UNIVERSITY OF THESSALY

SCHOOL OF ENGINEERING

DEPARTMENT OF MECHANICAL ENGINEERING

DIPLOMA THESIS

MAIN FAILURES AND MITIGATION STRATEGIES FOR PROTON EXCHANGE MEMBRANE FUEL CELL

By

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Submitted in partial fulfillment of the requirements for the degree of diploma in Mechanical Engineering at the University of Thessaly

Volos, 2024

ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΙΑΣ

ΠΟΛΥΤΕΧΝΙΚΗ ΣΧΟΛΗ

ΤΜΗΜΑ ΜΗΧΑΝΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ

ΔΙΠΛΩΜΑΤΙΚΗ ΕΡΓΑΣΙΑ

ΚΥΡΙΕΣ ΒΛΑΒΕΣ ΚΥΨΕΛΩΝ ΚΑΥΣΙΜΟΥ ΜΕ ΜΕΜΒΡΑΝΗ ΑΝΤΑΛΛΑΓΗΣ ΠΡΩΤΟΝΙΩΝ ΚΑΙ ΣΤΡΑΤΗΓΙΚΕΣ ΜΕΤΡΙΑΣΜΟΥ ΤΟΥΣ

υπό

ΚΑΚΑΝΗΣ ΑΝΔΡΕΑΣ

Επιβλέπων: Καθ. Τσιακάρας Παναγιώτης

Υπεβλήθη για την εκπλήρωση μέρους των απαιτήσεων για την απόκτηση του Διπλώματος Μηχανολόγου Μηχανικού του Πανεπιστημίου Θεσσαλίας

Βόλος, 2024

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Ο/Η Κακανής Ανδρέας, γνωρίζοντας τις συνέπειες της λογοκλοπής, δηλώνω υπεύθυνα ότι η παρούσα εργασία με τίτλο «ΚΥΡΙΕΣ ΑΣΤΟΧΙΕΣ ΚΑΙ ΣΤΡΑΤΗΓΙΚΕΣ ΜΕΤΡΙΑΣΜΟΥ ΓΙΑ ΚΥΨΕΛΕΣ ΚΑΥΣΙΜΟΥ ΜΕΜΒΡΑΝΗΣ ΑΝΤΑΛΛΑΓΗΣ ΠΡΩΤΟΝΙΩΝ» αποτελεί προϊόν αυστηρά προσωπικής εργασίας και όλες οι πηγές που έχω χρησιμοποιήσει έχουν δηλωθεί κατάλληλα στις βιβλιογραφικές παραπομπές και αναφορές. Τα σημεία όπου έχω χρησιμοποιήσει ιδέες, κείμενο ή / και πηγές άλλων συγγραφέων, αναφέρονται ευδιάκριτα στο κείμενο με την κατάλληλη παραπομπή και η σχετική αναφορά περιλαμβάνεται στο τμήμα των βιβλιογραφικών αναφορών με πλήρη περιγραφή.

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ACKNOWLEDGMENTS

This thesis is the final step in the completion of my academic cycle. I would like to express my thanks to my professor and supervisor, Prof. Panagiotis Tsiakaras for his valuable help, scientific competence and informative instructions that he offered me for the completion of this thesis. I thank him very much for his patience and the trust he showed me in this collaboration, as well as for the opportunity he gave me to work on this subject.

Of course, I would like to express my sincere thanks to my beloved family for both their financial and psychological support. In particular, I would like to thank my parents, Kakanis Georgios and Vakalopoulou Androniki as well as my sister Kakani Ekaterini. Of course, I do not forget friends who in their own way helped me through the academic years.

ΕΥΧΑΡΙΣΤΙΕΣ

Η παρούσα εργασία αποτελεί το τελικό βήμα για την ολοκλήρωση του ακαδημαϊκού μου κύκλου. Θα ήθελα να εκφράσω τις ευχαριστίες μου στον καθηγητή μου και επιβλέποντα, κ. Παναγιώτη Τσιακάρα για τη πολύτιμη βοήθεια, την επιστημονική επάρκεια και τις κατατοπιστικές οδηγίες που μου προσέφερε για την ολοκλήρωση αυτής της διπλωματικής εργασίας. Τον ευχαριστώ πολύ για την υπομονή του και την εμπιστοσύνη που μου έδειξε σε αυτή τη συνεργασία καθώς και για την ευκαιρία που μου έδωσε να ασχοληθώ με το αντικείμενο.

Φυσικά θα ήθελα να εκφράσω τις θερμές μου ευχαριστίες στην αγαπημένη μου οικογένεια τόσο για την οικονομική όσο και για τη ψυχολογική υποστήριξή τους. Συγκεκριμένα, θα ήθελα να ευχαριστήσω τους γονείς μου, Κακανή Γεώργιο και Ανδρονίκη Βακαλοπούλου καθώς και την αδελφή μου Κακανή Αικατερίνη. Σαφώς και δεν ξεχνώ και φίλους οι οποίοι με τον δικό τους τρόπο βοήθησαν στο πέρας των ακαδημαϊκών χρόνων.

ABSTRACT

The commercialization of Proton Exchange Membrane (PEM) fuel cells holds numerous advantages that contribute to the global pursuit of sustainable and efficient energy solutions. One of the key benefits is environmental friendliness. PEM fuel cells operate with hydrogen and oxygen, emitting only water vapor and heat as byproducts, making them a clean and environmentally friendly energy source. This aligns with the global push for reducing greenhouse gas emissions and combating climate change.

Efforts are directed toward scaling up production. The transition from laboratory-scale production to large-scale manufacturing is critical for meeting commercial demands. Streamlining production processes and ensuring the scalability of PEM fuel cell technologies are key points for bigger productions. Policy support and market adoption play pivotal roles. Governments and industries are encouraged to implement policies that incentivize the adoption of PEM fuel cell technologies. Building a supportive regulatory environment and fostering market acceptance are essential for widespread commercialization.

On the other hand, there are many challenges that operate as multiple obstacles for the commercialization of the PEM fuel cells. A lot of researches are trying to address these problems and find a way to bypass them.

In this thesis, we will focus on some problems and failures that today's fuel cells face, and we will suggest some mitigation ways against them. For the next years, the usage of PEM fuel cells will be increasing. So, it is important to make them more durable and effective, the operation time needs to be higher, and the general cost should be as low as possible.

ΠΕΡΙΛΗΨΗ

Η εμπορευματοποίηση των κυψελών καυσίμου με μεμβράνη ανταλλαγής πρωτονίων (PEM) έχει πολλά πλεονεκτήματα που συμβάλλουν στην παγκόσμια επιδίωξη βιώσιμων και αποδοτικών ενεργειακών λύσεων. Ένα από τα βασικά πλεονεκτήματα είναι η περιβαλλοντική φιλικότητα. Οι κυψέλες καυσίμου PEM λειτουργούν με υδρογόνο και οξυγόνο, εκπέμποντας μόνο υδρατμούς και θερμότητα ως προϊόντα, γεγονός που τις καθιστά καθαρή και φιλική προς το περιβάλλον πηγή ενέργειας. Αυτό ευθυγραμμίζεται με την παγκόσμια πίεση για τη μείωση των εκπομπών αερίων του θερμοκηπίου και την καταπολέμηση της κλιματικής αλλαγής.

Οι προσπάθειες κατευθύνονται προς την κλιμάκωση της παραγωγής. Η μετάβαση από την παραγωγή σε εργαστηριακή κλίμακα στην παραγωγή μεγάλης κλίμακας είναι κρίσιμη για την ικανοποίηση των εμπορικών απαιτήσεων. Η βελτιστοποίηση των διαδικασιών παραγωγής και η εξασφάλιση της επεκτασιμότητας των τεχνολογιών κυψελών καυσίμου PEM αποτελούν βασικά σημεία της επέκτασης. Η στήριξη της πολιτικής και η υιοθέτηση από την αγορά διαδραματίζουν καθοριστικό ρόλο. Οι κυβερνήσεις και οι βιομηχανίες ενθαρρύνονται να εφαρμόσουν πολιτικές που παρέχουν κίνητρα για την υιοθέτηση τεχνολογιών κυψελών καυσίμου PEM. Η οικοδόμηση ενός υποστηρικτικού περιβάλλοντος και η προώθηση της αποδοχής της αγοράς είναι ουσιώδεις για την ευρεία εμπορευματοποίηση.

Από την άλλη πλευρά, υπάρχουν πολλές προκλήσεις που λειτουργούν ως πολλαπλά εμπόδια για την εμπορευματοποίηση των κυψελών καυσίμου PEM. Πολλές έρευνες προσπαθούν να αντιμετωπίσουν αυτά τα προβλήματα και να βρουν τρόπους να τα παρακάμψουν.

Στην παρούσα διατριβή, θα επικεντρωθούμε σε ορισμένα προβλήματα και αστοχίες που αντιμετωπίζουν οι σημερινές κυψέλες καυσίμου και θα προτείνουμε ορισμένους τρόπους μετριασμού τους. Για τα επόμενα χρόνια, η χρήση των κυψελών καυσίμου PEM θα γίνεται όλο και περισσότερη. Έτσι, είναι σημαντικό να γίνουν πιο ανθεκτικές και αποτελεσματικές, ο χρόνος λειτουργίας τους πρέπει να είναι μεγαλύτερος και το γενικό τους κόστος πρέπει να είναι όσο το δυνατόν χαμηλότερο.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1

1. Introduction

Energy is the lifeblood of human civilization, serving as the driving force behind progress, development, and the fulfillment of basic needs. The importance of energy to humanity is immeasurable, influencing every aspect of our daily lives and shaping the trajectory of societies worldwide. One of the fundamental roles of energy lies in meeting the basic necessities of life. From heating our homes and cooking our meals to powering hospitals, schools, and industries, energy is indispensable for ensuring a decent quality of life. It enables access to clean water, sanitation, and healthcare, playing a critical role in promoting human well-being.

Beyond meeting basic needs, energy is a catalyst for economic growth and innovation. Industries rely on energy to manufacture goods, transport products, and conduct research. Innovation in energy technologies has historically driven advancements in other sectors, fostering economic development and job creation. The availability of affordable and reliable energy sources is a cornerstone of economic prosperity. In the context of transportation, energy powers vehicles that connect communities and facilitate the movement of people and goods. From cars and trucks to trains and airplanes, energy is the key enabler of modern mobility, supporting both local and global connectivity. Furthermore, the geopolitical landscape is significantly shaped by the quest for energy resources. Access to reliable and affordable energy has been a driver of geopolitical strategies, affecting international relations and global power dynamics.

Energy is also intricately linked to the environment. The type and source of energy we choose impact air and water quality, contributes to climate change, and influence ecosystems. As societies recognize the need for sustainable practices, the importance of transitioning to cleaner and renewable energy sources becomes paramount.

The intricate relationship between energy and the environment underscores a critical balance that modern societies must strike to ensure sustainability and a habitable planet. The production and consumption of energy have profound implications for the environment, influencing climate change, air and water quality, and overall ecological health.

One of the primary environmental concerns associated with energy is climate change. The burning of fossil fuels, such as coal, oil, and natural gas, releases carbon dioxide (CO_2) and other greenhouse gases into the atmosphere. These gases trap heat, contributing to the warming of the Earth's surface and leading to a range of climate-related impacts, including more frequent and severe heatwaves, storms, and disruptions to ecosystems.

Renewable energy sources, such as solar, wind, and hydropower, offer a more environmentally friendly alternative to fossil fuels. Harnessing energy from these sources produces fewer greenhouse gas emissions and reduces dependence on finite resources. The transition to renewable energy is a crucial step in mitigating the environmental impacts associated with conventional energy production. However, even renewable energy technologies are not entirely without environmental considerations. The manufacturing, installation, and decommissioning of renewable infrastructure can have ecological footprints, emphasizing the importance of responsible planning and resource management.

Beyond climate change, energy production influences air and water quality. Emissions from fossil fuel combustion can lead to air pollution, affecting respiratory health and contributing to acid rain. Similarly, the extraction and processing of energy resources may impact water sources, posing challenges to aquatic ecosystems and human water supplies. Proton Exchange Membrane (PEM) fuel cells stand at the forefront of the green energy revolution, representing a promising technology in the pursuit of sustainable and clean power solutions. These fuel cells are electrochemical devices that convert chemical energy from hydrogen and oxygen into electricity, with water and heat as the only byproducts.

One of the key advantages of PEM fuel cells is their environmental friendliness. Unlike traditional combustion-based power generation, PEM fuel cells produce electricity through an electrochemical reaction, avoiding the emission of harmful pollutants and greenhouse gases. This characteristic positions PEM fuel cells as a green energy option with the potential to significantly reduce the carbon footprint of various applications.

The primary fuel for PEM fuel cells is hydrogen, which can be derived from renewable sources such as wind, solar, and biomass. Green hydrogen, produced using clean energy methods like electrolysis powered by renewables, ensures that the entire fuel cell process is devoid of carbon emissions. This aligns with the broader goal of transitioning toward a sustainable energy future and mitigating the impacts of climate change.

PEM fuel cells find diverse applications in transportation, stationary power generation, and portable devices. In the transportation sector, fuel cell electric vehicles (FCEVs) equipped with PEM fuel cells offer a zero-emission alternative to conventional internal combustion engines, contributing to cleaner air and reduced reliance on fossil fuels. Stationary power generation utilizing PEM fuel cells provides an efficient and clean source of electricity for homes, businesses, and even entire grid systems. Their quick start-up times and flexibility make them valuable contributors to a decentralized and resilient energy infrastructure. The portability and scalability of PEM fuel cells make them suitable for off-grid and remote power applications, enabling access to green energy in areas where traditional power sources may be impractical or unavailable.

CHAPTER 2

Fundamentals of Electrochemistry

Electrochemical devices for energy conversion and storage

2.1 Introduction

Electrochemistry is the part of chemistry that is connected with electricity. In electrochemical processes, chemical reactions are caused by an electric current or electric power is generated by chemical reactions. Chemistry and electricity are connected by the motion of electrons, ions and holes which transfer between the different parts of an electrochemical device [1].

The science of electrochemistry is dealing with transfer of electrons at the electrode-electrolyte interface. The first electrochemical invention was invented by Alessandro Volta, in 1800. He invented the first battery, a sustainable source of electricity. With this invention, the world learned about this new scientific field and its development was very quick. Inventions like the upper one and others are shown in **Fig. 2.1** below [2].

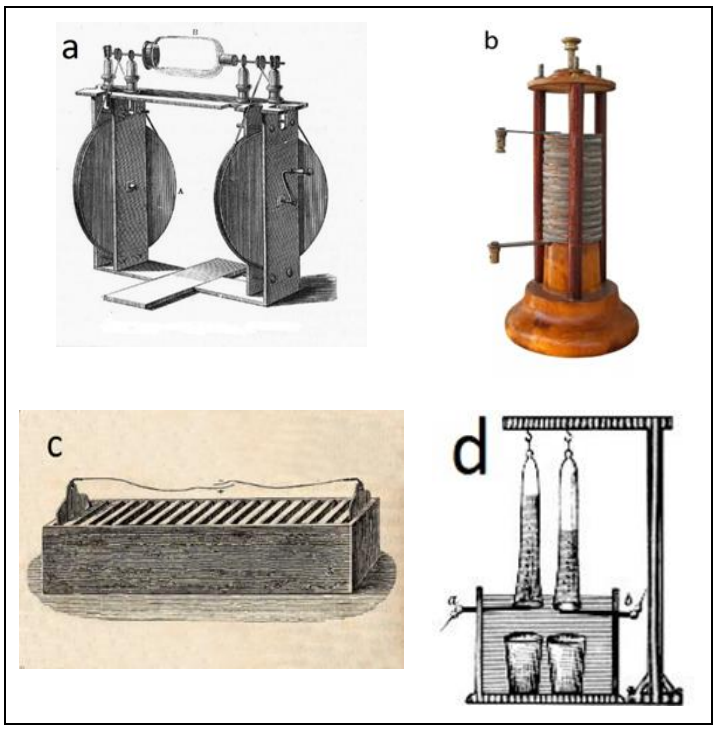

Figure 2.1: a) Francis Hauksbee's gas discharge lamp [3], b) Alessandro Volta's battery [4], c) William Cruickshank's battery [5], d) Johann Wilhelm Ritter's invention for electrolysis [6]

2.2 Fundamental Equations

2.2.1 Nernst Equation

The Nernst equation connects the instantaneous potential, E, to the standard potential, E°, and the reaction quotient, Q. The standard cell potential (E^{o}_{cell}) is the difference of the two electrodes' potential when all dissolved substances have concentration of 1 M. To find the difference of the two half cells, the following equation is used: $E^{o}_{Cell}=E^{o}_{Reduction}-E^{o}_{oxidation}$. Reaction quotient Q is the ratio of concentrations from products and reactants (Q=[Products]/[Reactants]) [2,7].

When a chemical reaction takes place, we have this equation: $\Delta G=\Delta G_o+RT *\ln(Q)$, ΔG is the Gibbs free energy change. We know that $\Delta G=-nFE$ and $\Delta G_o=-nFE_o$. Replacing the ΔG and ΔG_o from the upper relations, we have the equation below, which is the Nernst equation [2,7].

Nernst Equation: $E = E_o - (RT/nF) *\ln(Q)$ **[Eq. 2.1]**

Where:

- R: the gas constant (=8,3145 $J*mol^{-1}*K^{-1}$)
- T: temperature in Kelvin
- n: the number of electrons exchanged.
- F: Faraday's constant (= 96485 C/mole)
- E: instantaneous, non-standard cell's potential
- E_o: standard cell's potential
- Q: reaction quotient

Here it can be said that this relation is applicable at all temperatures. If the Q is unity, instantaneous, non-standard potential E is equal with the standard potential E_o. When Nernst equation is used at 25ºC, a form written in base 10 log is usually used [2,7]:

Used at only 25ºC (298K): $E = Eo - (0,059/n) * \log(Q)$

2.2.2 Equilibrium Constant

At equilibrium state of a reaction in a cell, instantaneous, non-standard cell's potential E is zero, because ΔG=0 and ΔG=-nFE, so E=0. In this situation, reaction quotient Q can be replaced by the equilibrium constant K. There are two relations, which extracted from the above equations, that can calculate this constant (from standard free energy change (ΔG^{o}) and from standard cell potential (E^{o})) ([2], [8]):

1. $\Delta G^{o} = -RT\ln(K)$ **[Eq. 2.2]**
2. $E^{o} = (RT/nF)\ln(K)$ **[Eq. 2.3]**

According to the value of the equilibrium constant K, it predicts the spontaneity of the redox reaction. If ΔG^o is less than zero, then E^o is greater than zero and K is greater than 1, so the direction of the reaction is spontaneous in forward direction. If ΔG^o is greater than zero then E^o is less than zero and K is less than one, so the direction of reaction is spontaneous in reverse direction. If ΔG^o is zero, E^o is zero and K is one, there is no net reaction and there is a balance between the two directions. **Fig. 2.2** shows the upper [2,8].

ΔG°	E°_{cell}	K	Direction of Reaction
<0	>0	>1	spontaneous in forward direction
>0	<0	<1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 2.2: Effect of Equilibrium Constant to the direction of the reaction [8]

2.2.3 Mass-Transfer Limited Current

The mass transfer rate to the electrode is directly related to the limiting current. The current that is measured when there is zero concentration on the surface of the reacting species is called limiting current. Mass-Transfer Limited Current (i) is calculated from the relation below [2]:

$$i = nFAmC \quad \textbf{[Eq. 2.4]}$$

Where,

- i: Mass-transfer limited Current (A)
- n: Number of transferred electrons.
- F: Faraday's Constant (=96485 C/mole)
- A: Area (cm^2)
- m: Mass-Transfer Coefficient (cm/sec)
- C: Concentration of electrochemically active substances which converted at the electrode ($mole/cm^3$)

2.2.4 Cottrell Equation

In electrochemistry, electrochemical reactions can be limited in many ways. The two main limitations are potential and diffusion. The potential is the driving force of a reaction, which is described by the Nernst Equation. But, if the potential is high enough to ensure a reaction, another problem occurs, depletion. The reaction occurring at the electrode consumes active substances in front of the electrode. These active substances are then depleted and are missing for the reaction to occur. New active substances are transported to the electrode by diffusion. Now the diffusion is determining the current at the electrode. Cottrell Equation describes the variation of the electric

current in time due to depletion and diffusion. This equation is usually applied when the potential is operated as the step function. To be well grounded, current should be limited by the diffusion of the substances to the electrode area [2,9]. The Cottrell Equation is below:

Cottrell Equation: $i(t) = (nFAD^{1/2}C)/((\pi t)^{1/2})$ **[Eq. 2.5]**

Where,

- **i**: current (A)
- **n**: number of electrons
- **F**: Faraday's Constant (=96485 C/mole)
- **A**: area of the electrode (cm^2)
- **D**: diffusion coefficient (cm^2/sec)
- **C**: initial concentration (mol/cm^3)
- **t**: time (s)

2.2.5 Faraday's Law

Faraday's Law is related the total charge passed through a cell to the absolute amount of analyte. The Faraday's Law is the below relation [2]:

Faraday's Law: $Q = nFN$ **[Eq. 2.6]**

Where,

- **Q**: total charge (C)
- **n**: number of electrons per mole of analyte
- **F**: Faraday's Constant (=96485 C/mole)
- **N**: moles of analyte

Faraday's Law can be used in many applications. With this equation, it can be found the amount of substance that have deposit on the electrode (electrogravimetry) and the total amount of electricity that is required for full electrolysis of a chemical compound [2].

2.2.6 Nernst – Planck Equation

Mass transfer can be achieved in three different ways or a combination of these. The first is diffusion, which is the random movement of molecules in one dimension, from a region of high concentration to a region of lower concentration. The concentration difference between two points in a solution affects the rate of a molecule diffusion. The second is migration that describes the motion of charged particles in response to an electric field. The charge of the ion, the ion concentration, the diffusion coefficient, and the magnitude of the electric field gradient that the ion experiences affect migration's contribution

to the overall flux. Finally, the third way is convection which is forced movement of solution species by mechanical (stirring) or other means ([2], [11]).

The total mass transport of material, or flux, to an electrode is described by the Nernst-Planck equation:

$$J_j(x) = - [D_j (\partial C_j(x) / \partial x)] - [(z_j F/ RT) D_j C_j(x)] (\partial \varphi(x) / \partial x) + C_j(x) \nu(x)$$ **[Eq. 2.7]**

Where, J is the flux (mol $cm^{-2}s^{-1}$), D is the diffusion coefficient of the solution species (cm^2/s), C is the concentration of the species (mol/cm^3), z is the charge, F is the Faraday's constant, φ is the potential and ν is the rate with which an element moves in solution ([2], [11]).

The first term on Nernst-Planck equation describes the contribution of the diffusion in the total mass transport, which is given by the Fick's First Law of Diffusion. The second term is the assistance of the migration and the third one is the contribution of the convection ([2], [11]).

2.3 Electrochemical Cell

The heart of an electrochemical operation is the electrochemical cell. There are two types of this, galvanic cells, and electrolytic cells. Galvanic cells are those in which chemical reactions take place and electricity is produced. On the other hand, in an electrolytic cell, electricity passes through and this results in the occurrence of chemical reactions [2].

2.3.1 Galvanic Cells

Galvanic or voltaic cells involve electrochemical reactions in which the two reactions are separated, and the current can flow through an external wire. The pot on the one side is called a half-cell and contains a solution with a piece of metal partially submerged (such as copper nitrate solution with copper metal submerged in it). The metal is an electrode and is undergoing oxidation ($Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$). So, this electrode is the anode. On the other side, the half-cell consists of the other metal electrode in a solution (such as silver electrode submerged in silver nitrate solution). The silver is undergoing reduction ($Ag^+(aq) + e^- \rightarrow Ag(s)$). Therefore, the silver electrode is the cathode. The anode and the cathode are connected with an external wire.

At this point, no current flows, because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution. As electrons flow from the one to the other side, through the electrode and wire, nitrate ions (anions) pass through the porous plug into the copper nitrate solution. This keeps the pot on the left electrically neutral by neutralizing the charge on the copper ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving, sodium ions (cations) move through the porous plug, and into the silver nitrate solution on the

right. These added cations replace the silver ions that are removed from the solution as they were reduced to silver metal, keeping the pot electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral, and no current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. Fig. 2.3 shows a galvanic cell [2,12].

