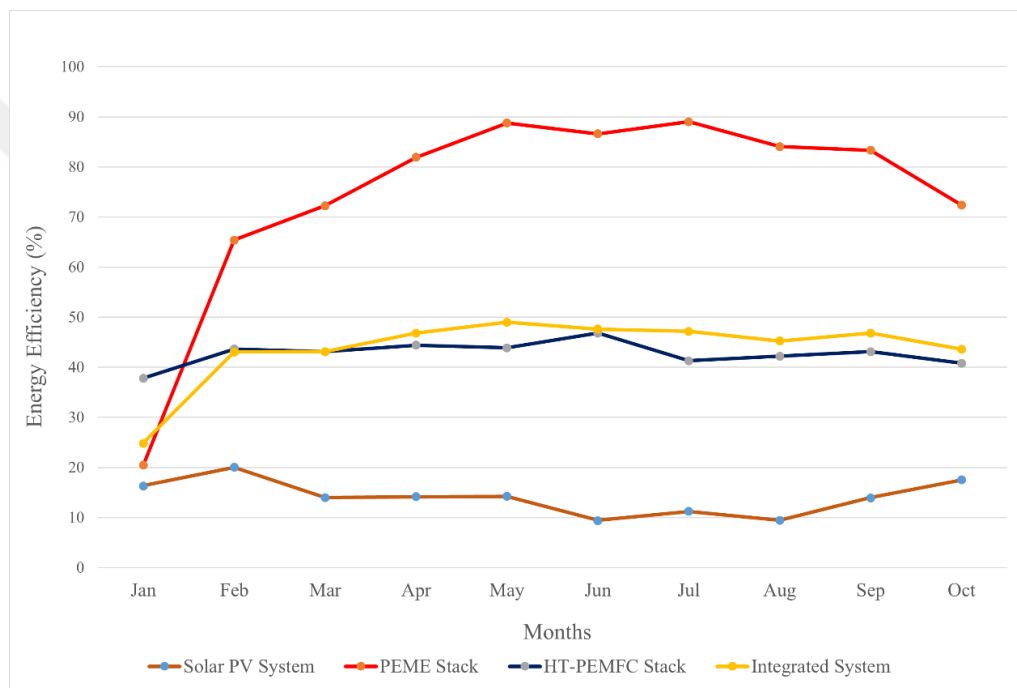


Figure 6.42. The energy efficiency of system components and integrated system.

The monthly exergy efficiency variation of all system components and integrated system is depicted in Figure 6.43. According to the figure, the minimum and maximum exergy efficiency of the solar PV system is determined as 7.09% in June and 15.02 in February. In addition, the minimum and maximum exergy efficiency of the PEME stack is calculated as 19.42% in January and 84.57 in July, whereas the minimum and maximum exergy efficiency of the HT-PEMFC stack is computed as 34.05% in January and 42.15 in June. Furthermore, the minimum and maximum exergy efficiency of the overall integrated system is determined as 21.91% in January and 44.84% in May, respectively.

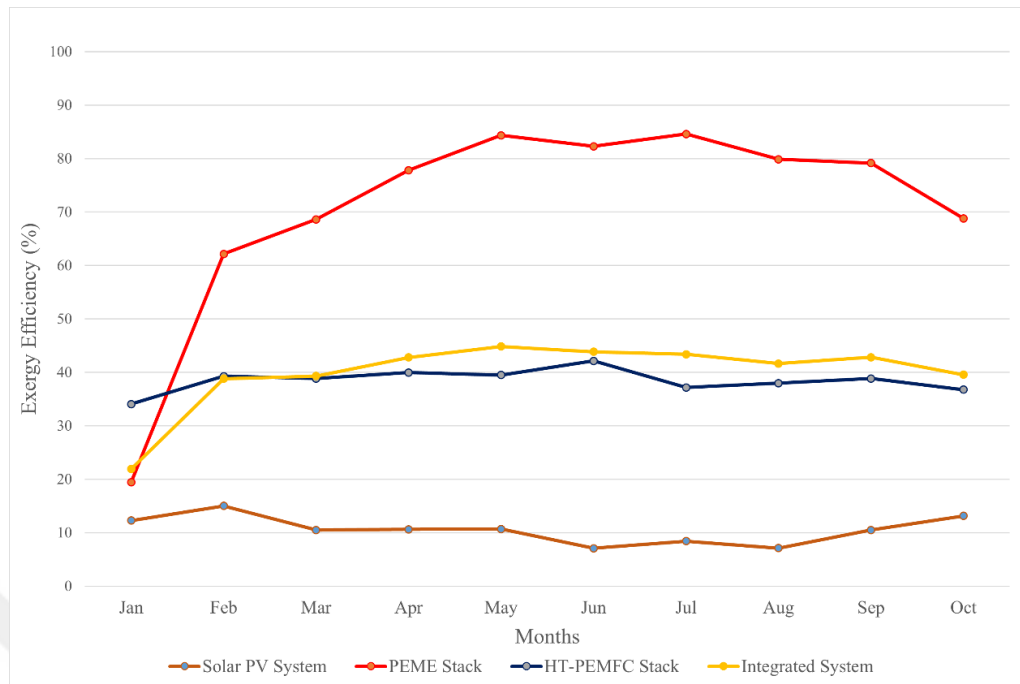


Figure 6.43. The exergy efficiency of system components and integrated system.