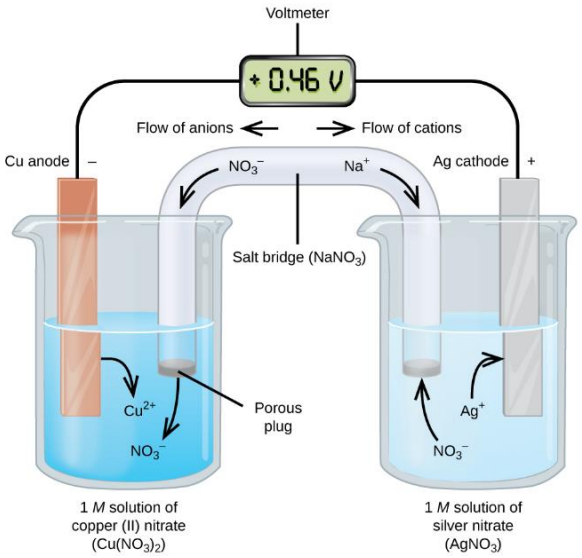

Figure 2.3: Galvanic cell [12]

2.3.2 Electrolytic Cells

It is possible to make a cell that operates by driving an electric current through the cell. These cells are called electrolytic cells. Electrolytic cells, like galvanic, consist of two half-cells, one is the oxidation half-cell, the other is the reduction half-cell. The direction of electron flow in electrolytic cells may be reversed from the direction of electron flow in galvanic cells, but the definition of both cathode and anode remains the same. The reduction takes place at the cathode and oxidation happens at the anode.

Electrolytic cells are very similar to galvanic cells, because both have a cathode and anode side, and both have a flow of electrons from the anode to the cathode. However, there are also differences between the two cells.

Let's use the example of molten NaCl in the container. If molten NaCl(l) is placed into the container and electrodes of C(s) are used, attached to the positive and negative terminals of a battery, an electrolytic reaction will occur. **Fig. 2.4** shows this exact electrolytic cell.

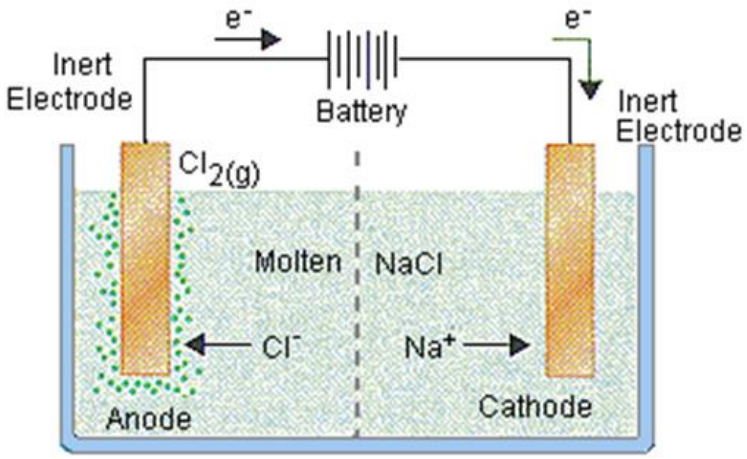

Figure 2.4: Electrolytic Cell [14]

Electrons from the negative terminal travel to the cathode and are used to transform sodium ions into sodium atoms ($Na^{+}+e^{-}\rightleftharpoons Na(s)$). The sodium will plate onto the cathode as it forms. The sodium ion is migrating towards the cathode [2,6].

The negative Chlorine ions transport towards the anode and release electrons as they oxidize to become chlorine atoms ($2Cl^{-}\rightleftharpoons Cl_2(g)+2e^{-}$). The chlorine atoms will combine together to form chlorine gas which will bubble away.

Note that the site of oxidation is still the anode, and the site of reduction is still the cathode, but the charge on these two electrodes is reversed. The anode is now positively charged, and the cathode has a negative charged.

The conditions under which the electrolyte cell operates are very important. The substance that is the strongest reducing will face oxidation and the substance that is the strongest oxidizing will be reduced. If an aqueous solution of sodium chloride were used, hydrogen would face reduction instead of sodium, because it is a stronger oxidizing agent than sodium [2,13].

2.4 Terminology

Here some terms of electrochemistry are explained [2]:

•**Anode**: electrode where oxidation happens

•**Battery**: one or a stack of galvanic cells

• **Cathode**: electrode where reduction happens

• **Cell's Potential**: the sum of electrical potentials in an electrochemical cell

• **Electrochemical Cell**: device that contains current as a result of chemical reactions. It can be either a galvanic cell or an electrolytic cell.

• **Electrode**: it is an electrical conductor or semiconductor in an electrochemical cell. It can be anode or cathode. In an electrode, the electrons are transferred through.

• **Electrolytic Cell**: device that converts electrical into chemical energy. It is composed of two electrodes and an electrolyte.

• **Equilibrium Potential**: the potential when all redox reactions are in equilibrium.

• **Fuel Cell**: device identical to a galvanic cell which produces electricity from chemical energy. It is fed with chemical reactants from outside the cell.

• **Galvanic (Voltaic) Cell**: device that generates electricity by chemical reactants. It also consists of two electrodes and an electrolyte. It is limited by the chemical reactants supply.

• **Half-Cell**: it is the anode and the cathode part individually, including all redox reactions that happens on them

• **Half-Reaction**: the redox reaction that takes place at one half-cell (the anode or the cathode)

• **Ideal Non-Polarizable Electrode**: it is an electrode that does not change its potential when current passes through

• **Ideal Polarizable Electrode**: it is an electrode that its potential changes a lot, when current passes through

• **Interface (Junction)**: it represents a location, in an electrochemical cell, where separate phases are in contact with each other or two liquids with different composition and concentration

• **Oxidant**: the chemical substance which phases the reduction and enables the oxidation for other substances

• **Oxidation**: is the process which chemical substance losses one or more electrons

• **Overpotential**: the deviation of a cell's potential from the equilibrium value. It can be negative or positive

• **Potentiometry**: it uses electrochemical methods to calculate the output potential, when current is close to zero

• **Redox**: process that occurs both an oxidation and a reduction

• **Redox Couple**: the chemical substances that at least two oxidation states (Fe2+, Fe3+)

• **Reductant**: the chemical substance which phases the oxidation and enables the reduction for other substances

• **Reduction**: is the process which chemical substance gains one or more electrons

• **Reference Electrode**: electrode that can keep constant potential when the conditions are changed

• **Supporting Electrolyte**: is an ionic substance that is in the solution to ensure conductivity. It doesn't take place in redox reactions. Usually, is called just electrolyte.

• **Working Electrode**: electrodes where the redox reactions take place.

2.5 Applications

2.5.1 Water electrolysis

The electrolysis of water can be used to produce oxygen and hydrogen. The heart of the electrolysis unit is the electrochemical cell, which is filled with pure water and has two electrodes connected with an external electrical power source.

At a certain voltage, which is called critical voltage, between both electrodes, the electrodes start to produce hydrogen at the negative electrode and oxygen gas at the positive electrode. The amount of gases produced per unit time is related to the current that passes through the electrochemical cell. In water, there is always a certain percentage found as ionic species, H+ and OH- represented by the equation: $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$.

Oxygen and hydrogen gas can be generated at noble metal electrodes by the electrolysis of water: positive electrode (anode):$4OH^-(aq) \rightleftharpoons 2H_2O(l) + O_2(g) + 4e^-$, negative electrode (cathode): $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$. In case of acidic or basic water, the reactions which occur at the electrode interface are slightly different. In water electrolysis there are no side reactions that can produce unwanted byproducts. **Fig. 2.5** shows how electrolysis of water works.

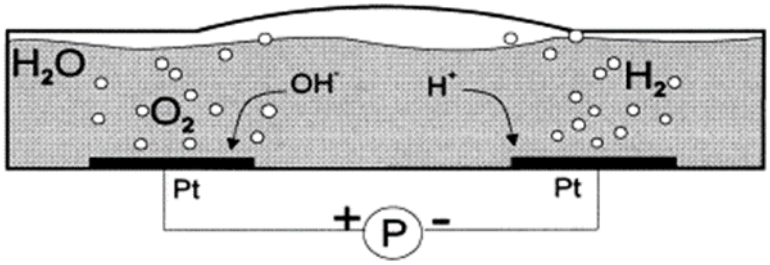

Figure 2.5: Electrolysis of water [15]

The minimum necessary voltage for the start of the water electrolysis, E^o_{cell}, is given under standard conditions (P, T constant) by the following equation: $E^o_{cell}=\Delta G^o/nF$ where ΔG^o is the change in the Gibbs free energy under standard conditions, n is the number of electrons transferred and F is the Faraday's constant [15].

By lowering the overpotential required to generate the same volumes of gases, efficient catalysts can lower the electric power which needed to produce the same volume of H_2. Modern electrocatalysts are materials based on single functional noble metals, such as Pt for the hydrogen evolution reaction (HER) and IrO_2/RuO_2 for the oxygen evolution reaction (OER). Currently, these catalysts still require a significant overpotential in order to proceed with the HER and OER. Unlike HER, OER happens at the anode and requires a fairly high overpotential due to its four-electron transfer process [16].

Pt and IrO_2/RuO_2 are now thought to be the most effective electrocatalysts for HER and OER, however, their high cost and scarcity seriously limit their practical use. Numerous non-precious metal catalysts have been studied in recent years and have been demonstrated to have good HER and OER capabilities. The state-of-the-art catalysts including carbon-based catalysts, transition metal borides (TMBs), transition metal carbides (TMCs), transition metal oxides (TMOs), transition metal phosphides (TMPs), transition metal sulfides (TMSs), and single-atom catalysts have been investigated toward both the HER and OER, and they showed comparable activities to precious catalysts. Further research into non-precious catalysts for water electrolysis holds immense potential for advancing sustainable energy technologies. Key areas warranting investigation include catalyst design, synthesis methods, performance optimization, and durability enhancement [17].

In addition to reducing the difficulty of producing different catalysts, studies have targeted on the creation of non-precious bifunctional electrocatalysts with improved performance. It has found that they can, also, prevent cross-contamination between the two reaction electrodes. The reaction mechanisms of HER and OER are entirely different, making the rational design of a bifunctional electrocatalyst difficult [18].

To develop efficient and effective bifunctional catalysts for water electrolysis, research should prioritize several key areas. Firstly, a thorough investigation into the molecular-scale mechanisms of both the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) is essential. This necessitates a combined approach utilizing computational studies and experimental data to understand the underlying processes. Such insights will enable the rational design of robust catalyst materials by manipulating electronic structures while also addressing catalyst degradation mechanisms over extended cycling periods. Secondly, efforts should focus on modulating the morphology and composition of bifunctional catalysts to enhance the exposure of catalytic active sites and facilitate reactant diffusion in solution media [18].

Engineering and fabrication processes must carefully consider various parameters to optimize catalytic activity, especially concerning industrial-scale applications. Lastly, harnessing the potential of heteroatom doping in nanostructured catalysts presents a promising avenue. These materials have demonstrated exceptional catalytic activities in electrochemical water-splitting processes, owing to their controlled molecular structures, abundant active sites, and resilience to harsh conditions. Advancements in in-situ characterization tools, coupled with computational estimations, are crucial for unraveling working mechanisms and refining performance. By addressing these aspects comprehensively, researchers can advance the development of bifunctional catalysts, contributing to the realization of sustainable energy production through water electrolysis [18].

Examples of bifunctional catalysts are cobalt nanoparticles encapsulated in nitrogen-doped carbon (Co@N–C). The Co@N–C catalyst displays high activity and durability for HER in a wide pH range and for OER in alkaline medium as a bifunctional catalyst. Similarly, it was discovered that ultrathin CoP NS was a strong and efficient catalyst material for overall water splitting. CoP NS/C has better OER and HER activity than the majority of modern catalysts, requiring an overpotential of just 0.277 V and 0.111 V for OER and HER, respectively, to achieve 10 mA cm−2. At 1.8 V, the current density was 335 mA cm−2, which is quite competitive with the most advanced Pt/IrO2 catalyst at a far cheaper cost. These results demonstrate the promise of CoP NS as readily available, affordable, environmentally benign, and bifunctional catalysts for electrochemical water splitting devices in the near future. They can also streamline the splitting process, enabling mass manufacture of energy devices ([19], [20]).

Further, the tested bifunctional catalyst Fe−Ni Nanoparticles (NPs) (25–40 nm) expresses remarkable catalytic activity and excellent performance. Last but not least, a study has checked a catalyst consisted of Cu-doped CoP nanosheet arrays grown on carbon paper (Cu-CoP NAs/CP). The results showed that this kind of catalyst can have increased active sites exposure, improved mass/charge transport, excellent activity and significantly enhanced conductivity ([21], [22]). Furthermore, powder of CuZr metallic glass was tested as a bifunctional catalyst. This cheap powder showed lower HER performance than the commonly used Pt/C but higher OER performance than the commercial IrO_2 and good stability ([21], [22], [23]).

For the HER exclusively, studies have tested numerous non-platinum catalysts. One of them is a C-N catalyst which exhibited an exceptional HER performance with a very positive onset potential and remarkable durability. The increase of the nitrogen input and doping with multi-heteroatoms (N, S, P) can effectively improve the electrocatalytic activity. Also, the pH value has a huge effect on the surface properties of the catalyst and so the electrochemical performance. Another one is molybdenum sulfide which, with the appropriate process, showed good catalytic activity, small overpotential and excellent electrical conductivity. Some other examples are Ni_{58}-Co_{42}, also, after a certain way of manufacturing, with similar positives for HER performance and durability, and well-designed monolithic etched copper foam-based Cu_2O layer decorated with TiO_2 nanoparticles heterojunction catalyst that providing superior HER activity, low onset potential and long-term stability in alkaline solution ([24], [25], [26], [27]).

Additionally, from another research, an electrocatalyst composed of a worm-like S-doped RhNi alloy has been successfully synthesized by a hydrothermal method followed by annealing in high temperature. It shows Pt-like catalytic activity and efficiency for HER, and good stability. Moreover, single-phase, well-characterized WC and W_2C thin film electrodes have been investigated as means of evaluating the suitability of these materials as micro thick precious metal HER catalyst supports. Both the WC and W_2C surfaces displayed comparable HER activity and durability to bulk Pt, making them suitable substrates for tiny quantities of Pt in electrochemical studies. Catalysts which are made by NiW alloy and especially $Ni_{59}W_{41}$, also, showed very high HER activity and performance ([28], [29], [30]).

OER's slow kinetics linked to the challenging 4-electron transfer significantly reduce the efficiency of hydrogen production overall. As a result, the goal of the effective electrocatalysts is to lower the OER overpotential, increasing water electrolysis' efficiency and minimizing power loss. The cheaper, than the expensive IrO_2, option of fluorine-doped cobalt molybdate (F-$CoMoO_4$) nanosheet arrays on graphite felt (GF) was tested. Results indicated that it can efficiently promote OER catalytic activity and the electrical conductivity. Another catalyst is $FeSe_2$ nanoplatelets, which also showed low overpotential, and high catalytic performance and activity ([31], [32]).

Hydrogen production can be achieved, as well, in a fuel solution. Alcohols are, particularly, interesting options among the fuels that can be converted into hydrogen because they break down quickly in the presence of water and produce an H_2 rich combination that is ideal for fueling fuel cells. Because it can be easily made from renewable resources and has a relatively high hydrogen concentration, bio-ethanol is very important. It was found that hydrogen selectivity was proportional to the H_2O/EtOH molar ratio. Ethanol decomposes to CO_x and H_2. According to an analysis, the NiZnAl catalyst has a high level of stability and catalytic activity for the ethanol reforming reaction. It was also discovered that, the performance of these catalysts depends a lot on the conditions and the nickel amount [33].

2.5.2 Batteries

2.5.2.1 Lithium-ion batteries

Lithium, in its elemental form, is very reactive. That's why elemental lithium, in many occasions, isn't used in lithium-ion batteries and contain lithium-metal oxide, such as lithium cobalt oxide ($LiCoO_2$). A battery is made up of several individual cells that are connected all together. Each cell contains three main parts: a positive electrode (cathode), a negative electrode (anode) and a liquid electrolyte [34].

When a device is powered by a lithium-ion battery, positively charged lithium ions (Li^+) go from the negative anode to the positive cathode, travelling through the electrolyte. On the other hand, electrons go from the anode to the cathode. **Fig. 2.6** depicts how lithium-ion batteries works [34].

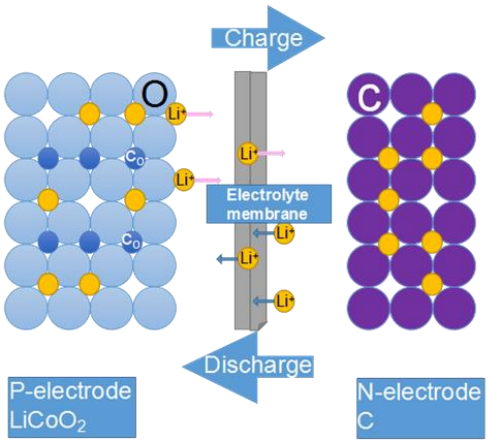

Figure 2.6: Lithium-ion battery operation [35]

The chemical reactions that take place on a lithium-ion battery are:

- At the cathode, reduction takes place. There, cobalt oxide combines with lithium ions to form lithium-cobalt oxide ($LiCoO_2$). The half-reaction is: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$,

- At the anode, oxidation takes place. There, the graphite compound LiC_6 forms graphite (C_6) and lithium ions. The half-reaction is: $LiC_6 \rightarrow C_6 + Li^+ + e^-$.

These batteries are rechargeable. When a lithium-ion battery is charged, the process is exactly the opposite. The lithium ions return to the anode from the cathode and the electrons are transferred from the anode to the cathode. The chemical reactions are totally reversed [34].

2.5.2.2 Li-O_2 Batteries

Researchers interested in lithium-oxygen (Li-O_2) batteries because of their exceptionally high theoretical energy density (~3500 Wh kg^{-1}). The reversible electrochemical reaction between O_2 and Li_2O_2 ($2Li^+ + O_2 + 2e^- \rightleftharpoons Li_2O_2$), which includes the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is the basis for discharging and charging processes. Nevertheless, a few problems need to be resolved before it is implemented widely. For instance, slow cycle performance, slow kinetics of ORR and OER, electrolyte degradation, and rapid capacity fading. **Fig. 2.7** shows how this works [36].

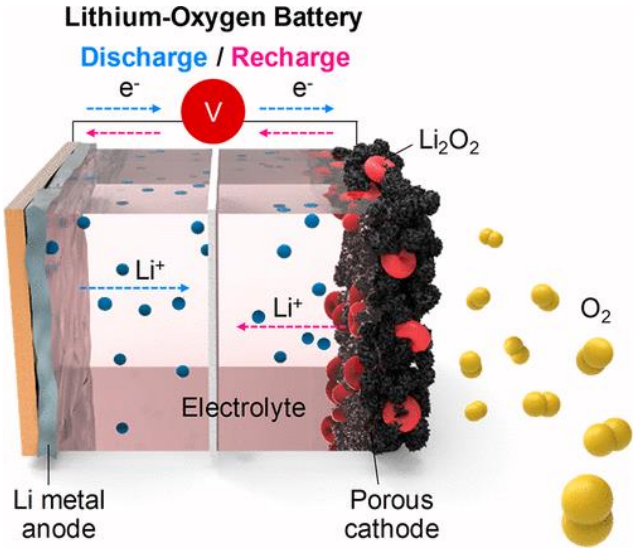

Figure 2.7: Schematic presentation of Li–O_2 battery [37]

The primary reason for the poor performance of Li-O_2 batteries is the slow cathode reactions, the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). Therefore, in order to make Li-O_2 batteries practical, bifunctional catalysts with high catalytic activity must be designed and prepared. Noble metals and their compounds, like Pt, Ru, Ir, and RuO_2, are unquestionably the top ones when it comes to lowering the overpotential and enhancing the cyclic stability of Li-O_2 batteries. Nevertheless, their high price and unavailability prevent large-scale commercialization. Many efforts have been undertaken to date to create low-cost, high-activity catalysts for Li-O_2 batteries [38].

Transition metal phosphides (TMPs) exhibit exceptional redox activity and outstanding electrical conductivity, making them attractive candidates for use as electrode materials. A catalyst that was

tested is NiFeP@NC/BC (BC = biochar), which delivered good electrochemical performance, good rate capability, and long cycle life and improved the catalytic activity of both ORR and OER. Additionally, a catalyst made of polyhedral and porous Mn_2O_3 rods was also examined. The analysis shows that the distinct porous structure of PP-Mn_2O_3 and the bifunctional catalytic qualities of Mn_2O_3 both improve the electrochemical performance of the Li-O_2 batteries. The catalyst, under specific process, has a high specific surface area and a mesoporous structure, which result in an abundance of active sites and better oxygen and electrolyte diffusion. As a result, the PP-Mn_2O_3 cathode batteries have exceptional specific capacity and strong cycling stability. One other example is a self-supporting Co-CoSe@NSeC/bioC cathode fabricated through growing cobalt-based metal organic framework (ZIF-67) on biomass and subsequent high-temperature selenization. It is proven to have decent oxygen reduction reaction/oxygen evolution reaction (ORR/OER) electrocatalytic activity, high specific capacity and maintains many stable cycles ([38], [39], [40]).

The insulating and insoluble Li_2O_2 will eventually block the electrode surface and obstruct the mass transfer channels as the discharge depth increases on the catalytic sites. Therefore, the key to creating a Li-O_2 battery with better performance is to design a unique cathode with a high carrying capacity of discharge products, an efficient electron transfer rate, Li^+ transfer, and oxygen transmission. For this reason, experiments took place for the NiFe@NC/PPC (PPC = carbonized pomelo peel) low cost catalyst, which shows that it has high performance, efficient diffusion rates for O_2 and electrolyte, good catalytic activity for oxygen reduction reaction and oxygen evolution reaction (ORR & OER), high specific capacity, low discharge and charge overpotential. One other catalyst with Ni, especially for the cathode, that is tested is NiCu-BTA (BTA = organic ligand, 1,2,4,5-benzenetetramine). This low-cost catalyst displays increased porosity, high activity, high discharge specific capacity and exceptional cycling stability ([41], [42]).

Self-supporting carbonized wood electrode was prepared by high temperature pyrolysis with $FeCl_3$/LiCl impregnated paulownia wood and melamine, which was used as the cathode of Li-O_2 battery. $FeCl_3$/LiCl can enhance the specific surface area, mesoporous ratio, and porous structure of carbonized wood. This can lead to an increase in the electrochemical three-phase reaction interface. By adding heteroatoms to carbonized wood, melamine improves the electrode material's degree of defect, which promotes increased electrochemical activity. The rapid mass transfer at the electrode benefited from the vertical channel structure inherited from the wood. Consequently, the Li-O_2 battery exhibited superior electrochemical performance and cycle stability [43].

2.5.2.3 Lithium-Sulfur batteries

Because of its low cost and high theoretical energy density, lithium-sulfur (Li-S) batteries, which use abundant elemental sulfur as the cathode material, have emerged as one of the most attractive options for

next-generation energy storage devices. Li-S batteries use a multi-electron-transfer electrochemistry, which is different from the intercalation electrochemistry of LIBs. Based on the conversion reaction of $S_8 + 16\ Li^+ + 16\ e^- \rightarrow 8\ Li_2S$, Li-S batteries offer a high theoretical specific capacity of 1675 mAh g^{-1}. Sulfur's low cost adds to the technology's benefits and attracts use in large-scale energy storage for renewable energy sources like solar and wind power. However, an inherent disconnect between basic research and real-world applications has hindered Li-S battery industry growth. The **Fig. 2.8** shows how it works [44].

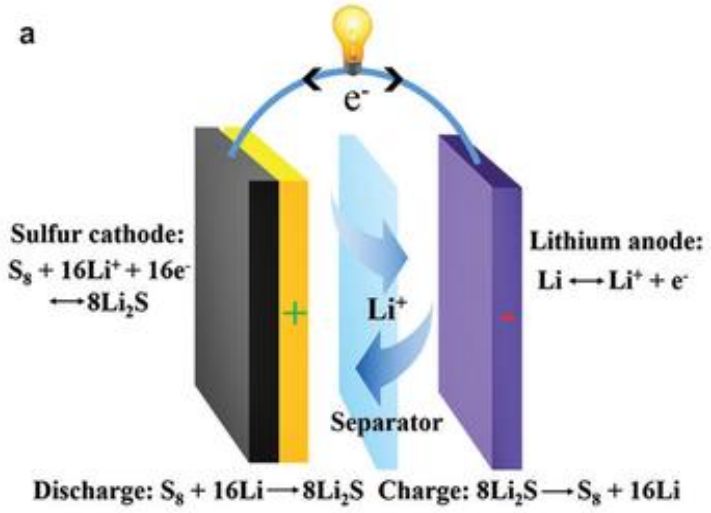

Figure 2.8: Schematic of the electrochemistry for Li–S batteries [45]

Nonetheless, the following issues hindered Li-S battery development for commercial use. Three things can happen when sulfur is totally reacted to generate Li_2S: 1) low conductivity, which causes the active material to react incompletely; 2) shuttle effect, where polysulfides dissolve in the electrolyte and shuttle back and forth between the positive and negative electrode for a parasitic reaction, resulting in a loss of active material, and 3) volume expansion, which can cause internal structures to be destroyed owing to the difference in density [46].

Many materials have been tested to address the aforementioned issues, and the most promising preparation technique makes use of porous carbon as the host of S. In a study, biomass (pomelo peels) and Prussian blue counterparts are used to prepare CoFe@NC/PPC composite. The process involves applying the CoFe-Prussian blue analogs (CoFe-PBA) to the pomelos in a solution setting, followed by a high-temperature calcination. Pomelo peel carbonization results in porous carbon doped with nitrogen during the calcination process, and Fe and Co ions are reduced to CoFe metal nanoparticles. In addition to having outstanding electrical conductivity, the nitrogen-doped porous carbon also binds sulfur in some way. The adsorption of sulfur can be improved even further by the coated CoFe nanoparticles. Following sulfur injection and button cell formation, it shows good rate performance and cycle ability [46].

2.5.2.4 Lithium-CO_2 Batteries

Fossil fuel consumption is rising in modern society, which increases CO_2 emissions and exacerbates global climate change. Li-CO_2 batteries, which have been reported recently, offer a potential remedy for this problem. Based on the reaction of $4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$, which accomplishes the usage of CO_2 and offers a new avenue for energy conversion and storage. The Li-CO_2 battery demonstrates a high theoretical energy density of 1876 Wh kg^{-1}. The **Fig. 2.9** below, describes the mechanism of this battery [47].

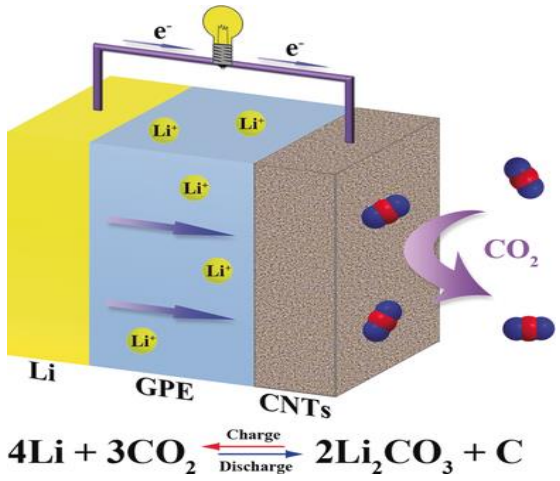

Figure 2.9: Schematic of the Li–CO_2 batteries [47]

The development of high performance Li-CO_2 batteries is really hampered by low specific energy density and poor cycle stability. High active catalysts for Li_2CO_3 decomposition have been developed in an attempt to increase the performance of Li-CO_2 batteries. The NiFe-Prussian blue analogues were deposited on the waste biomass (pomelo peels) to create the NiFe-PBA/PP precursor. NiFe@NC/PPC was eventually produced, and it underwent carbonization at 1000 °C in an Ar environment before being used as the cathode for Li-CO_2 batteries. It is confirmed that the 3D porous structure of carbon materials obtained from biomass is inherited to this cathode, providing ample space and enabling mass transmission. Furthermore, this cathode exhibits strong catalytic activity for the reduction of CO_2 and the breakdown of Li_2CO_3. High discharge capacity and outstanding cyclic stability with steady discharge and charge platforms were provided by Li-CO_2 batteries with NiFe@NC/PPC cathodes, which benefited from the distinctive 3D porous properties and the superior catalytic activity of the composite [48].

2.5.2.5 Zinc-Air Batteries

Even with their early start, Zn-air batteries today are still a long way from reaching their full potential. This is due to the fact that, on the one hand, the cathode's repeated proton-coupled electron transfers during the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are known to be sluggish, leading to significant electrode polarization and limited current density. On the other hand, most accessible zinc anodes have low cyclability due to zinc metal degradation and dendritic

development during recharging. So, Zn–air batteries are under revival. They have large theoretical energy density and potentially very low manufacturing cost compared to the existing Li-ion technology. Thus, their full potential will be fulfilled with the appropriate air cathodes and Zn anodes. **Fig. 2.10** shows how the Zn-air batteries works [49].

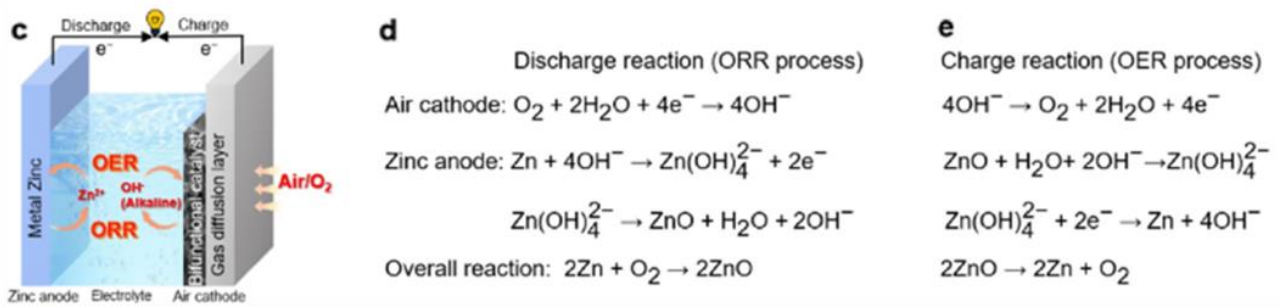

Figure 2.10: Schematic and reaction on Zn-air batteries [50]

They are composed of a Zn metal anode and a porous air cathode. These two, are separated by a membrane separator and are then loaded with a concentrated alkaline electrolyte. As the metallic zinc anode is oxidized to soluble zincate ($Zn(OH)_4^{2-}$) ions during discharge, oxygen from the ambient air enters the porous cathode and is reduced on the electrocatalyst surface. The aforementioned reaction can be reversed with the presence of an appropriate bifunctional oxygen electrocatalyst, allowing metallic zinc to be plated at the anode and O_2 to evolve at the cathode and be released back into the atmosphere [49].

Co_9S_8@N, S–C, a N, S co-doped carbon encapsulating Co_9S_8 nanoparticles, is effectively produced by using a novel precursor of Co-pyridine coordinated polymer, which consists of 4,4-dithiodianiline and 2,6-diacetylpyridine. With a low overpotential of 304 mV for the oxygen evolution reaction (OER) and rapid oxygen reduction reaction (ORR) kinetics with a high electron transfer number, the as-prepared Co_9S_8@N, S-C layer benefits from the abundant pore-structure (average pore-size ≈25 nm) and the distinct electronic characteristics of the Co_9S_8 and N, S–C layer [51].

Testing revealed that a material with single-site active Fe–Nx species on 2D porous nitrogen-doped carbon (PNC) that used as a bifunctional electrocatalyst for the oxygen electrode, confers functional Zn–air performance. OER/ORR bifunctional catalytic activity in an alkaline medium is exhibited by the as-synthesized FeNx-embedded PNC because of the combination of 2D porous nitrogen-doped carbon with outstanding conductivity, and a high specific surface area for integrating abundant active sites and Fe–Nx species with high intrinsic activity. The FeNx-embedded PNC based solid-state compressible and rechargeable zinc-air battery exhibits excellent mechanical durability and electrochemical performance thanks to the use of the high-performance bifunctional catalyst. Under compressibility and bending mechanical deformations, the electrochemical performance is highly maintained [52].

2.5.3 Fuel Cells

2.5.3.1 Solid Oxide Fuel Cell

A Solid Oxide Fuel Cell's (SOFC) fundamental structure is a solid electrolyte, typically ceramic, situated between an anode and a cathode. Fuel is provided to the anode and oxidant, commonly air, is provided to the cathode. The solid, porous electrodes allow the fuel and air to react near the electrolyte and the electrochemical reaction products to diffuse away from the electrolyte on the anode side. The oxygen ions produced by the electrochemical reduction of molecular oxygen, travel from the SOFC's cathode side to its anode side through the electrolyte. Fuel diffuses to the interface between the anode and the electrolyte via the anode. It initiates a catalytic reaction with the oxygen ions here, liberating electrons that travel through an external circuit to generate electricity. To increase voltage and power, individual cells are electrically connected in series with a metallic interconnect. They can be stacked to get the best stack size. A SOFC module can be made up of several stacks arranged in an enclosure. A SOFC power system can be formed by aggregating and integrating single or multiple modules with subsystems to deliver fuel and air, recover heat, and convert the generated electricity from direct current (DC) to alternating current (AC). **Fig. 2.11** shows how that operates [53].

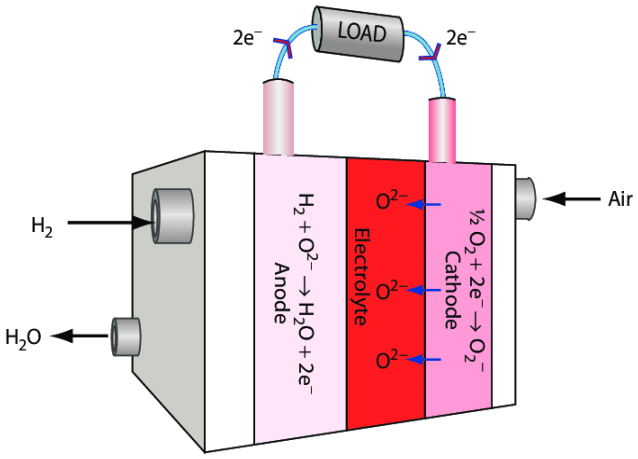

Figure 2.11: Solid Oxide Fuel Cell [54]

It is interesting to note that there is, also, SOFC based on proton-conducting electrolytes which some studies shown that this has higher efficiency values. **Fig. 2.12** shows how it works. A good example of an electrolyte for this application is the proton-conducting perovskite electrolyte, $Ba_{0.9}Sr_{0.1}Ce_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-\delta}$ (BSCZYSm). It exhibited unique characteristics in fuel cell application, showing a high-power density at intermediate temperatures. Using a particular technique and microscale particle sizes, BSCZYSm was successfully synthesized and demonstrated the potential for high ionic conductivity. It also had high proton conductivity and cubic symmetry. Compared to several other proton conductors, BSCZYSm has a better proton conductivity. A high-power density of 581.7 mW cm^{-2} was seen in several tests of the experimental

cell at 700 °C. Another good electrolyte is Y-doped BaZrO3 electrolyte (BZY), which need specific manufacture to be highly functional and efficient ([55], [56]).

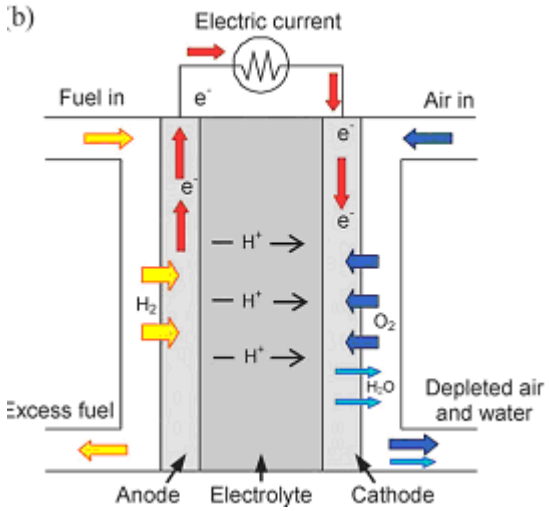

Figure 2.12: Solid Oxide Fuel Cell with proton conducting electrolyte [57]

It is critical to refer to the cathode's materials. A research, that was made for this reason, found one material that has the appropriate thermal and chemical properties to be used for the manufacture of the cathode. This material is $Ba_{0.5}Sr_{0.5}Co_{0.7}In_{0.1}Fe_{0.2}O_{3-\delta}$ [58].

This type of SOFC can be fed by different fuels, such as methane. This feeding requires an electrolyte that has a very good stability in carbon dioxide (CO_2) environments. Some experiments have been done about those electrolytes and specific research suggest an electrolyte by $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (SCY). This electrolyte can be recommended for use as an electrolyte for a temperature range of 600–800 °C, due to its decent proton-conducting ability ([59], [60]).

Especially for the methanol oxidation, a study has shown that the catalyst from $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ (LSCF) perovskite has good effects. It has decent electrical conduction and good catalytic activity. The main oxygen-containing products are CO, CO_2 and H_2O [61].

In general, selected fuel has a critical role in fuel cell's operation. Many fuel options such as methane, methanol, ethanol and gasoline are considered usable for SOFC operation, offering in fact a very significant ecological dimension in the issue of effective energy conversion. A simplified model that was created, shows that both electromotive force (emf) and efficiency are functions of the fuel type (oxygenated or not) its carbon atoms and of course the operational temperature. This model has also predicted that oxygenated hydrocarbons are less effective fuels than non-oxygenated ones for emf and system efficiency [62].

2.5.3.2 Anion Exchange Membrane Fuel Cell (AEMFC)

H_2 is supplied as a fuel and O_2 as an oxidant in hydrogen fuel cells. In an anion exchange membrane fuel cell (AEMFC), OH-ions are produced and then transported. Air can actually be used as an O_2 source. The anode and cathode sides receive H_2 and O_2, respectively. **Fig. 2.13** displays the AEMFC schematic diagram. The electrochemical reactions happen at the triple-phase boundaries. When water is present, O_2 at the cathode is reduced to OH^- ions, which cross the membrane to the anode side where they combine with H_2 to form H_2O. Since water is produced twice at the anode and consumed once at the cathode, improper water management can result in flooding at the anode and drying out the cathode. Electrons, generated on the anode side of the redox reaction, are gathered by the current collectors and moved to the cathode side via the external circuits. The membrane is chosen so that it transfers the OH^- ion exclusively [63].

The reactions are:

At the cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

At the anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Overall reaction: $O_2 + 2H_2 \rightarrow 2\ H_2O$

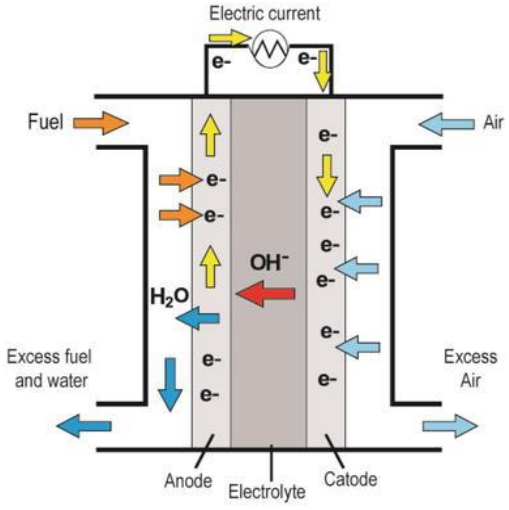

Figure 2.13: Operation of Anion Exchange Membrane Fuel Cell [64]

Developing effective, stable and low-cost electrocatalysts for alkaline media is highly desirable for the development of AEMFCs. So, there are many researches for catalyst without the precious platinum. One specific study suggests catalyst by Ni and Mo for the hydrogen oxidation reaction. Compared to Pt/C, the NiMo/C display a superior activity and durability [65].

AEMFCs can fed directly with glucose. Glucose has high power density, thus good performance for the cell itself. The complete oxidation to carbon dioxide can produce 24 electrons. More research is essential for the development of this technology [66]. The reactions are the below:

Anode: $C_6H_{12}O_6 + 24OH^- \rightarrow 6CO_2 + 18H_2O + 24e^-$

Cathode: $6O_2 + 12H_2O + 24e^- \longrightarrow 24OH^-$

Overall: $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

2.5.4 Photovoltaic Systems

A photovoltaic (PV) system is made up of one or more solar panels, an inverter, and other electrical and mechanical components that use solar energy to make electricity. From tiny rooftop or portable PV systems to enormous utility-scale generation plants, the size of a PV system can vary greatly. Through a process known as the photovoltaic effect, the light from the sun, which is made up of energy packets called photons, falls onto a solar panel and makes an electric current. Each panel only produces a small amount of energy, but when connected to other panels, a solar array can produce more. Direct current (DC) electricity is produced by a solar panel. Even though many electronic devices, like our phone or laptop, operate on direct current (DC) electricity, they are designed to provide electricity to the electrical utility grid, which uses alternating current (AC). So, an inverter is required to convert solar electricity from DC to AC before it can be utilized. The inverter's AC electricity can then be sent to the electrical grid for use elsewhere or used locally to power electronics. **Fig. 2.14 (a and b)** shows a simple solar panel and the system's diagram [67].

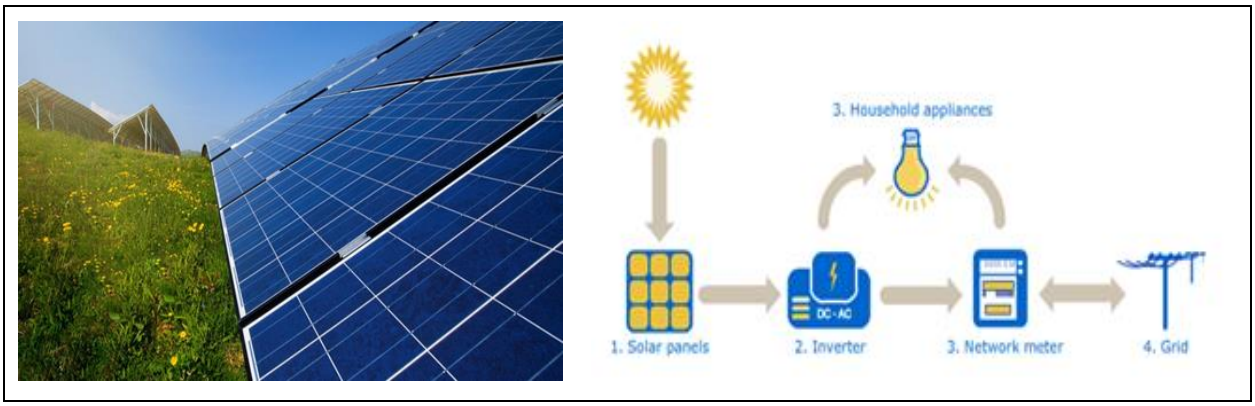

Figure 2.14: a) Solar panel and b) Photovoltaic System diagram [67], [68]

2.5.5 Photoelectrochemical Splitting

In the pursuit of sustainable and eco-friendly solutions, the field of photocatalysis has emerged as a beacon of hope, holding the promise of revolutionizing how we address energy and environmental challenges. As the world grapples with the detrimental effects of fossil fuel consumption, ranging from greenhouse gas emissions to resource depletion, there is an urgent need for alternative and cleaner energy sources.

Photocatalysis, a process driven by the interaction of light with specially designed catalysts, offers a pathway towards mitigating some of the profound issues associated with fossil fuels [69].

The current reliance on fossil fuels, marked by the burning of coal, oil, and natural gas, contributes significantly to air pollution, climate change, and geopolitical tensions. The extraction and combustion of these finite resources release vast amounts of carbon dioxide and other pollutants, exacerbating the global environmental crisis. Photocatalysis presents an innovative approach to circumvent these challenges by tapping into the abundant and renewable resource of sunlight to drive chemical reactions [69].

By harnessing the power of light, photocatalysis enables the conversion of solar energy into usable forms, such as hydrogen fuel through water splitting. This process not only provides a clean energy alternative but also addresses the issues of energy storage and transport associated with renewable sources. Moreover, photocatalytic materials have shown promise in environmental remediation, breaking down pollutants and contaminants under sunlight, contributing to a more sustainable future [69].

As the world seeks solutions to transition away from fossil fuels, photocatalysis stands at the forefront of research and development. Its potential applications span from clean energy production to air and water purification, offering a glimpse into a future where the harmful impacts of traditional energy sources are significantly reduced. In this context, exploring and advancing photocatalysis becomes imperative for shaping a more sustainable and resilient global energy landscape [69].

Water photocatalysis stands at the forefront of sustainable technologies, leveraging the power of sunlight to drive chemical reactions that hold great promise for clean energy and environmental remediation. At the heart of this process is a fascinating interplay between light, a photocatalyst, and water molecules. In water photocatalysis, a semiconductor material, often titanium dioxide (TiO_2) or other metal oxides, serves as the photocatalyst. Recent researches have targeted to invent and test new photocatalysts to enhance the production of hydrogen through water photocatalysis, such as single atoms catalysts (SAC) and especially single noble-metal atoms based on two-dimensional materials (SNA@2DM). When exposed to sunlight, the semiconductor absorbs photons, leading to the excitation of electrons from the valence band to the conduction band. This creates electron-hole pairs, where an electron is elevated to a higher energy state, leaving behind a positively charged hole. These electron(e^-)-hole(h^+) pairs play a pivotal role in redox reactions occurring on the catalyst surface. In the context of water splitting, the reactions involve:

1. Reduction Half Reaction: $2e^- + 2H^+ \rightarrow H_2$
2. Oxidation Half Reaction: $H_2O + h^+ \rightarrow O_2 + 2H^+$
3. Overall Reaction: $2H_2O \longrightarrow 2H_2 + O_2$

In this way, sunlight-driven water photocatalysis transforms solar energy into chemical energy stored in the form of hydrogen and oxygen gases. How the water photocatalysis works, is showed in **Fig. 2.15** ([69], [70], [71]).

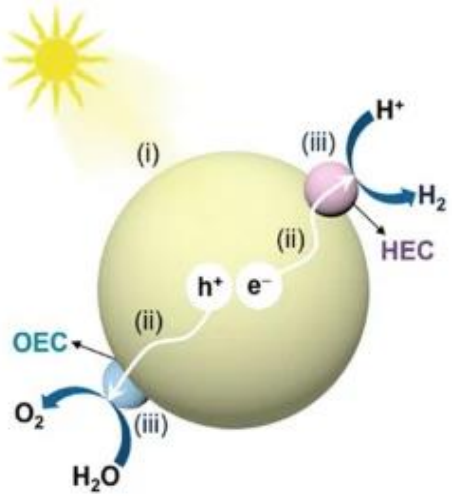

Figure 2.15: The reactions during water splitting on a photocatalyst [69]

Photocatalysis represents a groundbreaking approach in the quest for sustainable solutions, not only for water splitting but also for the transformation of carbon dioxide (CO_2), a major greenhouse gas. In the intricate dance of photons and catalysts, photocatalysis offers a glimpse into a potential avenue for mitigating climate change by converting CO_2 into valuable carbon-neutral fuels, such as CH_4 and CH_3OH. In CO_2 photocatalysis, a semiconductor material, often titanium dioxide (TiO_2) or other metal oxides, steps into the limelight as the catalyst. When exposed to sunlight, this material undergoes photoexcitation, generating electron-hole pairs that are subsequently engaged in a complex series of chemical reactions involving CO_2. One of the primary reactions in CO_2 photocatalysis is the reduction of carbon dioxide. This reduction reaction involves utilizing the energy from the excited electrons to convert CO_2 into carbonaceous products. The specific chemical products can vary, and their tuning is a subject of active research. CO_2 transformation poses thermodynamic challenges, requiring a considerable input of energy to drive the reduction reactions. Researchers are exploring ways to fine-tune catalyst properties, optimize reaction conditions, and integrate additional techniques, such as co-catalysts or external electrical bias, to enhance the efficiency of the process. Beyond carbon-neutral fuel production, this technology could find application in carbon capture and utilization, contributing to the reduction of CO_2 concentrations in the atmosphere. The development of efficient and selective catalysts is crucial for steering the reaction toward desired products while minimizing unwanted byproducts ([69], [72], [73]).

In the realm of photocatalysis, the synthesis of hydrogen peroxide (H_2O_2) stands as a captivating endeavor. Employing semiconductor materials as catalysts and utilizing light energy, this process

presents a sustainable pathway for generating H_2O_2, a versatile and eco-friendly oxidizing agent with applications ranging from water treatment to organic synthesis. At the heart of the photocatalytic production of H_2O_2 lies the reduction of oxygen (O_2) molecules under the influence of light-activated catalysts. The semiconductor catalyst, excited by photons, induces a cascade of electron transfers that eventually lead to the reduction of oxygen to hydrogen peroxide. The careful design of catalyst materials and the optimization of reaction conditions are paramount to enhancing the efficiency of this transformation. Semiconductor materials such as titanium dioxide (TiO_2), zinc oxide (ZnO), or new materials that are continuously tested on studies, often serve as the photocatalysts. These materials are chosen for their ability to absorb light and facilitate charge separation. Additionally, the introduction of co-catalysts, like metals or metal complexes, can further enhance the catalytic performance and selectivity ([69], [74], [75]).

The photocatalytic production of H_2O_2 faces challenges, including the need for improved efficiency, selectivity, and scalability for practical applications. Researchers are exploring advanced catalyst design, engineering techniques, and reactor configurations to overcome these hurdles and bring the technology closer to industrial implementation. Hydrogen peroxide produced through photocatalysis holds promise as a green oxidant. Its applications span from eco-friendly wastewater treatment and disinfection to serving as a feedstock in organic synthesis. By avoiding the traditional chemical routes to H_2O_2 production, photocatalysis contributes to reducing the environmental footprint associated with this valuable chemical. The photocatalytic synthesis of hydrogen peroxide exemplifies the boundless potential of sustainable chemistry. As advancements in catalyst design and process optimization unfold, this technology may play a pivotal role in providing environmentally friendly solutions for diverse industrial applications, furthering the quest for greener and more sustainable chemical processes ([69], [74], [75]).