CHAPTER 7

CONCLUSION

In this thesis, a comprehensive performance evaluation of an HT-PEMFC employing a PA-doped PBI membrane was performed with energy and exergy analyses, and the results were discussed. In order to determine the performance characteristics under different operational conditions, the HT-PEMFC was electrochemically modelled on both a cell and stack basis. Thermodynamic analyses were then applied to each model. Two effective methods, the 0-D & isothermal model and the 1-D & semi-empirical model, were used to obtain the electrochemical performance results at the cell level. In the 0-D & isothermal model, the polarization curve results were compared with two experimental studies conducted on 423 K and 433 K. Different statistical methods were applied to test and validate the proposed model. In addition, the effects of operating temperature, pressure, relative humidity, and membrane thickness on the cell performance were investigated, and the variation of energy/exergy efficiency, entropy production density, and exergy destruction rate was discussed [78]. In the 1-D & semi-empirical model, the polarization curve results were compared with four experimental studies performed at different operating temperatures from 393 K to 453 K at 20 K intervals. The regression models were derived for each temperature to prove how well the proposed model agrees with these experimental studies. Thus, the effects of leak current density and doping level on cell performance were investigated, and energy, exergy, and ecological analyses were performed [194]. Finally, apart from the cell-based models, the HT-PEMFC was also modelled in the stack-level based on the 1-D and semi-empirical model. In this study, the integration of an HT-PEMFC stack into a hybrid system consisting of a grid-connected SPP and a PEME stack to produce hydrogen was investigated to meet the energy demand of a residential area. Thus, the integration of HT-PEMFC into the proposed hybrid system was proven feasible, and the performance variation on a stacked basis with other system components was

analysed monthly. Accordingly, the following crucial concluding remarks were extracted from the findings of these studies [78]:

- One of the most significant parameters influencing the fuel cell performance is the operating temperature. Increasing the temperature to 453 K and 473 K enhances the energy efficiency by 6.7% and 39.71%, whereas the exergy efficiency by 6.92% and 38.67%, respectively, compared to the base case.
- The operating pressure has a negligible effect on the performance of the fuel cell. Raising the pressure from 1 to 4 atm contributes to an increase of 2.66% in energy and exergy efficiency.
- The relative humidity increases both efficiencies noticeably. Boosting the moisture to 11.4% improves the energy and exergy efficiency of 8.02% and 8.03%, respectively.
- Another critical characteristic that remarkably impacts the fuel cell performance is membrane thickness. Reducing the thickness to 0.01 cm contributes to an increase of 9.94% and 9.93% in energy and exergy efficiency, respectively.
- The derived results demonstrate that HT-PEMFC performs best in high temperatures (e.g., 453 K) because degradation can be a serious problem at 473 K, low membrane thickness (e.g., 0.01 cm), and optimal humidity environments (e.g., 11.4%).
- Increasing the leak current density from 0.005 to 0.5 Acm⁻² leads to a decrease of 5.77%, 5.88%, 5.44%, and 5.48% in the power density, net output voltage, energy efficiency, and exergy efficiency, respectively. In contrast, it increases the optimum entropy production density and exergy destruction density by 1.36% and 1.58%, respectively.
- Rising the doping level from 6.2 to 30 enhances the power density, net output voltage, energy efficiency, exergy efficiency, the optimum exergy destruction density, and the optimum entropy production density by 23.07%, 11.76%, 30.25%, 32.52%, 2.97%, and 6.25, respectively.
- Increasing the leak current density decreases the maximum level of all ecological functions and increases the theoretical improvement potential. In addition, increasing the doping level raises the ecological functions and reduces the improvement potential.

- The minimum energy consumption of the integrated system during the daytime is determined as 7140 kWh in June, whereas the maximum consumption is estimated as 7725 kWh in January.
- The minimum energy production of the solar PV system is observed as 6813.71 kWh in January, whereas the maximum production is obtained as 47065.72 kWh in July, which is far higher than the total energy demand.
- The monthly energy production of the HT-PEMFC stack is calculated to be 1152 kWh, which is adequate to meet the night-time energy demands of 15 residences.
- The minimum energy efficiency of the solar PV system, PEME stack, HT- PEMFC stack, and integrated system is determined as 9.46% in June, 20.43%, 37.83%, and 24.87% in January, respectively.
- The maximum energy efficiency of the solar PV system, PEME stack, HT- PEMFC stack, and integrated system is calculated as 20.02% in February, 89.02% in July, 46.83% in June, and 48.97% in May, respectively.
- The minimum exergy efficiency of the solar PV system, PEME stack, HT- PEMFC stack, and integrated system is computed as 7.09% in June, 19.42%, 34.05%, and 21.91% in January, respectively.
- The maximum exergy efficiency of the solar PV system, PEME stack, HT- PEMFC stack, and integrated system is estimated as 15.02% in February, 84.57% in July, 42.15% in June, and 44.84% in May, respectively.
- The energy and exergy efficiency of the HT-PEMFC at the stack level is lower than these efficiencies performed at cell size, including the 0-D and 1-D models.
- Considering these aforementioned results, integrating the HT-PEMFC into the proposed solar-based hybrid system is possible and feasible.

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RESUME

Mutlucan BAYAT started his undergraduate education at Mustafa Kemal University, Department of Mechanical Engineering in 2006 and graduated in 2011. In 2013, he was appointed as a research assistant at Karabuk University, Department of Mechanical Engineering, Energy Division. He completed his master's degree in Mechanical Engineering at Karabuk University in 2016 and continues his Ph.D. education in the same department. He is married and has two children.

The following scientific publications have been presented to the literature by using the data obtained with this thesis study.

- Bayat, M., Ozalp, M., and Gurbuz, H., “Comprehensive performance analysis of a high-temperature PEM fuel cell under different operating and design conditions”, *Sustainable Energy Technologies and Assessments*, 52 (C): 102232 (2022).
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- Bayat, M. and Ozalp, M., “Effects of leak current density and doping level on energetic, exergetic and ecological performance of a high-temperature PEM fuel cell”, *International Journal of Hydrogen Energy*, Under Review (10.11.2022).