Photocatalysis presents a powerful and eco-friendly solution to combat the environmental impact of pharmaceutical contaminants like tetracycline in water. Tetracycline, a widely used antibiotic, poses concerns for ecosystems and human health when it persists in water bodies. The process involves a semiconductor photocatalyst, often titanium dioxide (TiO_2), absorbing light to generate reactive oxygen species. These species break down the antibiotic's organic structure through redox reactions with oxygen and water. Efficiency hinges on factors like photocatalyst choice, light intensity, and environmental conditions. Researchers fine-tune catalyst modifications and operational parameters for optimal degradation, addressing challenges such as stability and the need for catalysts for specific contaminants. Photocatalysis operates under mild conditions, avoiding chemical reagents and minimizing harmful byproducts. It provides a green, sustainable approach to eliminate pharmaceutical contaminants, contributing to water quality and ecosystem health preservation. Ongoing research

focuses on advanced systems to bridge the gap from laboratory success to practical implementation in water treatment plants. Photocatalytic degradation represents a promising avenue for sustainable water treatment, illuminating a path toward a cleaner and safer aquatic environment ([69], [76]).

2.5.6 Sensors

2.5.6.1 pH Sensor

pH electrodes measure the difference in energy potential between two solutions, much like a voltmeter measures the difference in potential energy between two points in a circuit. A glass pH electrode uses a bulb made from pH-sensitive glass to measure a voltage when the electrode is submersed into a solution. This method can be customized to fit the majority of applications, is extremely accurate, and has an excellent response time. The voltage that is present in a charged battery can be easily measured by voltmeters but, the potential energy between two solutions does not typically exist between them, so a pH electrode must figure out a way to charge the solutions. The bulb is made of hydrogen ion sensitive glass to produce a potential gradient and charge the solution. Where the glass meets the solution, thin hydrated layers form. A gradient with measurable voltage forms if the number of hydrogen ions on one side of the glass differs from the other. The direction of current flow changes based on which side of the pH-sensitive glass has the highest concentration of H^+ ions. The two wires are connected by a liquid junction. This junction, which is made of a porous material, functions as a liquid wire by allowing a small amount of reference solution to flow out of the reference half-cell. It succeeds in separating the reference solution from the sample solution while still allowing current to flow, which is a challenging task. **Fig. 2.16** shows a pH sensor [77].

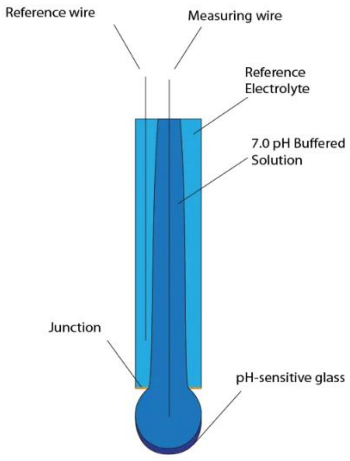

Figure 2.16: pH Glass Sensor [77]

2.5.6.2 Oxygen Sensor

The traditional oxygen sensor is a galvanic cell that employs an inert cathode and a lead sacrificial anode. The cell is low-cost and the reaction is powered by the net oxidation of lead to lead oxides

($2Pb + O_2 \rightarrow 2PbO$). When galvanic sensor is working, oxygen that diffuses into it, at a rate proportional to the pressure of oxygen in the solution, is reduced and consumed at the cathode. This reaction produces an electrical current that is directly related to the oxygen concentration. The ions (OH^-) transfer through the electrolyte from the cathode to the anode and the electrons (e^-) travel through the external circuit from the anode to the cathode ([78], [79]).

Anode (Pb) – lead oxidation reaction: $2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$

Cathode (Ag) – oxygen reduction reaction: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

Overall reaction: $2Pb + O_2 \longrightarrow 2PbO$

The sensor stops functioning when the lead is used up or when the solid PbO completely covers the lead surface. The rate at which oxygen diffuses in, which is regulated by the diameter of the inlet capillary, determines how long the sensor will last. A small capillary enables up to three years of sensor life. **Fig. 2.17** shows an oxygen sensor device ([78], [79]).

Figure 2.17: Oxygen Sensor [80]

2.5.6.3 Other Sensors

Gas electrochemical sensors are integral components in numerous technological processes, particularly those involving high temperatures, demanding precise analysis of gas mixtures. Their efficacy relies heavily on the electrolyte's processing, emphasizing the conductivity of solid electrolytes, their specific design, and the operational temperature. These sensors are adept at analyzing key gases such as H_2, H_2S, CO, O_2, SO_2, NO_x, and N_2, providing high-accuracy readings ([81], [82]).

In gas systems with oxygen and fuel gases, the sensors face challenges related to selectivity response, repeatability, and stability over time. Innovative solutions, such as the combined amperometric-potentiometric oxygen sensor, have been introduced to overcome these hurdles. Nitrous oxide (N_2O)

sensors are crucial, given N_2O's widespread use in medical anesthesia and food industry, and contributing to the enhancement of fossil fuel combustion engines ([83], [84], [85], [86]).

High-temperature proton-conducting ceramic materials (HTCP) play a pivotal role in sensor technology, enabling effective systems for controlling combustion processes, monitoring chemical pollutants, and determining gas concentrations. Hydrogen sensors designed for high temperatures are essential in the growing hydrogen economy, detecting leaks and measuring hydrogen content during production, transportation, and storage, ensuring safety and efficiency ([87], [88], [89]).

Measurement capabilities extend beyond hydrogen, covering gases like CO and CH_4. Sensors equipped with appropriate electrolytes ensure accuracy and reproducibility of responses. As the demand for hydrogen grows across various applications, these sensors become indispensable, providing a critical layer of safety and efficiency in industrial processes. Their versatility makes them valuable tools in analyzing and ensuring the quality of gas mixtures in diverse technological applications ([90], [91], [92]).

Electrochemical sensors play a pivotal role in various applications related to human health, demonstrating their significance in medical diagnostics and environmental monitoring. One of the notable applications is in glucose detection, particularly in low concentrations, showcasing their utility for diabetes management. These sensors enable real-time monitoring of glucose levels, offering patients a convenient and efficient way to track their blood sugar levels for proper disease management [93].

Moreover, the versatility of electrochemical sensors extends to the realm of infectious diseases, with notable applications during the COVID-19 pandemic. These sensors have been employed for the rapid and sensitive detection of viral components, aiding in the development of diagnostic tools. Their ability to provide quick and accurate results contributes to effective disease control and management [94].

In the realm of neurology and cardiovascular health, electrochemical sensors have proven instrumental in detecting neurotransmitters such as dopamine and ascorbic acid. Abnormal concentrations of these compounds are associated with conditions like Parkinson’s disease and atherosclerosis, respectively. The development of sensors capable of pinpointing these biomarkers allows for early diagnosis and proactive intervention in these critical health areas. Additionally, electrochemical sensors find application in the detection of hazardous environmental pollutants, such as hydroquinone (HQ) and catechol (CC), demonstrating their role in safeguarding human health by monitoring and mitigating exposure to potentially harmful substances. The ongoing advancements in electrochemical sensor technology hold promise for further breakthroughs in medical diagnostics and environmental health, contributing significantly to the well-being of individuals and communities ([95], [96], [97], [98]).

2.5.7 Carbon Dioxide Electrochemical Reduction

Carbon dioxide (CO_2) electrochemical reduction has emerged as a pivotal field in the quest for sustainable energy solutions and environmental remediation. As the concentration of CO_2 in the Earth's atmosphere continues to rise, driven primarily by anthropogenic activities, finding effective methods to mitigate its impact has become imperative. Electrochemical reduction offers a promising avenue to convert CO_2 into valuable fuels and unharmful chemicals through the application of renewable energy sources. This process not only addresses the environmental challenge of CO_2 emissions but also holds the potential to provide a renewable and carbon-neutral source of energy. In CO_2 electrochemical reduction, electrodes catalyze the conversion of CO_2 into various products, such as carbon monoxide (CO), methane (CH_4), and ethylene (C_2H_4), depending on the catalyst and reaction conditions. The development of efficient and selective electrocatalysts plays a crucial role in enhancing the performance of CO_2 reduction systems. Understanding the complex electrochemical processes involved in CO_2 reduction is essential for tailoring catalysts and optimizing reaction conditions to achieve desired product yields ([99], [100], [101]).

Electrochemical CO_2 Reduction Reactions systems, as shown schematically in **Fig. 2.18**, consist of an anode, a cathode, an aqueous solution electrolyte saturated with CO_2, and a membrane. The oxygen evolution reaction occurs at the anode, while the CO_2 Reduction Reactions occurs at the cathode. Transporting CO_2 to the surface of electrocatalysts is facilitated by the electrolyte. Protons can move to the cathode through the membrane, which forms a closed loop and separates oxidation and reduction products while preserving charge balance. The process of electrochemically reducing CO_2 is incredibly complicated. As shown, a variety of carbon-containing chemicals, including carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4), formic acid (HCOOH), methanol (CH_3OH), and ethanol (CH_3CH_2OH), can be created by transferring two, four, six, or eight electrons [100].

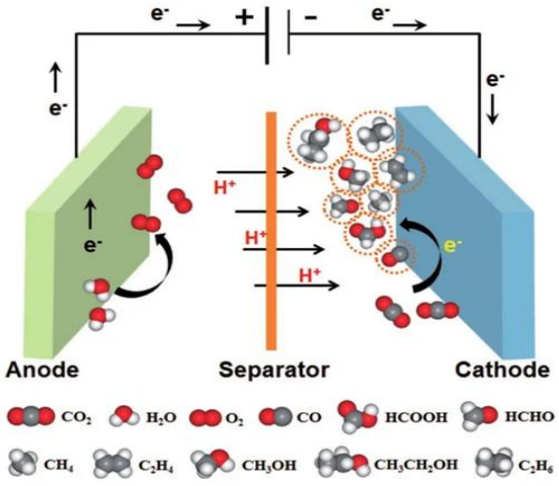

Figure 2.18: Schematic diagram of the electrochemical CO_2 reduction reaction system [100]

Catalysts play a pivotal role in carbon dioxide (CO_2) reduction reactions (CO_2 RR), serving as the key drivers to enhance the efficiency and selectivity of the electrochemical process. The pursuit of sustainable energy solutions and the conversion of CO_2 into valuable products heavily rely on the development of efficient catalysts. Among the diverse range of catalysts explored for CO_2 RR, metal oxides have garnered significant attention. Copper oxides, tin oxides, bismuth oxides, zinc oxides, cobalt oxides, and others have demonstrated varying degrees of catalytic activity and selectivity in reducing CO_2 to desired products. Metal oxide composites further enhance catalytic performance by synergizing the properties of different materials, leading to improved efficiency and stability. Gold (Au) based catalysts represent another noteworthy category in CO_2 RR research. Gold nanoparticles and Au-based composites exhibit unique catalytic properties that contribute to enhanced CO_2 reduction activity. The incorporation of gold into catalyst structures aims to optimize reaction pathways, improve selectivity, and boost overall electrochemical performance ([100], [102]).

It's a good timing to make a simple reference to Nitrogen Reduction Reactions. Nitrogen reduction reactions (NRR) have emerged as a critical avenue for addressing global challenges related to nitrogen utilization and management. Unlike carbon dioxide reduction reactions (CO_2 RR), which aim to mitigate greenhouse gas emissions, NRR targets the conversion of nitrogen molecules into valuable compounds, such as ammonia and other nitrogen-containing chemicals. This process is crucial for sustainable agriculture, as ammonia serves as a primary component of fertilizers, supporting crop growth and food production. The significance of NRR extends beyond agriculture, encompassing applications in the synthesis of nitrogen-containing chemicals such as fertilizer, explosive and dye, and pharmaceuticals. By unlocking efficient and sustainable methods for nitrogen transformation, NRR holds the potential to revolutionize industries reliant on nitrogen feedstocks ([103], [104]).

The reduction of nitrogen gas (N_2) to ammonia (NH_3) is a complex and energetically demanding process under ambient conditions. Hence, the development of efficient catalysts is paramount to facilitating NRR and making it economically viable. Various catalysts have been explored to enhance the selectivity and efficiency of nitrogen reduction, and these catalysts play a crucial role in determining the overall success of the reaction. Recent studies delve into the design of catalysts with tailored structures and compositions to optimize NRR performance. Notably, catalysts like FeAg/Si (FeAg nanoclusters loaded on silicon nanowire) exhibit promising results, leveraging the synergy between iron and silver nanoclusters on silicon nanowires. This configuration demonstrates enhanced catalytic activity [103].

2.5.8 Corrosion

Metallic surfaces slowly become covered in oxides or other metal salts due to corrosion. Some of the examples of corrosion are the development of green coating on copper and bronze, the rusting of iron and the tarnishing of silver. It significantly damages all metal objects, especially those made of iron, including buildings, bridges, ships, and other structures. A metal is oxidized during corrosion by losing electrons to oxygen and producing oxides. Iron corrodes (commonly referred to as rusts) in the presence of water and oxygen. **Fig. 2.19** depicts how corrosion is developed [105].

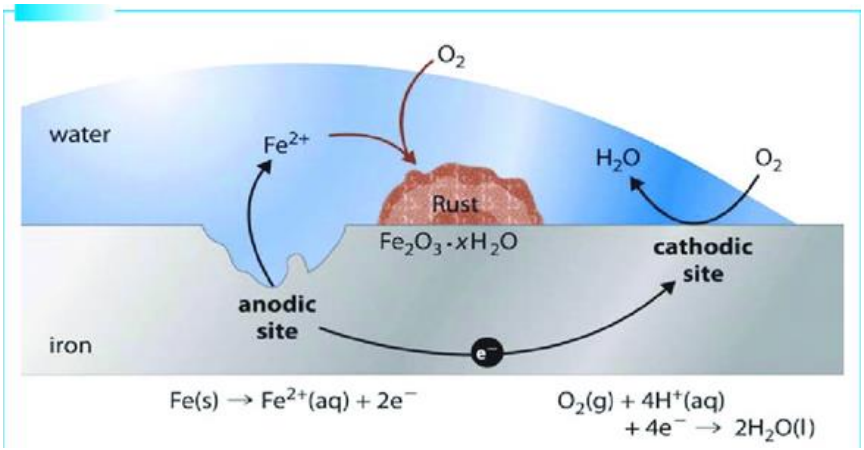

Figure 2.19: Corrosion's Formation [106]

Although corrosion's chemistry is quite complicated, it can essentially be described as an electrochemical phenomenon. An iron object undergoes oxidation at a specific location, which acts as an anode and allows us to record the reaction,

Anode: $2Fe\ (s) \longrightarrow 2Fe^{2+} + 4e^{-}$

Electrons released at the anodic point, migrate through the metal and go to another position on the metal where they reduce oxygen in the existence of H+, which is thought to be present from H_2CO_3 created when carbon dioxide from the air dissolves in water. Hydrogen ions may also be present in water, caused by atmospheric dissolution of other acidic oxides. This location acts as a cathode with the reaction,

Cathode: $O_2(g) + 4H^{+}(aq) + 4e^{-} \longrightarrow 2H_2O\ (l)$

The atmospheric oxygen continues to oxidize the ferrous ions, turning them into ferric ions that become hydrated ferric oxide, which is rust and produce more hydrogen ions. The reaction is the below,

Atmospheric oxidation: $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^{+}(aq)$

Corrosion’s prevention seems be of highest concern. In addition to saving money, it aids in avoiding accidents like bridge collapses or the breakdown of a crucial component due to rust. Since both the cathodic and anodic parts must take place for corrosion to occur, prevention of only one will stop corrosion. Preventing a metallic object's surface from coming into touch with air is one of the easiest ways to stop corrosion. This can be accomplished by painting the surface or applying various chemicals on it. Another straightforward technique is to coat the surface with other metals (Sn, Zn, etc.) that are reactive or inert in order to preserve the object. An electrochemical technique involves using a sacrificial electrode made of a different metal (such as Mg, Zn, etc.) that corrodes but protects the object [105].

CHAPTER 3

PEM Fuel Cells

3.1 Introduction

PEM Fuel Cells (as known as Proton Electrolyte Membrane) are made with polymer electrolyte membrane and are known to have low operating temperatures and high efficiencies. It is believed that they will be the main source of power for transportation (and not only) in the future, because the emissions are very low and they don't harm the environment. The emissions from fuel cells are notably cleaner because they convert fuel to energy electrochemically rather than through combustion. Just a reminder, the main product of these devices, is just water (H_2O). Furthermore, scientists and engineers are occupying more and more with these technological devices, because of the simplicity, the durability and the quick startup. **Fig. 3.1** shows some examples which use PEM Fuel Cell technology ([107], [108]).

Figure 3.1: Examples on which the power units are Fuel Cells [107]

An internal combustion engine (ICE) emits to our environment many gases such as oxides of sulfur, oxides of nitrogen, oxides of carbon, hydrocarbons which take part in so many phenomena in the environment, such as climate change, global warming, air pollution. Many organizations and scientists try to sensitize the humanity to understand the seriousness. So, this should result in taking measures to reduce the pollution in general. Thus, everyone can understand that with the use of a fuel

cell instead of an ICE, all these problems from the fumes, can stop existing in a large scale and the environment can become more and more clean and the air more breathable ([107], [108])

3.2 Structure and Components

PEM fuel cell consists mainly of two electrodes, anode and cathode, and an electrolyte which is packed between the electrodes. **Fig. 3.2** shows its components.

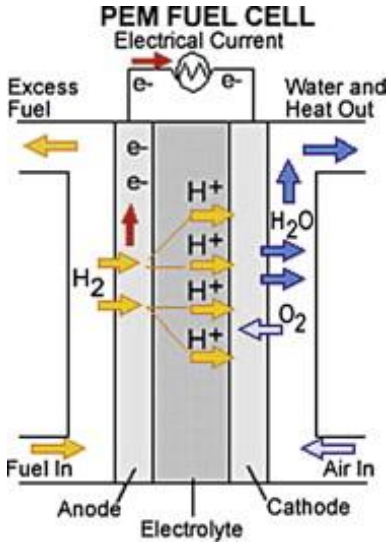

Figure 3.2: Components of a PEM Fuel Cell [109]

3.2.1 Membrane

The membrane (electrolyte) is the most important component of the Fuel Cell. Its main operation is to transfer protons (H^+) from the anode to the cathode. Also, there are some other operations such as keeping isolated the "fuel" hydrogen from the atmospheric oxygen, preventing from mixing of the two, bearing in difficult conditions and not letting electrons passing through itself ([110], [111]). So, a membrane must have:

- great proton conductivity,
- thermal and chemical stability,
- flexibility in conditions differences,
- low gas penetrability,
- high strength,
- dimensional stability,
- low-priced and
- be easily accessible and plenty.

The water amount is crucial for the membrane. The membrane must be hydrated, so it helps with the proton conductivity. Dehydration decreases the proton conductivity and it is difficult for protons to pass through it. But too much water on it, it has the opposite results. The excess water increases the volume of the membrane, making harder the motion of the protons. Also, on the cathode's side, water becomes a barrier for the oxygen to approach and react with the protons. That makes the cell less effective [110].

Many types of membranes have been used from the beginning of cell's research and production. Immediately, it became understandable that sulfonic groups are helping the membrane with the proton's transportation. Some membranes that used early were, membranes from phenol-formaldehyde sulfonic acid with phenolsulfonic acid and membranes with sulfonated polystyrene. These membranes were very weak and the lifespan didn't overtake 200 hours on operation [110].

Nowadays, the most used membrane is the membrane Nafion, which is a variant of the molecule Teflon. Nafion molecule is shown in **Fig. 3.3**. This membrane has the following advantages [110]:

- High chemical resistance
- High stability (strong carbon-fluoride chemical bonds)
- It can operate on relatively high temperatures (<= 190^0C)
- It has high proton conductivity
- The main chain is hydrophobic and the side chains are hydrophilic. So, it is created a group, which inside it, are placed the side chains and outside the main chains. With this placement, floods are prevented

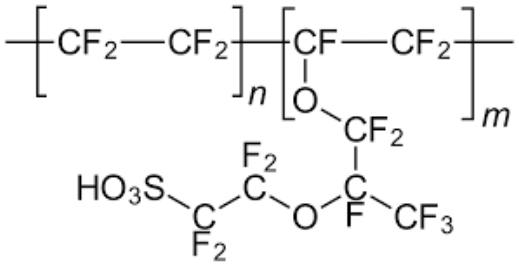

Figure 3.3: Nafion molecule [112]

3.2.2 Electrodes

Fuel Cells have two electrodes. The one that is fed with hydrogen is called anode and the other, where water is produced, is called cathode. It can be considered that the electrode consists of two layers, the catalytic and the gas diffusion layer. It is responsible for the transportation of the electrons to and from the outside circuit, the transportation and the reaction of the protons and the transportation of the reactants inside, and the products outside the fuel cell. Also, the electrode is trying to achieve the correct number of electrons, protons and atmospheric oxygen to have an effective reaction on the cathode ([107], [113]).

3.2.3 Catalytic Layer

The catalytic layer, as shown in **Fig. 3.4**, is in contact with the membrane and the gas diffusion layer. In this layer, the two electrochemicals reactions take place (the one on the anode and the other on the cathode). So, it is necessary for the catalyst to be as close as possible to the membrane, to rise the efficiency of the reactions. Properties that a catalyst must have are high diffusivity, high electrical and ionic conductivity, and satisfying hydrophobicity. Usually, platinum particles are used as catalyst, supporting on a carbon base. This catalyst has high efficiency but is very expensive. Technological advance has achieved the reduction of the quantity of platinum, lowering significantly the cost. Moreover, platinum alloys (with nickel, cobalt or krypton) have been discovered to be more active than plain platinum. For more efficiency and/or lower cost, catalysts from other materials are tested, such as palladium, ruthenium and combinations of metals with polymers ([107], [111], [113]).

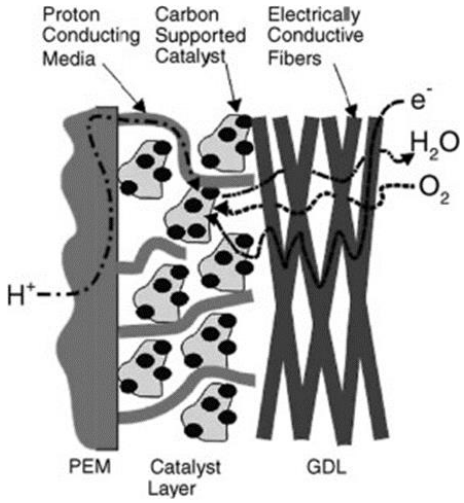

Figure 3.4: Catalyst Layer [113]

Because of platinum's cost and poor durability which extremely restricts the commercialization of PEMFCs, studies continually try to low Pt usage on catalysts. One way is proven to be the combination of Pt with Pd. Pd itself has high catalytic performance in many applications, and high stability under harsh reaction conditions. Also, Pt and Pd form solid bimetallic alloy structures because they have almost the same lattice constant and the same face-centered cubic geometry. So, Pt-Pd catalyst, after specific production method, has a superior performance for the reactions and shows remarkable durability. Pt usage can become even lower, when a trace concentration of Pt-Ni precursors is deposited on Pd nanosheets. With the appropriate thickness, the Pd-Pt-Ni catalyst can achieve excellent catalytic activity and durability. The union of Pd, Pt and Ni can be an ultra-small nanoparticle. Thus, this technique combines the improvement of the catalytic active site with the enhancement of the Pt electronic structure and the synthetic method to prepare Pt-based small-sized catalysts for ternary alloy ([114], [115]).

On recent years, a big number of studies were focused on binary Pt-Co catalysts. More specifically, a study has done a research about Pt-Co nanodendrite in nanoframe with Pt skin. After a specific and detailed process, this Pt-Co ND NF catalyst shows improved catalytic performance and activity with effectively exposed catalytically active sites, enhanced stability and durability. Additionally, it reported on another research an easy $Mg(OH)_2$/ZIF dual-template strategy for synthesizing PtCo catalysts on Co, N co-doped mesoporous nanocarbon (PCN-MC). It showed that on these catalysts, PtCo clusters can be carefully fabricated with proper size and composition (tiny size PtCo catalyst particles with a high Pt atom utilization) and achieve optimized catalytic activity and durability ([116], [117]).

Furthermore, over the last several decades, a new class of functional materials in the field of catalysis has emerged, metal-organic frameworks (MOFs), also called coordination polymers (CPs), which are built by metal centers and organic ligands. MOFs are advantageous because of their controlled surface area and controlled structures, and well defined and organized connections. After pyrolysis and acid leaching, coordination polymer frameworks' metal/metal oxide are thought to be effectively removed, producing the final cavities of porous carbon materials. Because interpenetrated MOFs contain a high density of metal cations in their interlaced packing structure, pyrolysis of these materials may result in effective porous channels in the resulting structure. One example of a catalyst of this kind is carbon materials doped with nitrogen with a hierarchically mesoporous structure, produced by pyrolyzing an interpenetrated non-porous MOF. These catalysts could have positive effects on mass transfer, kinetics and durability when used to construct non-Pt electrocatalysts for electrochemical processes. This carbon catalyst looks prospective for widespread use in various fuel cell types due to its aforementioned properties [118].

Much attention has drawn the non-precious metal catalysts because of the lower cost than platinum. One example that was tested is MnCo-NC/C NanoTubes(CNTs) from mixed-metal zeolitic imidazolate frameworks (ZIFs). This catalyst shows superior functionality and activity, high electrochemical performance and durability in acidic and alkaline electrolytes. Another general example for non-precious metal catalyst is the catalyst W_2N supported by carbon black (W_2N/C). This catalyst exhibits good electrocatalytic performance and decent stability due to the possible existence of WO_2 oxides on the surface. It, also, exhibits high electrical conductivity and exceptional resistance to corrosion ([119], [120]).

Just to be mentioned, single-atom catalysts (SACs) is a new technology that provides unparalleled control over catalytic activity at the atomic level, making them a state-of-the-art advancement in the field of catalysis. SACs are made up of isolated individual metal atoms anchored on a support material, usually carbon-based, as opposed to conventional catalysts, which are made up of nanoparticles or bigger clusters. The unique advantage of SACs lies in their ability to maximize the use of scarce and expensive catalytic metals, such as platinum and non. By dispersing these metals

as single atoms, the catalytic sites are exposed and accessible, leading to higher efficiency and reactivity. The design and engineering of SACs have broad applications in catalyzing various chemical reactions. The development of single-atom catalysts has spurred considerable interest and innovation in the quest for more efficient and sustainable catalytic systems. More research is needed because this technology has some barriers to overcome to become fully commercialized [121].

Finally, it's nice to make a simple reference about Non-faradaic electrochemical modification of catalytic activity (also known as NEMCA). This was discovered in 1980s and makes possible to enhance remarkably the catalytic reactions or significant changes in the catalytic properties of a conductive catalyst in the presence of electrical currents or interfacial potentials ([122], [123], [124]).

3.2.4 Gas Diffusion Layer

Many times, behind the catalytic layer (both anode and cathode), right after the flow channel (or the bipolar plates), is placed a gas diffusion layer. **Fig. 3.5** shows where the gas diffusion layer is.

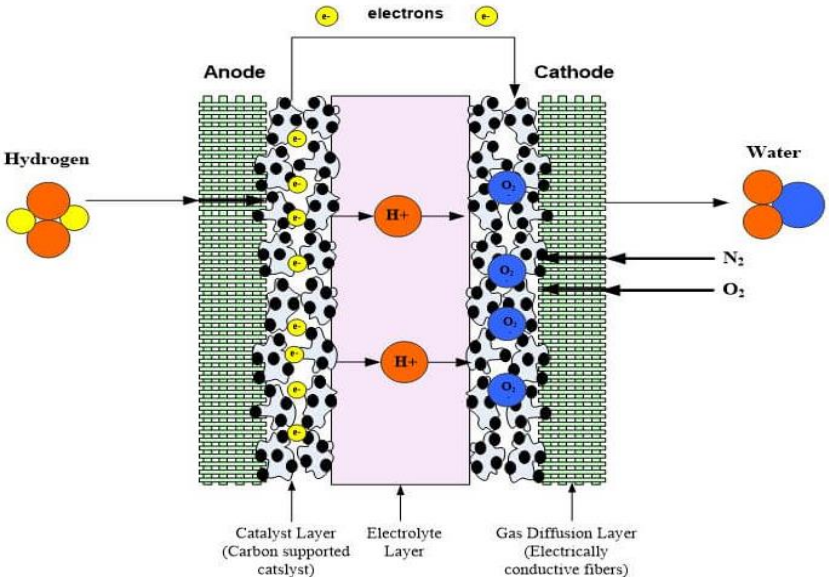

Figure 3.5: Gas Diffusion Layer [126]

This porous layer guarantees that reactants successfully diffuse to the catalyst layer. Additionally, this layer is the electrical conductor that moves electrons to and from the catalyst layer and guarantees that reactants are evenly distributed across the electrode. For this reason, it must have low electronic resistance. Furthermore, it helps in the operation of the cell, throwing away the product water (cathode). Generally, this layer has multiple functions in cell operation because they are controlling mass, heat, and electron transport. It also provides solid mechanical support and protection for the catalyst layer and membrane during installation and operation. The void areas help the transport of the reactants and the products ([112], [125]).

This layer must be made of porous, conductive material that helps the reactants to diffuse, on an almost perfect way, on the two electrodes. Usually, the material, which is selected is water proofed, carbon paper or cloth, (two additional advantages are that, it is water proofed and stable in acid environment) and its thickness doesn't overtake the 300μm. More, to prevent the pores from being clogged with liquid water, gas diffusion layers are often coated with Teflon to make them wet-proof. The Gas Diffusion Layer can be one layer or consisted of two individual layers, a macroporous and a microporous layer. This is also shown in **Fig. 3.6** ([125], [127]).

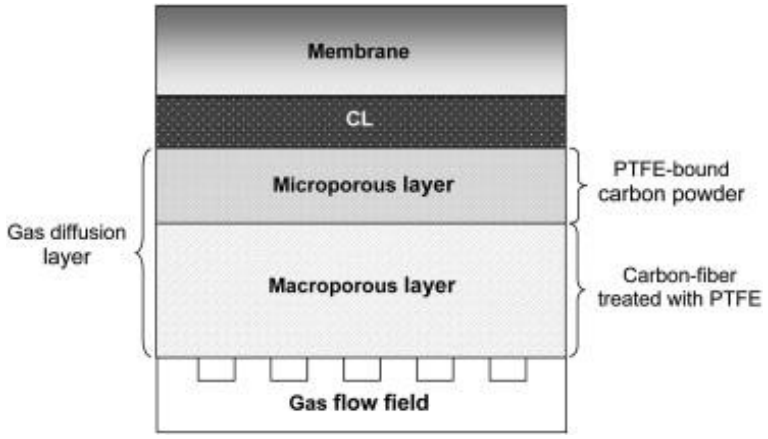

Figure 3.6: Two-layered Gas Diffusion Layer [128]

Macroporous layer (or substrate) is carbon-based layer and it is responsible for the evenly distribution of the reactants on the electrodes and for the water removal. So, it is required to be coated by hydrophobic substances (such as polytetrafluoroethylene and fluorinated ethylene propylene). Also, it is a support for the catalyst and has elastic properties, which is necessary when the assembly happens, because it handles compressions ([125], [127], [129]).

Microporous layer is made by carbon powder enriched by hydrophobic substances like the upper one. It helps reducing the contact resistance and strengthen the electronic contact between the catalytic and the macroporous layer and removing the water. So, it decreasing the possibilities of a destructive flood [129].

3.2.5 Bipolar Plates

Bipolar plates do not exist in a single cell, the electrodes from the two sides of the membrane are assumed to be these. In this situation, it can be said that the bipolar is the two electrodes [130]. The bipolar plates are placed in a stack of cells. Where it is placed is shown in **Fig. 3.7**. Their role is to [100]:

- Connect cells in series electrically,
- Isolate the gases from neighboring cells,
- Support the stack structurally,
- Conduct heat from the active cells preventing overheating and

- House the flow channel of reactants and products.

So, bipolar plates' properties must have high electrical and thermal conductivity, low penetrability to gases, high strength and durability, excellent corrosion resistance and low cost, and to be lightweight and convenient for mass production.

Materials that are usually used for manufacturing bipolar plates are metals and graphite-composite [111].

Metallic plates are excellent for mass production because are easy to access and process. They can be very thin, lightweight and strong, but they have a big disadvantage. The environment inside a fuel cell is very corrosive, and normal metals like steel and aluminum dissolve and release ions. These ions can penetrate into the membrane, resulting in reducing the electrical conductivity and in general the life of the cell. Using metals, it is necessary to have them coated with a noncorrosive layer. The selection of the material must be careful because this layer can react and reduce the electrical conductivity of the plates. This is something that manufacturers and researchers don't want to face. Apart from the above, the coat's efficiency depends on cracks that the layer can have from the production or during operation and the difference between the metal's and the coating's thermal expansion coefficients. Thus, layers that can be used are from graphite, conductive polymers, metal nitrides or carbides, organic polymers etc. ([111], [131]).

Graphite-Composite plates are constructed from thermoplastics or thermoset resins with carbon fillers and fiber reinforcements. These plates can be produced with various types of molding that haven't got super high cost and combined with the low cost of the graphite, the total cost is limited. Another advantage is that these materials are chemical stable in the cell's environment. On the other hand, these plates have more thickness and they are more brittle than the previous one. Also, some leaks can be appeared and, so, they lose their functionality. Also, it would be a good measure is to check them for improvements in material's configuration and properties. That can have an impact on the cost. While their electrical conductivity is lower than the metallic plates, they have very little resistive losses ([111], [131], [132]).

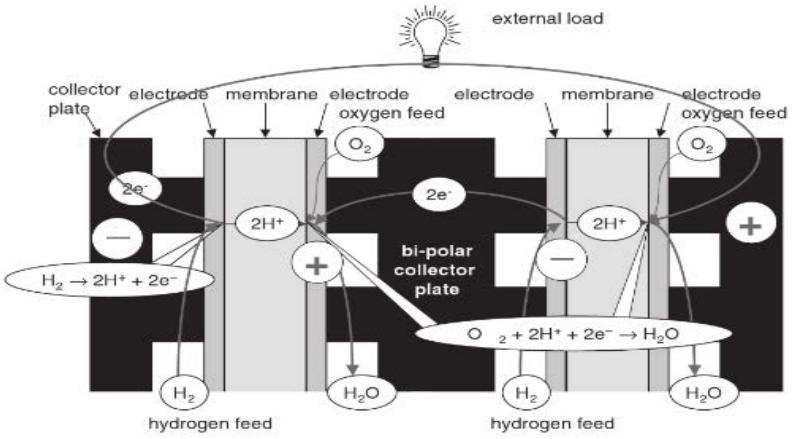

Figure 3.7: Bipolar plate [133]

3.2.6 System Control

Mainly, in a stack of Fuel Cells, it is required a system to control many parameters to ensure that the stack operates in the most effective way. This system, as it's shown in **Fig 3.8**, is consisting of four subsystems: 1) reaction, 2) thermal, 3) water management and 4) power electronics subsystem [134].

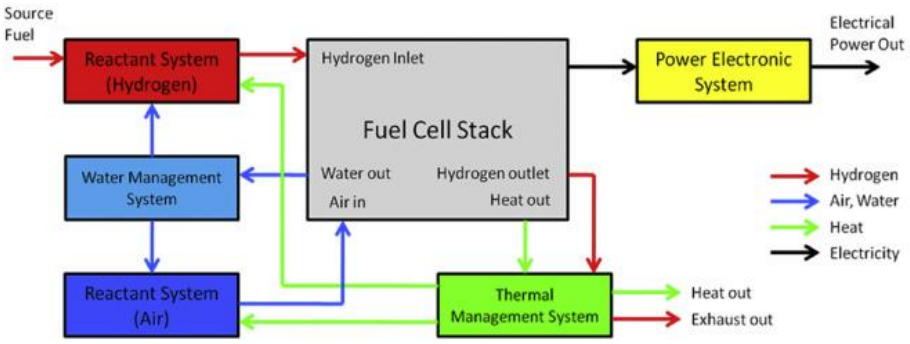

Figure 3.8: Diagram of System Control [134]

3.2.6.1 Reaction Subsystem

First, in the reaction subsystem, the reactants, hydrogen and air, are entered in a specified stoichiometric ratio into the stack, where they react to produce electrical power and water. Hydrogen is provided from reforming fuel (such as natural gas, methanol) or from a hydrogen tank. The pressure of the hydrogen flow is continually controlled by a pressure regulator. On the other side, the atmospheric air can be assisted from a blower or a pressurized air tank and the pressure is controlled, to achieve the precise air flow to ensure the stoichiometric ratio between hydrogen and air. This subsystem must be well produced, because any changes in the load, changes the effective stoichiometric ratio. So, the subsystem should get familiar quickly with the different situations and adapt the parameters. Therefore, phenomena like hydrogen starvation, which can weaken the cell and in general the stack, can be avoided [134].

3.2.6.2 Thermal Subsystem

Secondly, the thermal subsystem is very important because the heat that the fuel cells produces can influence the operation of the fuel cell. **Fig. 3.9** shows an example of a thermal subsystem. Heat (or rise of temperature) can help the electrochemical reactions to be more effective and quick, but there will be consequences to the membrane. Membrane will be shrunk, creased and cracked and all these would low the cell's performance or even worse, the cell will stop working. So, it is crucial for the subsystem, to keep the temperature on specific tolerances to have a balance between the two, achieving the maximum performance that can be possible. Just to mention, on stacks that produce power up to 1500W, temperatures can be controlled only by an air cooling system. This has an extra advantage that the fan, which is referred upwards for feeding the cathode with air, can be used for cooling the stack also. On stacks with higher power production, is necessary to use water cooling systems with radiator, which can expel higher load of heat [134].

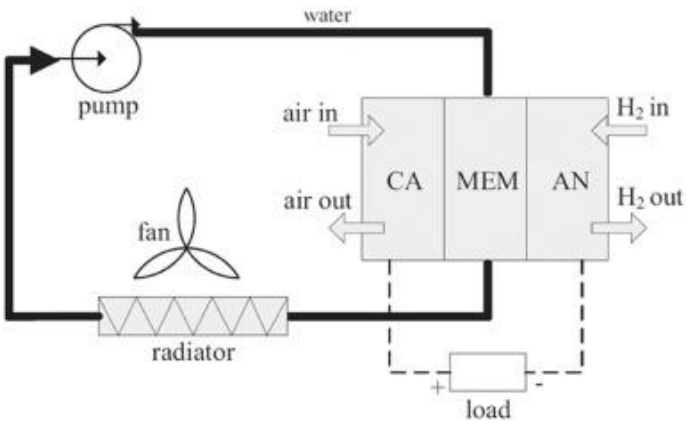

Figure 3.9: Example of a Thermal Subsystem [134]

3.2.6.3 Water Management Subsystem

Furthermore, water, on some levels, facilitates the proton's transport through the membrane and the catalytic layer. Water, also, is a product from the electrochemical reaction on the cathode. Here comes the water management subsystem, which its role is to keep the membrane perfectly hydrated to ensure conductivity and stability, but, in addition, it tries to remove extra water, preventing the cell from flooding. Flooding possibilities are bigger, when the air flow is small because the water isn't pushed out fiercely and when the temperature is low and the water is not evaporated in huge amounts. Even, the precipitation of water in the porous gas diffusion layer can cause floods and they degrade dramatically the efficiency. Also, the subsystem must control the humidity of the reactants that can cause troubles. There are referred two options, external and internal humidification. In the external, the subsystem controls the humidity of the reactants by changing their temperature and their passing time in an external humidifier. On the other hand, in internal humidification, water is injected directly to the membrane to make sure that humidity is on the right level [134].

3.2.6.4 Power Management Subsystem

Last, power management subsystem is required to rule the unstable electric power and passing it from a series of electrical devices for processing and filtering. **Fig. 3.10** shows an example of a power management subsystem. This aims to transform the power into smooth and efficient electricity. Just to mention, the output electrical current is direct (DC).

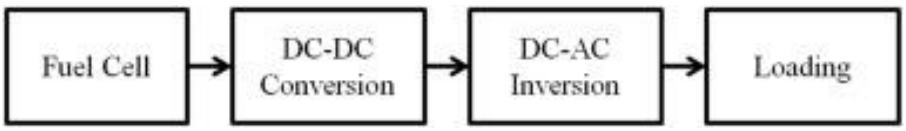

Figure 3.10: Example of a power management subsystem [134]

Many times, the voltage, that the stack produces, is reduces because of bigger current that is drawn when higher loads are required due to ohmic losses. So, the main operation of this subsystem is to provide adequate power from the cells to the load and to keep checking continually to please the

changeable demands. This subsystem can be consisting of voltage regulators, DC/DC converters and chopper circuits, which can adjust by increasing or decreasing the output voltage from the stack. If the subsystem increases the voltage, it can be called boost converter, if it reduces it, it can be called buck converter and if it can do both, it called buck-boost converter. The electric power can also adjust from an external circuit that contains a rheostat of a transistor. Therefore, the most applications need alternative current (AC), thus, this subsystem requires to has a DC/AC inverter to transform directly, the output direct current to alternative. So, it can be used immediately [134].

3.3 How a PEM Fuel Cell works.

Atoms of hydrogen aren't free in the environment. We can take them from hydrocarbons or from electrolysis of water. Each atom of hydrogen has one proton (H^+) and one electron (e^-). An electrochemical reaction happens at the surface of the catalyst in the contact area between the one electrode and the membrane (electrolyte). The reaction is the following one: $\boldsymbol{H_2 \longrightarrow 2H^+ + 2e^-}$. The electrode from the side of the pure hydrogen is called anode and is the negative one. The hydrogen, which is inserted in the device from the one side, splits into protons and electrons. The proton (H^+) passes through the membrane while the electron's path is through the electrically conductive electrodes. The electron ends up in the other side of the membrane after it passes the outside circuit. In the outside circuit, the motion of the electrons gives a direct electrical current. That current is what we can take and use it for many applications that humans have ([111], [135]).

Next, at the catalyst, between the other electrode and the membrane, happens another electrochemical reaction, which is the following one: $\boldsymbol{O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O}$. The electrode, which is from the other side with the atmospheric oxygen, is called cathode and it is the positive one. In this area, the protons which have passed through the electrolyte, the electron from the electrode and atoms of oxygen from the atmospheric air meet and react all together to give clean water. Then, the water is pushed out from the device. This operation is repeated over and over again to have stable result ([111], [135]).

Every one of these Fuel Cells generates a voltage that is about 1V according to sources. To produce higher voltage for more demanding applications, it is needed to construct a good amount of these cells and connect them in series. So, the total voltage is the sum of the voltage that each one can generate. Depending on the application, the total voltage can be 200V or even more. Certainly, this stack can create some problems, but these will be referred further down ([110], [132]).

3.4 PEM Fuel Cell's Losses

The voltage that a fuel cell or a stack of this can produce is changing continually because of the load and losses owing to operating conditions. There are three types of losses, ohmic, concentration and activation losses [111].

- Ohmic Losses: The resistance of each individual part of the fuel cell. All together are forming the ohmic losses.
- Concentration Losses: These losses are result of the local reduction of the concentration of hydrogen and oxygen at electrodes. After certain reactions, new quantity of gases must be, directly, on the surface of the catalyst. Also, with high concentration of water at the cathode, the catalyst surfaces are covered in water and the oxygen can't approach the catalyst.
- Activation Losses: Are the energy that is necessary for the fuel cell to start reacting. In consequence, this is the effectiveness of the catalytic layer. If a catalyst is effective, the activation energy is reduced and the losses are less.

3.5 Today's some alternatives

3.5.1 Direct Ethanol PEM Fuel Cells

Today, hydrogen is not fully commercially distributed and producing hydrogen by fuel processing, the product is not ~100% clean. So, scientists and manufacturers, looking for some alternatives, found that PEM Fuel Cell can fed with ethanol. Ethanol is renewable, non-toxic fuel and can be easily produced by sugarcanes (or other raw materials that contains sugar). Particularly for small-scale applications, Direct Ethanol Proton Exchange Membrane Fuel Cells (DE-PEMFCs) are interesting options for power sources. The way that this fuel cell operates is shown in **Fig. 3.11** [136].

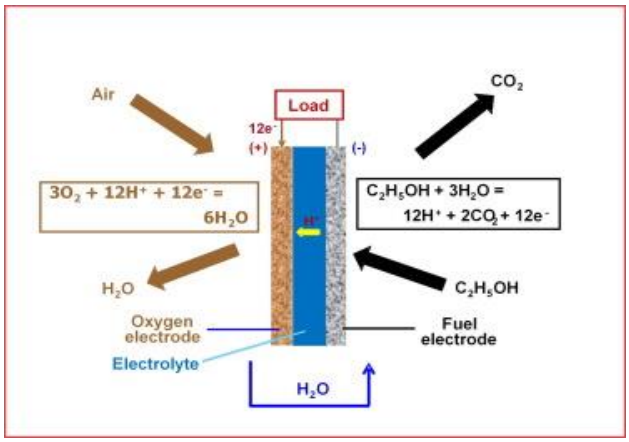

Figure 3.11: Direct Ethanol PEM Fuel Cell [136]

Due to their benefits, PEMFCs, that are directly fed by ethanol, have been the subject of increasing attention for many years. Nonetheless, there are certain obstacles that must be surmounted, for example, ethanol present at the cathode catalyst, which restricts oxygen reduction and causes a mixed overpotential to occur. The Direct Ethanol PEM Fuel Cell operates, almost, like the PEM Fuel Cell. The main difference is that on the anode, ethanol reacts with water to produce protons and electrons but, also, carbon dioxide is produced. In addition to past and today's technology, carbon dioxide is the only emission that is produced, and the quantity is lower on these. One problem that needs to be fully addressed is the ethanol

crossover. This presents a negative consequence on the open circuit voltage and the cell performance of DEFC and some countermeasures have already proposed [136].

3.5.2 Direct Methanol PEM Fuel Cell

It was also found that PEM Fuel Cells can, also, directly fed with methanol. Direct methanol fuel cells (DMFC) are appealing for portable applications including phone chargers, LEDs, and sensors, because of their high-power output. Liquid methanol is simple to work with, has a high energy density, and is safe for the environment. Additionally, methanol is safe to handle at normal temperatures and pressures, easy to store, and simple to refuel. The **Fig. 3.12** below shows how it operates [137].

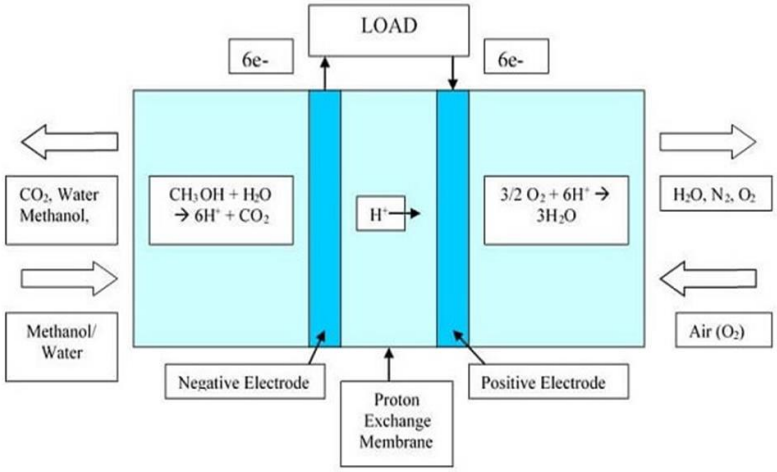

Figure 3.12: Direct Methanol Fuel Cell [138]

However, there are challenges and problems that need to address, to become fully commercially used. Main issues are about the membrane and the electrodes-catalysts. On these fuel cells, methanol crossover and low ionic conductivity are observed. These problems can be solved by using new kind of membranes. Some researchers have done some experiments and found that, for example, a sulfonated polyether sulfone/polyvinyl alcohol membrane with tungsten disulfide nanosheets or a Nafion membrane with graphene oxides and a sulfonated derivative, have increased proton conductivity and reduced methanol crossover [137].

The main catalysts that are mostly used are Pt for both electrodes and Pt-Ru for the electrode that Methanol Oxidation Reaction takes place, because in such fuel cells, these catalysts continue to work exceptionally well in the methanol oxidation and oxygen reduction reactions. One big issue is that both Pt and Ru are very expensive and are increasing the total cost for commercially development. Also, both elements have high sensitivity to CO, which is produced from methanol electrooxidation. This not only continually reduces activity but also results in a decent decrease in cell performance. Thus, it is still very desirable to use new types of Ru-free, more stable, and effective electrocatalysts for methanol electrooxidation. Thus, designing extremely effective, inexpensive, durable electrocatalysts that optimize Pt utilization rate and minimize Pt loading is a crucial part of fuel cell manufacturing ([139], [140]).

Firstly, because of their excellent hardness, high melting point, and strong resistance to wear, oxidation and corrosion, tungsten carbides (WC) have found extensive application in machinery. When processed properly, they have been shown to have a positive impact on Pt catalysts' activity in the methane oxidation reaction and their resistance to CO poisoning. These catalysts also show excellent performance, high activity, and desired stability. Moreover, it has also been demonstrated that alloying Pt with non-noble metals is a useful and cheap way to increase catalytic capability. A wide range of bimetallic Pt–M alloys with different nanostructures (M = Cu, Ni, Co, Pb, Ag etc.) have been created and showed to be successful in increasing the electrocatalytic activity for both reactions. Compared to other reported Pt-based catalysts, because Ni is readily available at a reasonable cost and Pt-Ni alloys have good catalytic capabilities and high durability, they are among the most promising electro-chemical catalysts. ([139], [140]).

3.6 Why should we use PEM Fuel Cells?

PEM Fuel Cells (and in general Fuel Cells) are believed to be the power source of the future. They have many advantages of using them instead of today's energy conversion devices. Some of that are ([108], [132], [135], [141], [142]):

- They have higher efficiency (up to 50%) than the internal combustion engines. So, Fuel Cells are considered to be the future of automotive industry and scientists are trying to make them commercially operated,
- They are more efficient than today's power plants. Thus, it is believed that in the future, a huge part of electricity will be generated in stacks of fuel cells,
- They can operate on lower temperatures, usually between 80 and 100^{o}C. This means that short warm up periods are required, usable for almost immediately use when needed,
- PEMFCs have high power densities. Their power ranges, usually, from 5 watts to over 500 kilowatts. This power is generated in a relatively smaller volume when compared to other types of fuel cells. This high-power density makes PEM Fuel Cells ideal for many daily applications.
- PEM fuel cells (and in general all the types of fuel cells) are small and light and the stacks are compact. Adding the high-power density that can produced, in many applications, the power source will change, from conventional to fuel cell's powered,
- Fuel Cell's products are, theoretically, only water and unused air. This is very important for the environmental pollution that most people are concerned with it. Thus, with the usage of them, pollutants are going to reduced. These risk-free products make them to be convenient for indoor use, such as residential areas or even more submarines.
- Because, fuel hydrogen is not yet an option for the general public, fuel cell needs a fuel processor to generate hydrogen or it can operate with ethanol. With these two options, carbon

dioxide emits to the environment. Even if people use these methods, the emissions are very lower than the today's technology's pollutants.

- The noise level when a fuel cell operates is zero or very low. Today, many people on big cities are suffering from big noises. So, the more people use them, the cities become more and more quiet. This can have only benefits for the societies, because it is understandable, how frustrated can be for anyone, in many terms, to be exposed to high noise.
- Fuel Cells are not using oil products to operate but only hydrogen. Fuel hydrogen can be produced by electrolyzing water or by reforming hydrocarbon fuels. Using these methods, countries become more and more independent from oil, which some countries are lucky to have on their lands and seas. Because, oil is a major source of huge incomes for a country, there are many examples, in past and present, that the desire of oil control started entire wars and killed many people.
- If the general public gradually accept to use continually for as many applications as it can, conventional fuels and oil products will limit. So, the pollution of extracting and transporting oil will be reduced on land and sea.
- Fuel Cells are simple devices that don't have moving parts and they are consisted of repetitive parts. This is a huge advantage because, it fits for mass production
- Many people who are involved in these, are promising that with technological advance, materials that are effective and relatively cheap, will be discovered, lowering their price. Mass production will have, also, an impact on lowering the cost.

3.7 Applications

As it mentioned before, PEM Fuel Cells can produce, from couple watts to hundreds of kilowatts. This, and not only, makes PEM Fuel Cells suitable for many applications. From huge power plants to cars and to small mobile phones.

Because of the small size, there are attempts to power a bike or a scooter with these cells. **Fig. 3.13** shows a bike powered by them. This bike is from Fraunhofer ISE, and it is an alternative to today's electric bike. It is said that in nominal operation, the fuel cells can produce 70 watts [143].

Figure 3.13: Bike powered by PEM Fuel Cells [143]

Some others examples of scooters are added below in the **Fig. 3.14 a** and **b**.

Figure 3.14: **a)** Fuel Cell scooter by URE [144], **b)** Yamaha FC-AQEL [145]

Car manufacturers are also investing billions to this technology, because environmentally friendly laws are becoming stricter and stricter [132]. Some examples are shown in **Fig. 3.15 a** and **b** below.

Figure 3.15: **a)** Toyota Mirai [146], **b)** Hyundai Nexo [147]

PEM Fuel Cells are going to be a main power source for various machines on industrial sites. Below, in **Fig. 3.16 a**, is showing a forklift that uses them except for an engine. Also, they have manufactured buses, which use PEM Fuel Cells. **Fig. 3.16 b** shows one.

Figure 3.16: **a)** Toyota's Fuel Cell Forklift [148]**, b)** Hydrogen bus by Ballard [149]

Aircrafts' manufacturers are, also, trying to keep up with hydrogen technology, as shown in **Fig. 3.17 a**. Submarines will also adopt fuel cells for their power units [132]. Nowadays, fuel cells with an electric motor are operating together with an internal combustion engine. An example is the German submarine below in **Fig. 3.17 b**.

Figure 3.17: **a)** Airbus' concept airplane for hydrogen aviation [150] **b)** German Submarine U-35 (S185) [151]

Ships are trying to be more environmental friendly on the near future [132]. A complete example is below in **Fig. 3.18 a**. This catamaran is powered by fuel cells and is travelling around the world. PEM Fuel Cells are suitable for small portable power generators. This generator, in **Fig. 3.18 b**, can generate up to 175 watts and supports many commercial and industrial applications [153].

Figure 3.18: **a)** Ship Energy Observer [152], **b)** BOC HYMERA Hydrogen Fuel Cell Generator [153]

Also, many companies are making huge stationary power generators as in **Fig. 3.19a**. This company assures us that this generator can produce decent amounts of megawatts of electricity. Individually, a power block can generate 1,5 MW and many blocks are combined together to achieve huge amounts of megawatts [156].

NASA was first to introduce the use of PEM fuel cells in space and it was, also, a message to all, that fuel cells can be operating. NASA used them for the first time in program Gemini (1965-66) and they were providing electric power for spacecraft's applications. The device is shown below in **Fig. 3.19b** [155].

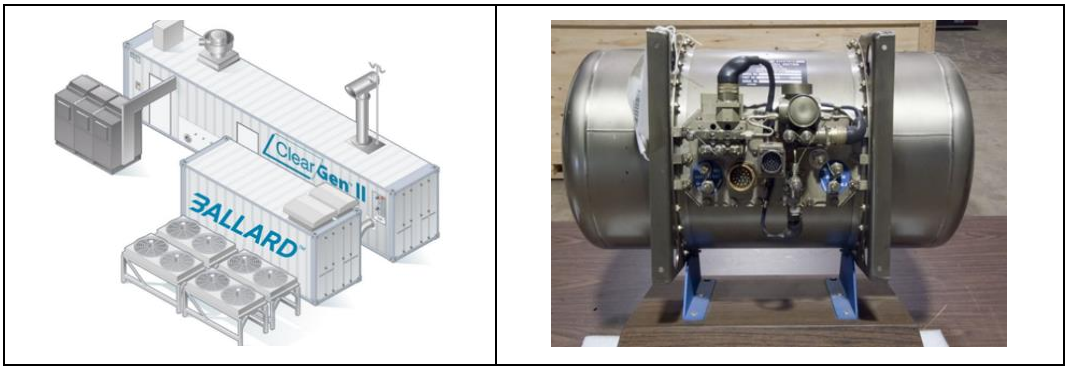

Figure 3.19: **a)** Ballard Clear-Gen™ II [154], **b)** Fuel Cell used on spacecraft Gemini (built by NASA) [155]

PEM Fuel Cells can be used, as well, in the military, as it's shown in **Fig. 3.20**. These can be used to reduce the weight of soldier's equipment.

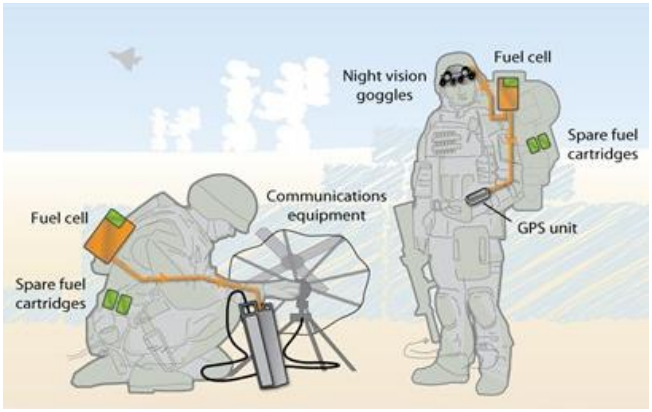

Figure 3.20: Military applications [157]

Attempts are being made, every day, to manufacture everyday products that are powered only by hydrogen fuel cells. Some examples are below, in **Fig. 3.21a** and **b** which show a phone charger and a MP3.

Figure 3.21: a) UPP Phone Charger [158], **b)** Toshiba's Fuel Cell MP3 [159]

CHAPTER 4

Main Failures and Mitigation Strategies

for Proton Exchange Membranes Fuel Cells

4.1 Introduction

As it was described upwards, PEM Fuel Cells are believed to be the future for many applications. There are many advantages by using them, such as non-pollute emissions and clean energy. But, as many technological inventions at the start, they have some problems which they make difficult to be commercialized now, for the general public. It is necessary for us, to focus on these problems and failures, to understand the current situation and to find some means for mitigation. An example of a failure is shown below in **Fig. 4.1**.

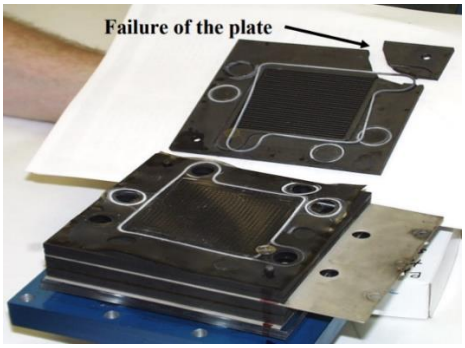

Figure 4.1: Example of a failure [160]

4.2 Cold Start

4.2.1 Failures

Fuel cells may deteriorate as a result of cold starts. Degradation is mostly caused by water freezing, damaging important parts like the catalyst layer and membrane. Ice on a fuel cell is shown in **Fig. 4.2**. It was shown that while there is no big performance deterioration with a dry state cold start, there is significant performance degradation with a wet state cold start after testing freeze/thaw cycles under both dry and wet conditions. It is determined that more flooding is caused by the freeze/thaw cycles by measuring the stack's resistance. The performance of the stack significantly declines during wet cycles [161].

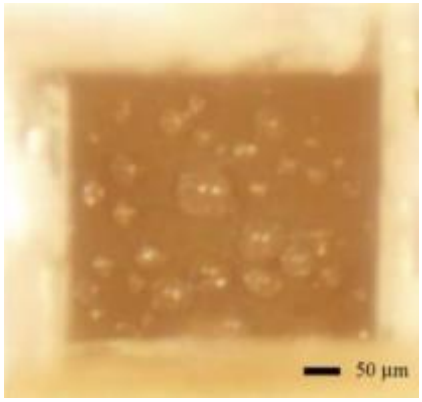

Figure 4.2: Visualization of water and ice on MEA surface [161].

For PEM fuel cells, membrane breakdown is a crucial problem. The membrane surface, which is connected to the catalyst layer, is where freezing-induced thermal deterioration of the membrane often takes place. The freezing point of the membrane is significantly reduced because the majority of the water is trapped in the polymer chains. Therefore, this portion of the water in the membrane is not significantly altered by the subfreezing process. When the majority of the water within the membrane flows out, water freezing is more likely to happen on the membrane's surface. A number of issues arise when ice forms on the membrane surface: the gap between the membrane and catalyst layer widens, electric resistance rises, water absorption from the catalyst layer into the membrane slows down, and, most dangerously, the catalyst layer (CL) peels off the membrane surface and is damaged. The cold start can also alter the mechanical characteristics of the membrane. The clamping force may cause the membrane to become more fragile [161].

One of the main variables influencing the catalyst layer's degradation is the pace of heating and cooling. It is discovered that an ideal purge procedure prior to cold start cycles reduces catalyst layer cracking. There are still a lot of platinum particles entering the membrane from the CL, though. In addition to affecting cold start capability, phase change in the CL also promotes CL deterioration [161].

The Gas Diffusion Layer's (GDL's) porous structure may alter as a result of ice forming in the pores. It has the capacity to alter the GDL's hydrophobicity and gas permeability, among other characteristics. These characteristics are necessary for reactant movement and water draining to function properly. In an experiment, it was noticed that after ten cold start cycles at −10°C, the GDL contact angle changes from 131° to 112°. On the other hand, cold start performance is also significantly impacted by hydrophobicity. **Fig. 4.3** shows how operation temperatures affect the GDL [161].

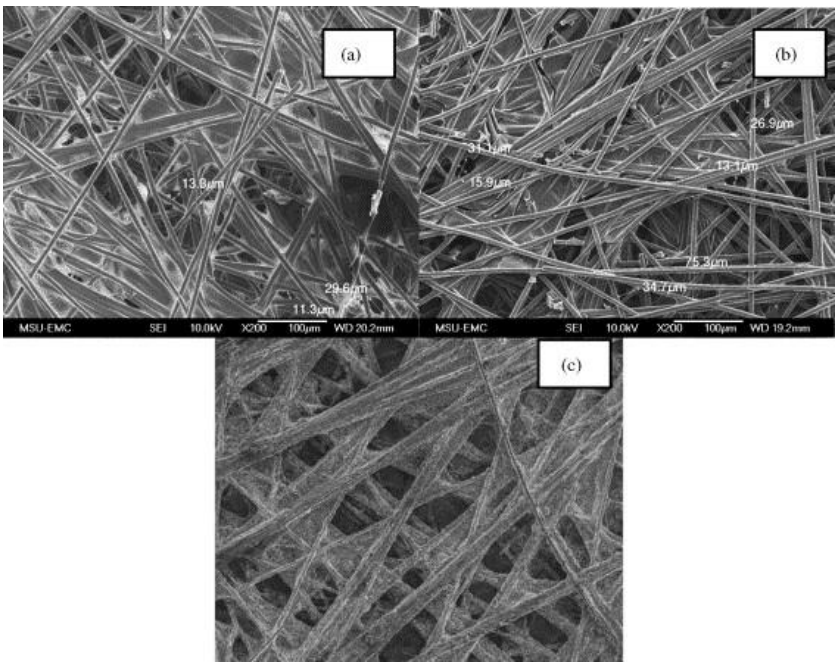

Figure 4.3: Effect of sub-zero temperature on GDL. (a) Fresh carbon paper, (b) carbon paper after operation at room temperature and (c) carbon paper after operation at −15 °C [162]

4.2.2 Mitigation Strategies

Basic research on the PEM fuel cell cold start has shed light on the critical variables affecting the start-up performance. Practically speaking, these important variables can provide useful information for cold-start optimization, enabling the achievement of more demanding cold-start performance standards. Enhancing cold-start performance involves more than just quick heating. It ought to be investigated alongside fuel efficiency, system stability, and ease of use [161].

Better design choices and material selections can maximize the cold-start performance of PEM fuel cells. Research indicates that cold-start performance can be enhanced by optimizing crucial cell components (such the membrane, CL, GDL, and Bipolar Plates (BP)) and effective designs at the stack and system levels [161].

The ability of the membrane to absorb water and its conductivity at subfreezing temperatures are the main areas of optimization. The concept is straightforward, less ice will develop and the start-up will have a higher chance of success if more water can be absorbed in the membrane. Lowing the membrane's thickness is one way to accomplish this. Three distinct thickness varieties of NafionTM (NafionTM 117, 115, and 112) were examined. The thinner membrane (NafionTM 112) was discovered to be the most advantageous for the cold start. The thinner membrane exhibits a higher gradient in water concentration than the thicker membrane. Because of the increased rate of water absorption that follows, ice builds up more slowly with the thinner membrane. Using cutting-edge materials can also increase the membrane's water capacity. The SiO_2 and $Zr(HPO_4)^2$ composite

membrane was compared to the pure NafionTM membrane. According to the experimental results, the composite membrane had a higher water content, which improved the cold start's efficiency [161].

Important parameters in the catalyst layer that impact the cold start include the thickness, composition, Pt/carbon ratio, and ionomer content. Since a greater ionomer percentage in the CL can absorb more water and cause more water to permeate into the membrane, it is possible to effectively minimize the rate of ice accumulation. It was concluded that the benefits of greater ionomer fractions stem from improved oxygen permeability in the ice-blocked catalyst layer based on experimental confirmation of these benefits [161].

The membrane's ability to hold water is also impacted by electrode thickness. It was discovered that a thick electrode (e.g., 14.1 μm) had a lower maximum water content in the membrane than a thin electrode (e.g., 3.5 μm). While a cold start promotes a thick layer of catalyst, it also increases the loading of precious metals and can reduce durability. Flooding can occur with an ultrathin CL, particularly at lower beginning temperatures. Several approaches were suggested, including the use of a thicker membrane and drying the membrane prior to startup, to address the performance loss brought on by the ultrathin CL [161].

Additionally, the impacts of the catalyst layer cathode's platinum-to-carbon support ratio were investigated. The pace of ice formation was shown to be more likely to be slowed down by a lower platinum/carbon support ratio. With regard to the composition of CL materials, it was discovered that adding silica to the cathode catalyst layer might increase water capacity and, thus, help on the duration of the cold start [161].

Two important variables that affect the GDL's cold-start performance are its pore size and thickness. The impacts of GDL pore size were investigated. Since the GDL operated longer at a steady current at -5°C, they discovered that a GDL with smaller pores is better suited for cold starts. After doing additional research on how ice formation affected the catalyst layer's reaction area, they discovered that it remained intact even after ice formation and apparent cell potential decline. Others studied the properties of melting ice in the GDL. Their formula established a relationship between thermal conductivity and GDL thickness. According to this calculation, a thinner GDL is better for the cold start since it can hasten the melting of ice [161].

PEM fuel cell flow channel designs that are frequently utilized include serpentine, parallel, and interdigitated designs. Since the interdigitated flow-field improves water removal from under-land GDL by convective mass transfer, it is preferred over the parallel design in the constant current start-up mode. The fuel cell with an interdigitated flow channel was able to start up successfully at −6 °C at a lower start-up current density, whereas the fuel cell with a parallel flow channel could only maintain −4 °C in the same conditions [161].

The material and structure of bipolar plates are the two main parameters that influence cold start ability in PEM fuel cell stack design. Applying metallic materials on bipolar plates has several benefits. Metallic bipolar plates have the ability to lower the stack's thermal mass, which will quicken the cold start. Nevertheless, at the cold start, metallic bipolar plates are more prone to experience severe mechanical stress and corrosion. Vanadium oxide polycrystalline deposits can be made to function better in metallic bipolar plates. Since the film turns into a self-heating source during the cold start procedure, its negative temperature coefficient property is advantageous [161].

A solution is to use electric heating. The main benefit of electric heating is its controllability, which is advantageous for aided cold-start tactics that are somewhat complex. Electric heating is the foundation of many suggested patents for aided cold-start techniques. One person demonstrated a brand-new load-control assisted cold-start technique that used an electric heater as the heating source and variable heating. A multi-cell stack has a 100 W electric heating source dispersed throughout it. In order to successfully cold start the stack at -20°C, the inner cells are typically started first, and the waste heat is then used to warm up the surrounding cells [161].

Moreover, the aided cold start technique employing coolant heating is covered by multiple patents. According to certain research, hot coolant can be passed through the stack during a cold start, allowing it to warm up quickly. This approach has the benefit that hot coolant can be produced from a variety of sources in real-world scenarios (e.g., fuel cells and internal combustion engine in a hybrid car). This approach also has the advantage of allowing for a uniform and effective warm-up procedure because the coolant channels are dispersed uniformly throughout the stack. An advantage of this technology over direct electric heating is that it eliminates the need for further accessory installation [161].

But, if the only option is the direct heating of the coolant, the comparatively large heat capacity of the coolant poses a disadvantage to this method. This could result in increased energy usage. Due to the coolant's high thermal mass which result in longer heating time, this problem could slow down the cold start procedure [161].

4.3 Fabrication

4.3.1 Failures

In a study, a PEM Fuel Cell with the membrane Nafion® 112 as the electrolyte and carbon-supported platinum as the catalyst, was found to have six morphological anomalies, including cracks, thickness variations, delamination, catalyst orientation, electrolyte clusters, and platinum clusters. **Fig. 4.4** shows these anomalies. During the fabrication process, solvent vaporization from the inner mixing catalyst powder to the top layer breaks the CL in thin regions, and the MEA is bent and stretched during the

assembly and application processes. The membrane experiences a concentrated force as a result of CL cracking, which could hasten membrane cracking [163].

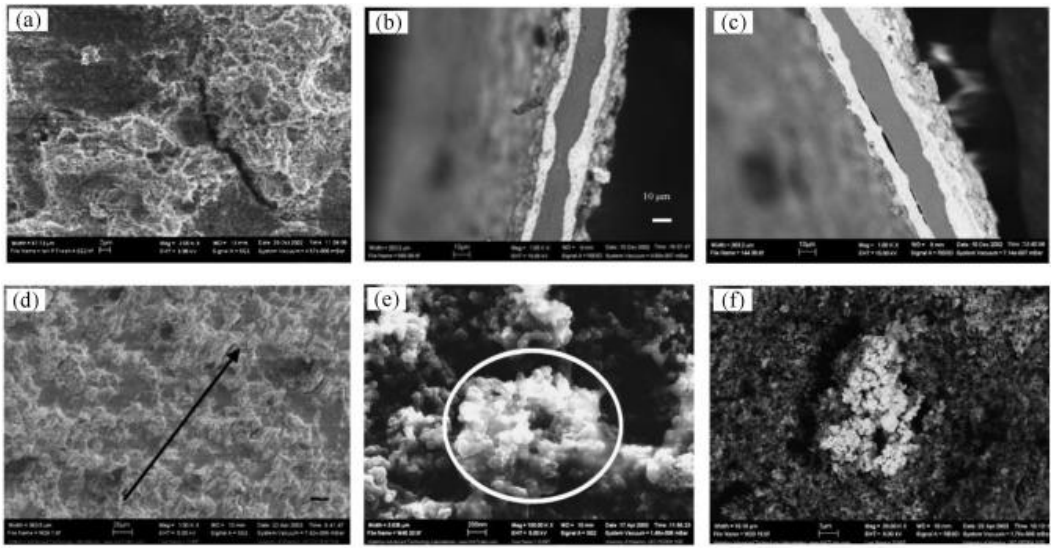

Figure 4.4: Typical defects of membrane: a) cracks, b) thickness variations, c) delamination, d) catalyst orientation, e) electrolyte clusters, and f) platinum clusters [163]

Large catalyst agglomerates or the process of making membranes, produce thickness variation. Due to uneven catalyst casting and a fault in the freeze-fracturing process, the delamination creates a space between the membrane and catalyst. When mixing catalyst and creating catalyst particles, it is important to consider the uneven catalytic properties of orientation, electrolyte clusters, and catalyst clusters. The mechanical strength, contact resistance, inhomogeneity of reaction efficiency, flooded area, heat generation, and catalyst erosion caused by these flaws, make the membrane degrade more quickly. The working circumstances of the fuel cell have an impact on the propagation of faults as well [163].

4.3.2 Mitigation Strategies

To raise membrane quality, the fabrication process must be improved. It has been shown that PTFE-reinforced membranes are more resistant to mechanical degradation. According to experiments, reinforced PTFE membranes have an order of magnitude longer lifetime than unreinforced membranes of pretty similar thickness. A membrane's chemical and mechanical interest properties, such as working temperature, proton conductivity, mechanical strength, and response to water content, can be altered by the addition of an inorganic material. As a result, considerable effort has been put into developing the composite membrane made of SiO_2, ZO_2, TiO_2, graphene oxide (GO), zirconium phosphate (ZP), etc. For instance, compared to pure Nafion, the Nafion/TiO_2 composite membrane exhibits better mechanical durability, exhibiting a 40% reduction in creep at 25 °C and 100% RH and a lower decrease in elastic modulus when exposed to water. In H_3PO_4/Nafion-PBI

membrane (20 wt.% Nafion and 80 wt.% PBI, immersed in 85% H_3PO_4 at 60 °C for 60 min), higher elastic modulus and yield stress are also obtained [163].

A bigger thickness can increase the durability of the membrane but reduce the proton conductivity. As membrane thickness is increased, the H_2 and O_2 crossing rates will decrease. According to an accelerated test on a four-cell stack using Nafion® membranes (N117, N115, NR212, and NR211) of various thicknesses, the fuel cell with the thinner membrane (NR211) has a lower open circuit voltage (OCV) due to a higher hydrogen crossover, but it produces the highest performance before degrading. In comparison to the cell with NR211 (0.26 mVh^{-1}), the cell with N117 has a higher thickness and a considerably lower deterioration rate overall (0.09 mVh^{-1}) [163].

In order to enhance cell efficiency and lessen mechanical deterioration, there should be good initial contact between the membrane and CL. Ion beam morphology is employed prior to coating the membrane in order to flatten its surface, and it appears that the interface between the membrane and catalyst layer is flatter as a result. Additionally, useful for enhancing contact between the membrane and electrodes is the hot-pressing technique. The benefits of this process to performance and durability are still established, notwithstanding some worries regarding a potential decline in porosity after pressing. In the work, the membrane with hot-pressing shown smaller ionomer layers thinning, higher cell function, and significantly less degradation after Accelerated Stress Test [163].

It has been demonstrated that the addition of a diffusion medium (DM) between the membrane and the gas diffusion layer (GDL) can slow membrane deterioration. The membrane can be protected against wrinkling and buckling brought on by hydrothermal conditions in an operating fuel cell by a static friction force created between the membrane and the DM. It supplies a barrier against membrane expansion, excessive water infiltration and freeze/thaw cycle conditions [163].

4.4 Membrane Degradation

Proton exchange membrane (PEM) fuel cells are susceptible to various forms of degradation that can significantly impact their performance and lifespan. The degradation of PEMs encompasses chemical, mechanical, and thermal processes that lead to the slow deterioration of the material's structural integrity, microstructure, and associated properties. Mechanical stress, often induced by the fuel cell stack assembly or repeated start-up and shutdown cycles, can result in mechanical degradation, leading to a decline in the PEM's integrity. Moreover, chemical degradation occurs due to the effects of reactive gas penetration, the generation and migration of harmful compounds like H_2O_2 and HO-free radicals, and ion contamination. These intricate degradation mechanisms collectively affect gas permeability, proton conductivity, and other critical properties of the PEM, ultimately impacting the overall performance and longevity of fuel cells ([164], [165]).

Assessing the condition of PEMs is vital to understanding and addressing degradation. This involves evaluating structural properties like thickness variations and identifying defects such as cracks or perforations. Additionally, monitoring changes in parameters compared to healthy membrane states, including fluoride ion release rate, voltage drop, and hydrogen permeation, is integral to failure analyses. Overall, a comprehensive understanding of the various degradation mechanisms and their effects is essential for developing resilient PEMs and ensuring the sustained performance of fuel cells in the long term. ([164], [165])

4.4.1 Chemical Degradation

4.4.1.1 Chemical Degradation

Chemical degradation happens more gradually than mechanical deterioration. The degradation is severe at high temperatures and RH values between 40 and 60%, according to some findings, which also demonstrated that the membrane thinning caused pinhole development and hastened gas crossover. The proton conductivity declines, the fluorine ion release rate rises, and the gas permeability increases with time when PEM undergoes chemical degradation. The side chain's sulfonic acid groups and the carboxylic acid end group sites of the primary chain will be attacked by the radical chemical species, causing the chemical bonds to break and the defects to spread. The main causes of membrane chemical deterioration are considered to be radical attacks on the membrane: oxygen molecules permeate from the cathode side to the anode side, and oxygen from the anode side can decrease the Pt catalyst to create HOO and HO radicals, which would further cause membranes to degrade significantly. These radicals are results of the unregulated interaction between the transition metal ions (Fe^{2+}, Co^{2+}, and Cu^{2+}) present in PEMFCs and hydrogen peroxide (H_2O_2). According to a number of studies, the electrochemical reaction that mostly produces hydrogen peroxide at the anode side is supported by the anode's lower potential and the membrane's operating circumstances ([164], [165], [166]).

The production of the aforementioned free radicals is shown in the following chemical processes.

$M^{2+}+H_2O_2 \rightarrow M^{3+}+\bullet OH+OH^{-}$ (1)

$M^{2+}+H_2O_2 \rightarrow M^{2+}+\bullet OOH+H^{+}$ (2)

$H_2+\bullet OH \rightarrow \bullet H+H_2O$ (3)

where M is a transition metal that is present in the membrane, such as a result of manufacturing errors, and the ensuing radicals react with the hydrophilic sulphonic acid side chains of the PTFE hydrophobic backbone, changing the primary backbone and side chain terminals at the molecular level [166].

Numerous earlier investigations have noted that hydroxyl radical attacks are the primary cause of membrane chemical deterioration. Reducing free radical production is the most efficient strategy to stop chemically driven membrane deterioration. The number of hydroxyl molecules could be significantly decreased by reducing the supply of one of the reaction's ingredients. The transition metals in PEMFC are a result of component corrosion during storage and operation as well as contaminants during manufacture. In order to increase the membrane's endurance, contaminants should be kept to a minimum and materials with excellent corrosion resistance should be used [161].

Radiation-induced damage to PFSA membranes results in the fluorocarbon backbone being destroyed, which has an immediate impact on the membranes' mechanical strength and proton conductivity. Radicals can connect to the carboxylic acid end groups of the main chain, which is how they primarily alter the chemical composition of PFSA membranes. Furthermore, as shown in **Fig. 4.5**, the reaction that breaks down the PFSA membranes can be caused by the production of carboxyl groups by the scission of main chains ([164], [165]).

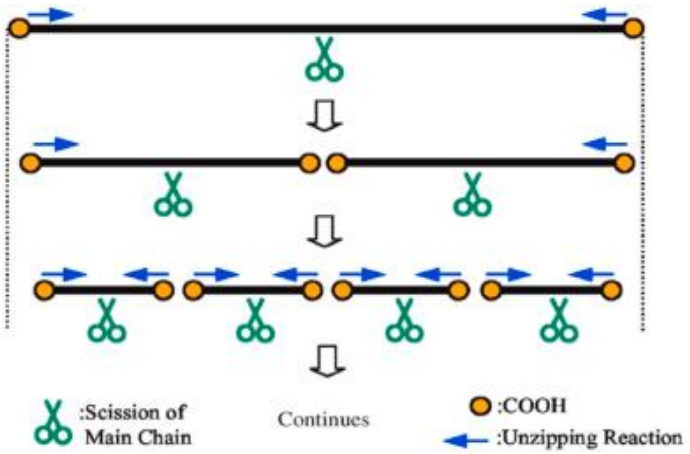

Figure 4.5: Chemical degradation mechanism of PFSA membranes [164]

The main membrane damage brought on by attacks from radical chemical species is the development of pinholes and a decrease in proton conductivity. It is commonly accepted that the high temperature, high cell voltage, high reaction gas pressure and low relative humidity in the fuel cell, contribute together to the chemical breakdown of the membrane. At higher temperatures and lower humidity, in particular, the degree of chemical breakdown is more apparent. An essential component of the vehicle operation state is the idling condition. The idling circumstances in fuel cell electric vehicles keep the cell voltage close to OCV, which is known to cause significant chemical deterioration [165].

Furthermore, the equivalent weight value of the proton exchange membrane could be decreased by increasing the number of sulfonic groups. On the other hand, the ohmic loss could be decreased by decreasing the thickness of the membrane. In addition, when membrane thickness drops, gas transport resistance also reduces, making it easier for reactant gases to infiltrate and causing chemical deterioration.

Therefore, the chemical degradation of perfluorosulfonic acid PEM is not only a problem in the use of fuel cells, but also an inevitable problem in the design and development of PEM [165].

Generally, the Nafion polymer structure is vulnerable to radical assault via four main pathways, as depicted in **Fig. 4.6** [165].

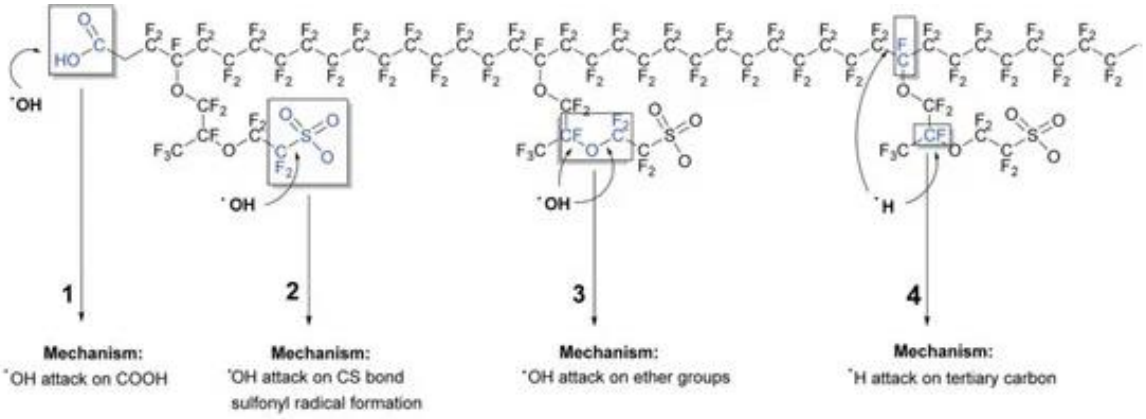

Figure 4.6: Mechanisms of radical attack on the Nafion® polymer structure [165]

As seen in **Fig. 4.7a**, the first attack of the free radicals targets the side chain's outermost ether groups, cleaving it. The membrane loses its hydrophilic channels, which are essential for membrane ion conductivity, as the reactants proceed to propagate along the side chain, disintegrating the C-F units. Numerous experimental studies link the breakdown of the side chains to the emission of fluoride and the mass loss of the PTFE membrane.

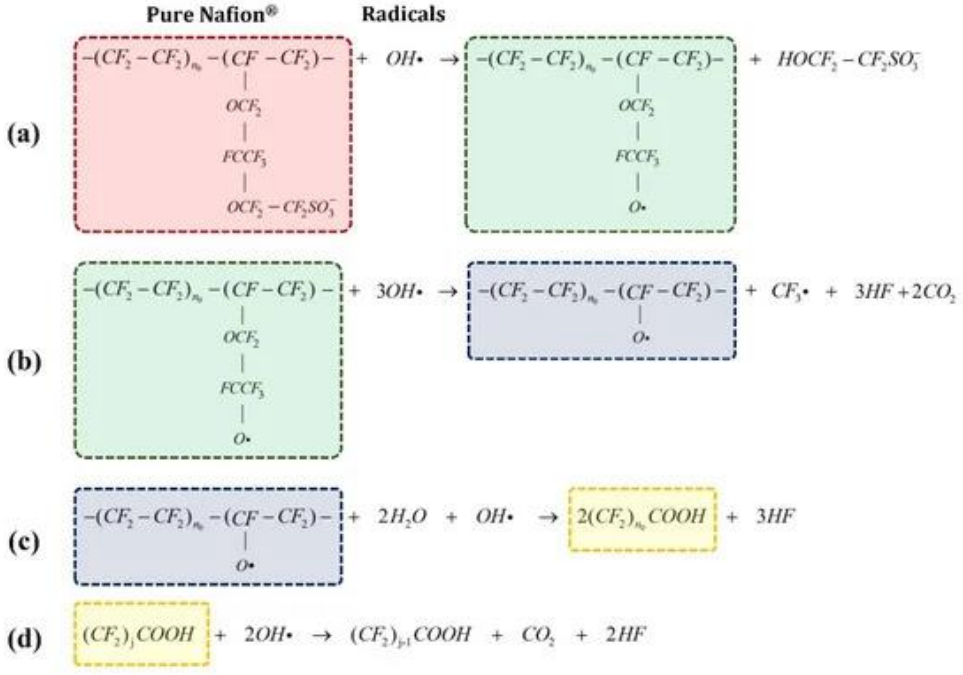

Figure 4.7: Molecular degradation mechanism of PTFE: (a) hydroxyl radical attack on the sulphonic termination of the side chain, (b) decomposition of the CF group along the side chain, (c) intermediate ionomer cleaving, (d) final unzipping of the main backbone [166]

Fig. 4.7b, c shows how the side chains continuously break down, leading to membrane mass loss through membrane thinning and pinhole/crack formation, which speeds up gas crossover. In the catalyst layer, the crossing over of oxygen and hydrogen to the opposing side of the membrane results in an exothermic reaction and small hotspots that lead to coupled thermochemical membrane breakdown. The primary PTFE backbone eventually breaks at the side chain junction at the conclusion of the hydroxyl radical attack, resulting in a number of fragmented carbocyclic acid groups and subsequent mass loss of the membrane. The membrane becomes brittle as the deterioration progresses and loses its ductility as a result of the absence of its hydrophilic transport channels. **Fig. 4.7d** depicts the sequential chain reaction between hydrogen radicals and pure Nafion® [166].

4.4.1.2 Mitigation Strategies

The ways to prevent membrane failure were put out, from several perspectives in accordance with the various membrane degradation mechanisms. Improvements in membrane manufacturing processes upgrade chemical stability, which can significantly lower membrane failure rates. According to studies, the 3,4-dihydroxycinnamic acid applied to the Nafion membrane as an antioxidant can scavenge HO- radicals. Others verified that the reducing agents Fe^{2+} in Nafion/CeO_2 and Nafion/YSZ membranes decreased in comparison to pure Nafion membranes, which would minimize the generation of radicals in the membranes. Therefore, by including radical scavengers to membranes, chemical deterioration can be postponed. The designed characteristics of the membrane are another method to lower the degree of membrane failure, in addition to constructing the outstanding membrane using unique materials. For instance, it is vital to set the membrane parameters to the proper level in order to increase cold start success rates and prevent damage to fuel cell components [164].

The generation of peroxide free radicals during fuel cell operation is primarily responsible for the chemical deterioration of the membrane. Radical scavengers or hydrogen peroxide breakdown could be introduced to the membrane in order to remove oxidation free radicals or prevent the production of oxidative free radicals in order to lessen the chemical degradation of the membrane. The researchers discovered that doping composite PEM with heteropolyacid, oxide, Pt catalyst, and other materials made the PEM more resistant to chemical deterioration. According to studies, adding TiO_2, CeO_2, MnO_2, ZrO_2, and other oxides to the membrane improves membrane deterioration by an order of magnitude. The breakdown of hydrogen peroxide in aqueous solutions of nanometer-sized SiO_2, Al_2O_3, TiO_2, CeO_2, and ZrO_2 particles was identified by experiments. It was discovered that H_2O_2 breakdown takes place on the surface of the oxide, and that the rate of decomposition increases with the oxide's surface area. However, it is possible that the quantity or effectiveness of the reaction sites may be more significant than the oxide's overall surface area. It has been demonstrated that the rate of H_2O_2 breakdown increases in the order of $SiO_2<Al_2O_3<TiO_2<CeO_2<ZrO_2$ [165].

Cerium-based additions have received the most research attention among these additives. Ce had the ability to effectively scavenge free radicals, and this ability was derived from the reversible redox couple Ce (III) and Ce (IV). The chemical deterioration of the membrane was lessened because the reaction rate of the free radical with Ce (III) was quicker than that of the free radical with ionomer membrane. By scavenging free radicals before they can damage the ionomer, cerium could considerably increase the durability of proton exchange membrane. Additionally, the power density and ion resistance of the fuel cell were not significantly affected by the low concentration of CeO_2 added to the membrane. There are commercialized membranes with CeO_2 scavengers, for example, Nafion XL. Cerium oxide nanoparticles were added to perfluorosulfonic acid membranes, and their capacity to increase in-situ membrane durability was examined by putting them through tough tests [165].

Typically, a hot-pressing technique is used to prepare Membrane Exchange Assembly (MEA), which promotes interface contact between the membrane and catalytic layer. The porosity, internal structure, thickness, and other characteristics of the membrane will alter during this procedure. Due to the membrane's pre-hot-pressing existence of microscopic pinholes or micropores, the hot-pressing procedure may reduce the membrane's surplus pores and electrode thickness, decreasing the electrode's response route. Additionally, during hot pressing, the structure of the Nafion molecules in the composite membrane may be reformed by heat treatment, reducing the gas permeability. Some researchers suggested hot pressed MEA by hot pressing two gas diffusion layers and catalyst coating membrane at 110 °C and 1 MPa. After conducting RH and loading cycle accelerated stress test studies, it was discovered that hot pressed MEA had superior performance and durability than unheated MEA because of its effective proton transfer and less chemical deterioration. However, others discovered that the performance of MEA made by hot pressing dropped quickly, which may be related to the increased likelihood of water collection in the gas diffusion layer and catalytic layer as a result of the catalytic layer losing porosity as a consequence of hot pressing. The hot-pressing process parameters (hot pressing temperature, pressure, and duration) need to be further researched to fulfill the application requirements in order to lessen the detrimental influence on cell performance [165].

4.4.2 Chemical Ionomer Degradation

4.4.2.1 Chemical Ionomer Degradation

We can be more specific on some certain failures. Hydrogen peroxide radicals are responsible for the PFSA-ionomer's chemical breakdown, which results in membrane deterioration and pinhole development. When oxygen and protons are present in an acidic environment and hydrogen oxidation is taking place, radicals can be created at a potential below 0.682 V. These conditions can exist at the anode, where oxygen is present due to membrane permeability, or at the cathode catalyst, where

hydrogen peroxide is produced as an intermediate product of the oxygen reduction reaction. It is evident that the anode side at the lowest current densities is where the conditions are most favorable for the existence of radicals, stable enough to cause membrane breakdown. The generated radicals have a higher stability as the voltage reduced [167].

Furthermore, the development of radicals through thermo-catalytic processes is facilitated by the presence of metal ions, primarily Fe^{2+} and Cu^{2+}. The functional end groups or C-H bondings in the PTFE chain, which originate from the manufacturing process or replaced C-F bondings, are the weak areas of the ionomer where the hydrogen peroxide radicals induce decay. New C-H bondings are formed as a result of the radical attack, end groups are removed, and the main chain or side chains of the ionomer are broken down. As a result, it accelerates on its own, causing pinhole formation, membrane weakening, and ionomer decay ([167], [168], [169]).

This phenomenon upwards can result in changes on membrane's water properties, increase of membrane's resistance, membrane thinning, increased gas crossover rate, peaks in local temperature and damage to the active layer and ionomer, development of pinholes in the membrane (pinholes allow the dilution of hydrogen with nitrogen causing fuel starvation), decrease of the active catalyst surface, reduction of the mechanical strength of the membrane and the electrodes and release of fluoride, and sulphuric acid ([167], [170], [171], [172]).

4.4.2.2 Mitigation Strategies

This problem can be limited by some ways. Firstly, minimizing idle load time and extremely transient operation that causes voltage overshoots and undershoots through optimized operating strategy and energy buffer management for the intended application. This is the most crucial step in preventing ionomer deterioration and, ultimately, pinhole formation. Second, ionomer degradation rates can be slowed down by a lower hydrogen pressure, a moderate cell temperature, and a stable, uniform humidification distribution inside the cell. The uniform distribution of cell temperature as well as an appropriate and consistent ionomer humidification must be guaranteed by the flow field design, the characteristics of the gas diffusion layers, and the cooling concept. Also, it is crucial to prevent the possible entrance of metal ion contaminants, particularly Fe^{2+} and Cu^{2+}, which are released from system impurities or metal corrosion into the ionomer [167].

4.4.3 Ionomer Inhibition by Impurities

4.4.3.1 Ionomer Inhibition by Impurities

The cause of ionomer inhibition is the blocking of the functional sulphonic end groups of the ionomer. By blocking the functional groups of the ionomer from being used for proton transport, impurities

make the membrane more resistant. At 25 °C in distilled water, a Nafion® membrane's H^+-form conductivity is more than 10 times greater than its M^{n+}-form conductivity. Similar reductions in conductivity are caused by contamination by earth alkali metal ions, transition metal ions, or Na^+ ions. The proton conductivity decreases more gradually as a result of the NH_4^+ pollution. A Nafion membrane's complex water-cation groups and successive water absorption behavior are affected by the presence of cationic species in the hydrophilic zone, which greatly affects the membrane's conductivity ([167], [173], [174]).

4.4.3.2 Mitigations Strategies

In response to this issue various mitigations have been proposed to address this concern. First, Applying ISO 14687, a standard on hydrogen purity, to NH_3 ion contaminants. A detectable ionomer inhibition requires that contaminants surpass a specific limit value. Concentrations below the standard's lower limit (0.1 ppm) shouldn't have an impact on the conductivity of protons. Moreover, avoidance of the enter of NO_x and sulphur containing air impurities into the fuel cell system. The concentration of pollutants and the time of inevitable exposure must be as low as possible. Other measures are the evasion of bipolar plate degradation (leading to cooling liquid leakage), metal system component and metal bipolar plate corrosion (that cause the release of metal ions), and silicone elastomer gasket degradation (releasing alkaline metal ions) [167].

4.4.4 Mechanical Degradation

4.4.4.1 Mechanical Degradation

Another important component that shortens membrane lifetime is mechanical degradation, which is brought on by mechanical stresses generated within the membranes in a dynamic environment. According to studies, there is a significant correlation between operating factors including stress, temperature, and relative humidity and membrane fatigue. The membrane's sandwich structure makes it resistant to complicated stresses, and the resistance rises as compression pressure rises. Additionally, the membrane's dimensional change is quite sensitive to humidity. Fuel cells will absorb water at startup, causing the membrane to swell and produce swelling pressure. Researchers studied the membrane lifetime under cyclic mechanical and chemical loadings using modeling techniques. According to some simulation results, a minor rise in humidity amplitude can result in a large decrease in membrane lifetime and can damage membranes more than a small variation in temperature [164].

The most frequent mechanical degradation forms of PEM include material fatigue, creep, and the development of wrinkles, delamination, pinholes, or fractures, as determined by the examination of the failure forms and position of the membrane’s failure. The primary cause of fuel cell failure, early on, is

typically attributed to the mechanical breakdown of the membrane. There are several causes for the mechanical failure of PEM, including poor structural design and material matching of MEA or fuel cell stack, uneven assembly or compression, temperature variations, particularly during frequent start/stop cycles, humidity changes, changes in gas flow and pressure during fuel cell operation, which could result in non-uniform mechanical stress or localized concentrated stress, and uneven assembly or compression [165].

Fuel cell membranes are subjected to vibrations and shocks in addition to clamping pressure and humidity cycling, which may gradually change and cause mechanical problems. For instance, the fuel cell engines used in transportation are exposed to a variety of erratic vibrations with varying amplitudes and frequency ranges. Under arbitrary vibration excitations, membrane cracking and delamination from catalyst layers are the fuel cell membrane's most vulnerable failure modes. They came to the conclusion that the fuel cell components' thickness, density, and Young's modulus could all be adjusted in order to calibrate the minimal natural frequency. In order to analyze the delamination propagation of the membrane from the catalyst layer at different frequencies (5 Hz, 10 Hz, 20 Hz, and 40 Hz) and amplitudes (1 g, 2 g, 3 g, and 4 g) of the stimulated vibration. They discovered that the damage propagation was three times greater when the excitation's frequency and amplitude were 40 Hz and 4 g, respectively, than when they were 5 Hz and 1 g [166].

The cracks or pinholes in the joint area between the MEA frame and gas diffusion layer (as shown in **Fig. 4.8**) are a typical mechanical failure from the failure position of MEA. In contrast to a severe loss of chemical function groups, the sudden increase in gas permeation and OCV drop in cycles indicate that pinholes or cracks appeared in some region of the MEA. Significant cracks were found at the PEM and frame junction area close to the hydrogen inlet after they disassembled the failed MEA. Shear stress will increase as a result of significant deformation that takes place at the PEM and frame boundary area when the upper and lower frames are aligned. According to a simulation, plastic deformation even happened in the PEM near the edge region and that the stress-strain concentration in the junction region increased with temperature and water content [165].

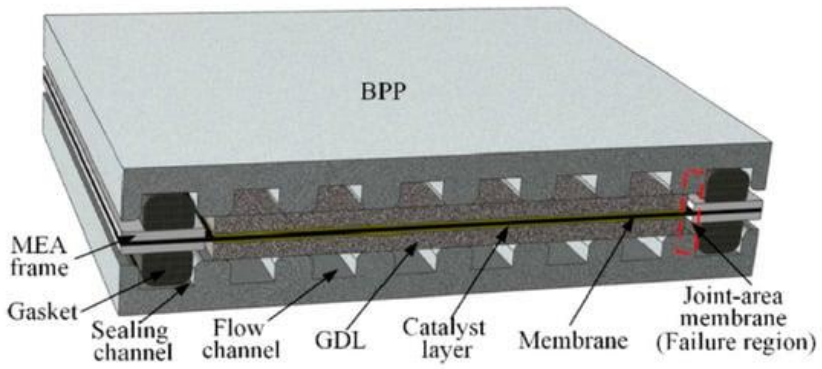

Figure 4.8: Schematic diagram of PEMFC and failure area [165]

Additionally, it is discovered that when the pressure difference between the anode and cathode sides exceeds 10 kPa, the stress concentration and plastic deformation rapidly increase throughout the entire active region of the PEM, particularly in the area where the membrane and frame meet. As a result, the weak point of the MEA is the junction area between the PEM and the frame, which is easily susceptible to membrane thinning or cracking as a result of mechanical stress during the short-term operation phase. Fuel cells' power demand characteristics dictate that the PEM will experience a variety of periodic loads, heating-cooling cycles, and start-stop operations. When water is absorbed and lost during this process, the membrane's hydration state will also change dynamically, and the PEM will exhibit anisotropic swelling and shrinking. The frame and bipolar plates on either side of the membrane restrict in-plane expansion and contraction under the operating conditions of the fuel cell. This geometric restriction will subject the PEM to mechanical tensile and contraction stresses. The stress and strain cycle will cause mechanical fatigue of the PEM with time accumulation, such as thinning, delamination, cracks, and pinholes, which will cause the fuel cell to fail. Inherent membrane flaws or slight fuel cell stack assembly deviations would also exacerbate the mechanical damage. Through external water supplement and dehydration experiments, investigated the water swelling and shrinkage behavior of PEM and the corresponding elongation. It was discovered that the effects of tension during the cycles of swelling and shrinkage accumulated and caused the mechanical creep and fatigue of the membrane [165].

In addition, it was discovered that PEM contacting the catalyst layer, has a high mechanical stress concentration effect on it, which encourages PEM crack propagation. This effect is particularly strong for cracks on the cathode side of the catalyst layer. Additionally, some theoretical simulation experiments demonstrated that the mechanical degradation behavior of PEM is influence by the hydration state of PEM and that the constant and cycled stress in the cell also influences the development of this behavior. Additionally, scientists demonstrated a relationship between membrane crack growth behavior and temperature, relative humidity, and the amplitude of stress change [165].

The consistency of the material, the uniformity of the pressing force, and the rationality of gas distribution are extremely challenging during the manufacturing of MEAs and the assembly of fuel cell stacks, which may result in the generation and change of local stress concentration in the fuel cell. When assembling a fuel cell, the packaging fixture presses the bipolar plate and MEA together with a specific amount of force. The fuel cell continuously applies pressure to the MEA. Under the influence of continuous pressure and cumulative effect, the existing manual assembly procedure and manufacturing error of the components may be magnified, which may hasten membrane failure. According to an analysis of the mechanical failure process of PEM in various places, the amount of stress rose as the amount of dislocation grew. The membrane at the edge of the seal ring will experience stress concentration even with a small manufacture

error. Therefore, it is impossible to overlook the impact of even a tiny deviation in the manufacture and assembly of fuel cell parts on the stress-strain distribution of PEM [165].

Membrane cracking, pinhole formation, membrane delimitation, and thickness loss are symptoms of mechanical membrane degradation. These failure scenarios are mostly brought on by the process of assembling the fuel cell as well as various conditions for cell operation and cycling. Since the membrane is a fragile component of PEMFCs, even a small amount of pressure irregularity during assembly could cause the membrane to deform and creep under constant clamping tension. Mechanical-based membrane degradation, as opposed to chemically-induced progressive deterioration, can result in an abrupt failure of the fuel cell. PEMFCs need a specific amount of clamping force to produce an ideal current collection and appropriate gas sealing. Additionally, it has been demonstrated that improving the clamping force can enhance the membrane's mechanical attributes. However, because of the flow-field's geometrical structure, the clamping force exerts a non-uniform pressure distribution in the membrane. Heterogeneous transport qualities between various compressed layers are produced by the non-uniform pressure distribution [166].

The gradual wear and tear of the membrane under humidity cycling is another often occurring mechanical source of failure. This sort of deterioration occurs when the membrane expands and contracts (membrane breath) in response to changes in humidity during fuel cell operation. Due to wear and tear, the membrane eventually fails as a result of its cycle nature. For fuel cells operating in extremely hot environments, thermally induced compression and the membrane's expansion both affect how long the membrane lasts [166].

In general, all of the mechanical degradation processes mentioned above might occur in sequence or simultaneously. Operational degradation, such as humidity cycling and vibration loading, invariably replaces the membrane defect brought on by manufacturing and/or assembly error. Enhancing the physical characteristics of the membrane itself or improving the manufacturing tolerances of the fuel cell components are all excellent ways to reduce membrane mechanical deterioration [166].

4.4.4.2 Mitigation Strategies

During operation, mechanical damage is prone to happening because of the significant heterogeneous stress in the region where the frame and membrane converge. The MEA's structure design is crucial in enhancing the membrane's mechanical toughness. A simulation of several MEA frame materials, structures, and contact behaviors revealed a zone with significant nonuniform stresses in the membrane beneath the terminal edge of the frame/membrane. In comparison to the aligned frames assembly, they discovered that the stepped frames assembly and the bonded contact behaviors have more uniform stress distributions. The findings may aid in the researcher's choice of frame materials

and frame designs as well as serve as a manual for assembling fuel cell stacks. After accelerated stress test trials for MEA without edge protection, it was discovered that tiny cracks started to form in the PEM close to the hydrogen input (as shown in **Fig. 4.9a**). The MEA's periphery, in particular the edge along the electrodes and membrane, needs to be carefully covered in order to increase fracture resistance (as shown in **Fig. 4.9b**). It has been demonstrated that the edge protection layer can permit long-term operation while preventing unexpected mechanical breakdown in its early stages [165].

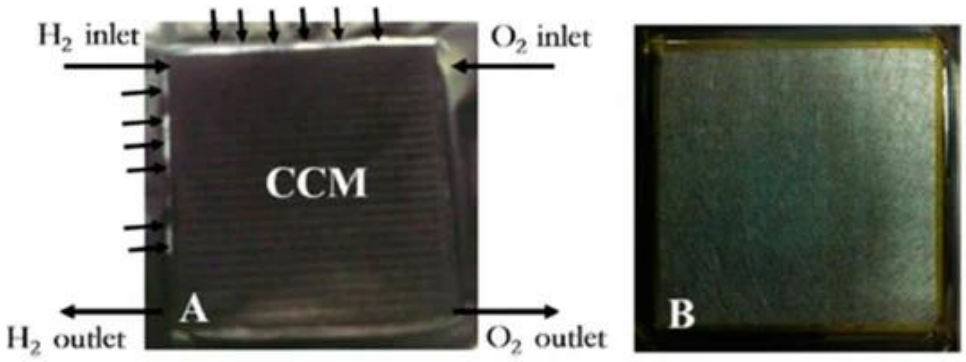

Figure 4.9: (a) The picture of MEA edge damage image, (b) The picture of MEA with edge protection [165]

Proton conduction and water reverse diffusion are improved when the proton exchange membrane's thickness decreases, but its mechanical qualities like strength and ductility are lost, making the membrane more brittle and susceptible to damage. Introduce more stable materials into PEM as a composite to increase its mechanical strength and dimensional stability and prevent the formation of cracks and plastic deformation is one technique to increase its mechanical durability. A sulfonated poly (amic acid) membrane was submerged in a Nafion solution before being thermally imidized into sulfonated polyimide (SPI) via solvent evaporation to create a NF-SPI-NF multilayer membrane. The stability and toughness of the NF-SPI-NF multilayer composite membrane were much better than those of native SPI and Nafion membrane. Because the composite membrane has high mechanical qualities, it can keep strength even when it thins (by about 20 m), extending the fuel cell's useful life. As the reinforcement supporting layer of composite proton exchange membrane, some porous reinforcement materials, such as expanded polytetrafluoroethylene (ePTFE) microporous membrane, poly (vinylidene fluoride) electrospinning microporous membrane, and polyvinyl alcohol microporous membrane, have been employed. Nafion XL and Gore Select are the only commercially improved movies available so far. In the middle of the ionomer is the microporous support layer of the reinforced membrane. Ionomer fills the microporous support layer, forming a continuous proton transport channel and facilitating water transport across the membrane's thickness. This reinforced structure boosts the yield strength and modulus of the modified PEM by two times over native Nafion membrane while decreasing in-plane swelling. The mechanical reinforced membrane has a life that is much longer than the unreinforced membrane because it is relatively stable over the relative humidity cycle. Under relative humidity cycle test settings, researchers examined the

performance of original Nafion membrane and ePTFE/Nafion reinforce composite membrane. Given that the cyclic stress brought on by swelling and shrinkage has a significant impact on the reinforcing membrane, the results demonstrate that the ePTFE/Nafion composite membrane is more durable than the native Nafion membrane. As a result, the ePTFE microporous supporting layer could effectively stop cracks from forming and spreading [165].

For mechanical reinforcement of PEM, a variety of nano-fillers, such as carbon nanotubes, nanofibers, inorganic particles, clay, and others, are also utilized in addition to porous reinforcers. The quantity of fillers, the natural characteristics, and the physico-chemical interaction between the fillers and Nafion matrix are the key variables determining the preparation and processing parameters of the reinforced membranes. In order to create a composite membrane, some added graphene oxide (GO) to a Nafion solution. The adding of GO increased the membrane's tensile strength and dimensional stability. The mechanical properties of the 3 wt.% GO/Nafion composite membrane were improved while the cell performance was comparable to the Nafion membrane's. Sulfonated graphite oxide (SGO) was created by changing the hydroxyl group in graphite oxide (GO) into a sulfonic acid group through a sulfonation reaction. The number of sulfonic acid groups increases with the addition of SGO, a proton transfer network forms in the Nafion membrane, and the Young's modulus and tensile strength of Nafion composite membrane are both enhanced. CeO_2-TiC (titanium carbide) with high crystallinity was employed by others as the filler in the Nafion membrane. Due to the addition of TiC, the thermal stability and tensile strength of the composite membrane were enhanced by 1.4 and 1.3 times, respectively. To ensure the commercial application of the modified membrane, we should also take into account the cost of the additives, dispersion uniformity, environmental protection of the synthesis method, and the overall impact of the additives on the performance of the membrane [165].

A combination of electro spun nanofiber web and SSC-PFSA membrane improved the composite membrane's mechanical strength and dimensional stability while maintaining its excellent conductivity. Jiao et al.'s comparison of three different Nafion membrane types (Nafion TM 117, 115, and 112) with various thicknesses revealed that a thinner membrane produces better cold-start performance. Another method to reduce membrane breakdown is to apply the proper amount of mechanical stress to the membrane [165].

4.4.5 Mechanical Degradation Through Chemical Degradation

4.4.5.1 Mechanical Degradation Through Chemical Degradation

Mechanical degradation can be related to chemical. The mechanical characteristics of the membrane are changed by chemical membrane breakdown. It becomes more vulnerable to the impacts of changes in pressure, temperature, and humidity. The material becomes brittle and less durable if

chemical membrane degradation drastically reduces the molecular weight of the high molecular weight glassy regions of the membrane. Localized ruptures are brought on by small deformations, whereas chain slippage is brought on by huge deformations ([167], [172], [175], [176], [177]).

Cracks are encouraged to grow larger by localized physical stress brought on by particles, uneven conditions inside the cell and clamping tension. Gas crossover rates are accelerated by cracks, which results in chemical membrane deterioration. The membrane's reaction and non-reaction zones enlarge to varying degrees. Also, the membrane swells and shrinks when in use, especially in environments with high humidity levels, resulting in permanent plastic deformation. The electroosmotic drag under current load causes a reduced water content at the membrane's anode side. The cathode side experiences greater localized plastic stresses and strains as a result. The membrane's humidity level has a significant impact on the ionomer's yield stress and modulus. In contrast, cycling at higher humidification levels, higher humidification cycle amplitude, and increased mechanical load brought on by vibrations increases membrane deterioration. Hygrothermal cycling, or the periodic drop and increase of humidity and temperature, happens particularly during start-up operations ([167], [176], [177], [178], [179], [180], [181], [182]).

This has multiple effects for the operation of the fuel cell. Firstly, membrane proton conductivity decreases due to structural and water-absorbing alterations and increased gas permeability and a rise in internal current density result in modest voltage losses. Furthermore, high gas crossover rates following membrane ruptures or fissures produce current reversal [167].

4.4.5.2 Mitigations Strategies

Mitigations for limiting this happening involve a range of strategic measures. These measures aim to address key challenges such as membrane humidity management, mechanical degradation, and heat-related issues. Avoiding air supply with supersaturated steam, humidity cycling, especially at high humidification levels, and operating conditions that cause membrane dry-out can improve the membrane's ability to control humidity. Also, efficient removal of any remaining liquid water by thoroughly draining and purifying the area can help. Excessive pressure cycling, overpressure, and pressure gradients should be avoided to prevent mechanical stress. Uniform contact pressure, facilitated by an optimized bipolar plate and cell design, helps mitigate membrane cracking, which is prone to occur under the bipolar plate channel regions [167].

Moreover, the introduction of a diffusion media between the catalyst-coated membrane and the gas diffusion layer serves as a protective barrier, moderating mechanical degradation by preventing membrane wrinkling and buckling caused by hygrothermal cycling. A thicker gas diffusion layer with a microporous smooth surface further reduces membrane buckling. To enhance stability and reduce stresses associated with shrinkage during membrane drying, reinforcement with polymers or oxides

is an effective strategy. These mitigations collectively contribute to the improved reliability and overall performance of PEM fuel cells, addressing the various challenges encountered during their operation ([167], [183], [184]).

4.4.6 Thermal Degradation

4.4.6.1 Thermal Degradation

High temperatures can somewhat speed up the electrochemical reaction rate and improve the membrane's ability to transport ions. However, if the temperature is too high, both material deterioration and a decrease in water content may lead to membrane collapse. The heat deterioration of PFSA membranes has been the subject of numerous investigations and reviews. The breakdown of the side sulfonate acid group is the start of the thermal degradation of Nafion, which is similar to chemical degradation. The membrane heat degradation process is illustrated in **Fig. 4.10** [164].

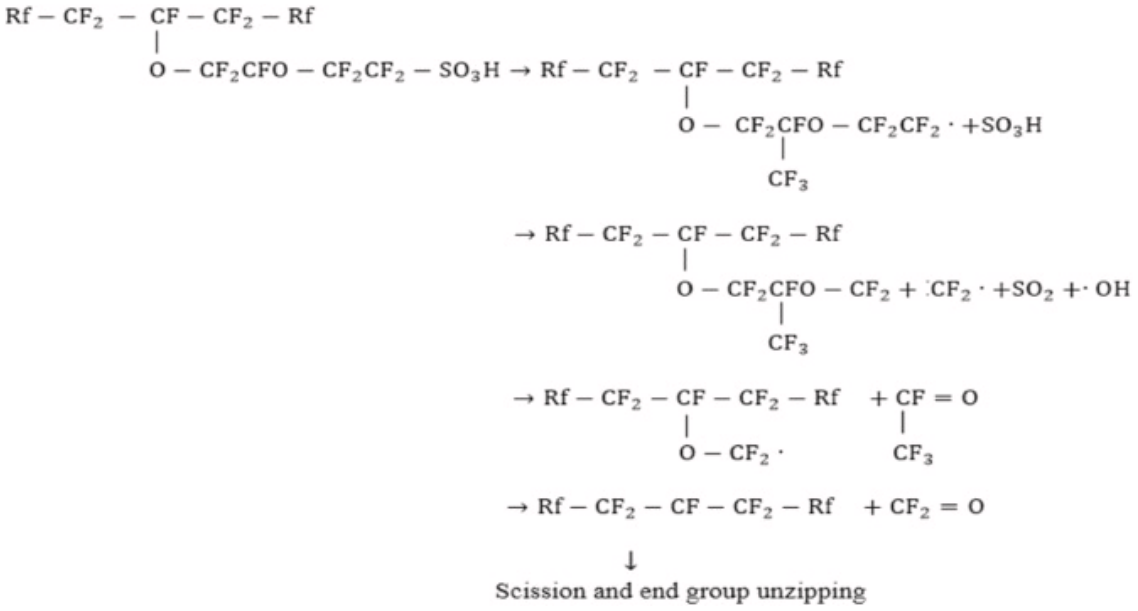

Figure 4.10: Degradation mechanism of Nafion materials [164]

Fuel cell membranes typically experience thermal deterioration under high working conditions and temperature cycling. Typically, a large range of temperature variations that fuel cells run under, has an adverse effect on the membrane's life. A well-hydrated membrane is said to perform best at a temperature between 60 and 80 °C. The widespread commercialization of PEMFCs continues to face temperature-related issues, such as quick startup from below-freezing temperatures and normal functioning above 100 °C. However, due to the post-mechanical degradation conditions of the membrane, thermal breakdown in fuel cell membranes might begin under typical working conditions (<100 °C). At a temperature of 95 °C, has been noticed that a considerable decrease in the membrane's proton conductivity. They have established a connection between the decline in conductivity and the breakdown of the hydrophilic proton-conductive sulfonic acid groups. Without sufficient

humidification, high-temperature operation of fuel cells results in the membrane's decreased protonic conductivity due to its lower water content. Additionally, dry membranes are vulnerable to cracking, which has a negative impact on their mechanical stability and encourages the growth of pinholes and gas crossover. Higher gas crossing rates that lead to hotspots in the membrane as a result of faster chemical reactions, are the typical characteristics of membrane pinholes. The small hotspots' temperature increases, in turn, cause the membrane to further deteriorate physically, chemically, and thermally. Membrane thickness irregularity might potentially be the first step in thermal deterioration. The rate of gas crossover considerably rises at extremely thin portions of the membrane where the anode and cathode are in close proximity to one another, leading to the emergence of hotspots. Using thermochromic pigments, were able to measure temperatures up to 140 °C in the vicinity of the hotspot locations. Nafion® membrane experiences its glass transition at about 110 °C. However, macro level thermal polymer degradation may take place at considerably greater temperatures [166].

The membrane thermal deterioration takes place both during the cold start procedure and at high temperatures. The majority of water in the membrane is trapped in polymer chains, delaying the freezing point until the water in the membrane reaches saturation. The membrane's internal water is carried out and is more prone to form ice on its surface. A number of issues with the membrane's structure and functionality can be brought on by the thermal degradation of the membrane brought on by freezing and thawing processes. For example, the expanding amount of ice that forms between the membrane and catalyst layer can cause damage to the membrane surface (such as cracks, pinholes, etc.) and potentially cause the catalyst layers to delaminate. After cold-start cycles, pinholes can be seen to form on the surface of membranes, as depicted in **Fig. 4.11** [164].

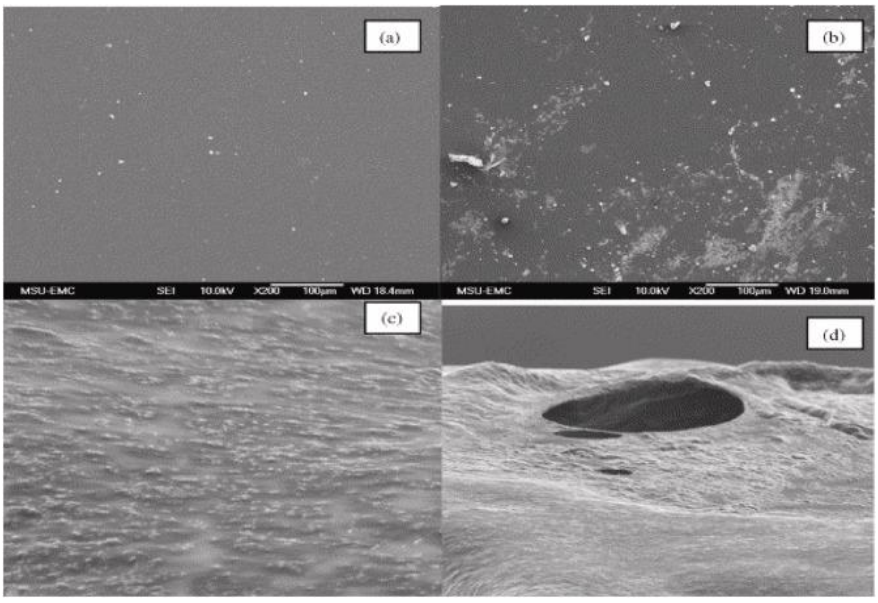

Figure 4.11: Effect of cold start on Nafion membranes: (a) fresh membrane, (b) membrane operated at normal temperature, (c) membrane operated at −15 °C, and (d) membrane operated at −15 °C located at cathode outlet [164]

4.4.6.2 Mitigation Strategies

Reduced fuel cell deterioration can be achieved by keeping the fuel cell at a specific temperature. Decreased humidity, drying, and the formation of hot spots are avoided. An apparatus that regulates temperature can be used. A controller may be implemented by introducing a thermal switch and allowing the system to function within a temperature set-point band. A thermal-switch actuator receives a signal from a temperature sensor once data are taken [185].

Furthermore, in order to reduce heat degradation and enhance PEMFC performance, choosing the right cooling method is crucial. Proper design and control of cooling systems are essential to prevent excessive heating and associated thermal degradation, ultimately contributing to the long-term reliability and efficiency of fuel cells. PEMFC cooling can be accomplished by a variety of techniques, including phase change heat transfer, liquid cooling, air cooling, and heat spreaders. In general, raising the air stoichiometric ratio can enhance cooling for a stack with power less than 100 W, but it also dries up the membrane. Extra air channel is needed for cooling when the PEMFC's output is between 200 W and 2 kW. Liquid cooling is necessary for PEMFCs with power outputs greater than 2 kW [186].

Advanced materials in Proton Exchange Membrane (PEM) fuel cells offer significant potential for mitigating thermal degradation and improving overall system performance. These materials, including high-temperature-resistant polymers and thermally stable catalyst supports, can enhance the fuel cell's ability to withstand elevated operating temperatures and reduce susceptibility to thermal degradation. For example, the use of thermally stable materials like PBI (Polybenzimidazole) as the polymer electrolyte can lead to improved durability in high-temperature PEM fuel cells. Additionally, advanced catalyst supports, such as carbon nanotubes, have shown promise in enhancing the catalyst's resistance to thermal degradation. Researches has demonstrated the advantages of advanced materials in reducing the impact of thermal degradation on PEM fuel cells, making them a critical element in improving the technology's long-term reliability and performance [187].

4.5 Electrodes' Failures

4.5.1 Electrochemical Carbon Corrosion

4.5.1.1 Electrochemical Carbon Corrosion

Under fuel cell operating circumstances, a high voltage, at which carbon loses its passivity, and a high kinetic resistance for oxidation to carbon dioxide, are the usual causes of electrochemical carbon corrosion. Carbon is only thermodynamically stable in acidic environments below 0.207 V, but it has a high kinetic oxidation resistance. Platinum particles reduce the kinetic oxidation resistance at the carbon surface. However, the corrosion rate considerably increases at potentials higher than 0.8 V with the unavoidable presence of oxygen or water. Since high cathodic potentials (>0.8 V) are needed, carbon

corrosion at the fuel cell cathode is theoretically possible. Under fuel cell working circumstances, there would be a negligible carbon corrosion rate in the absence of a platinum catalyst ([167], [188]).

Due to the extreme cathodic potential generated by the lack of local fuel, the anode must convert oxygen to water. The resultant decrease in pressure in the region of fuel starvation increases the oxygen penetration rate through the membrane, and the electrons are delivered in a plane. The cathode is pushed to raise its potential to the same extent because the potential of the oxygen reduction reaction is high. This leads to very high values above 1.4 V, which permit carbon corrosion and water splitting with an in-plane electrode flow. The proton flow is reversed in the local area of fuel shortage. Due to the high anodic potential induced by the lack of fuel, the anode is forced to create electrons and protons through the oxidation of carbon and water. The anode's potential rises to extremely high values. The cell voltage drops to the same extent since the cathode remains unaffected. **Fig. 4.12** shows this scenario ([167], [189], [190]).

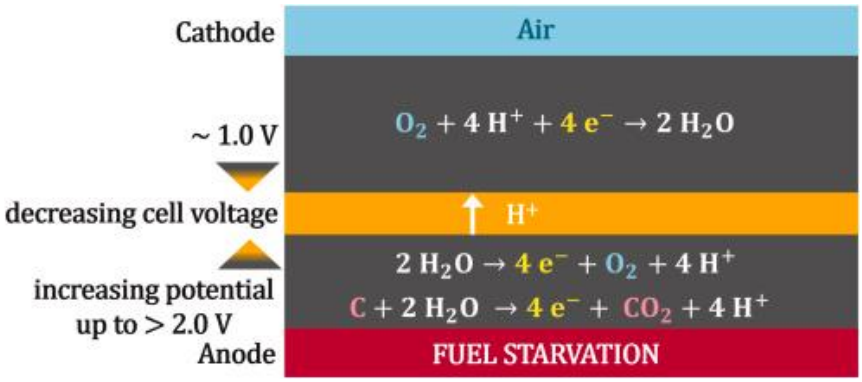

Figure 4.12: Illustration of the reactions at the anode and the cathode at fuel starvation [167]

These identified points encompass a range of factors that can significantly impact the performance and efficiency of fuel cells. Irreversible reductions in catalytic activity and increased activation overvoltage, stem from issues related to the contact loss between the carbon support and the catalyst. Such contact loss can compromise the effectiveness of the electrochemical reactions taking place within the cell. Changes in the hydrophobicity of the pores, linked to alterations in the electrode and gas diffusion layer pore structures, have far-reaching consequences. These changes can lead to a heightened risk of cell flooding, hampered cell performance characterized by sluggish dynamic behavior, and increased diffusion overvoltage. The thinning of the electrode and gas diffusion layer is responsible for elevating the cell's ohmic resistance. While reduced thickness reduces ohmic resistance within the layer, the contact resistance in the fuel cell increases, especially when the distance between the membrane and the bipolar plate remains constant. This scenario can lead to less efficient electron transport and hinder overall cell performance ([167], [191], [192])

The degradation of the porous structure in the carbon bipolar plate exacerbates contact resistance, impacting critical aspects of fuel cell operation. This includes an increased risk of cell flooding, less

uniform gas distribution and the potential for localized fuel or air shortages, due to changes in flow field parameters. Together, these effects underscore the intricate interplay of structural and material factors that influence the functioning of fuel cells, highlighting the need for careful design and maintenance, to maximize their efficiency and longevity [167].

4.5.1.2 Mitigation Strategies

Mitigations for electrochemical carbon corrosion in fuel cells are crucial to maintain the long-term efficiency and durability of these energy conversion devices. To address this challenge effectively, it is essential to avoid operating at excessively high cell voltages or very low current densities, as extreme conditions can accelerate carbon corrosion. Similarly, erratic and transient operations that result in overshoots and local hydrogen depletion should be minimized to prevent undue stress on the cell components. Optimized shut-down and start-up procedures play a significant role in reducing the dwell period of the hydrogen-air front at the anode. This helps in preventing detrimental carbon corrosion effects that may occur during startup and shutdown phases. Furthermore, during shutdown, the removal of any remaining liquid water is vital to prevent the formation of ice crystals within the stack, which can lead to damage [167].

The mitigation of cell reversal occurrences and the avoidance of cell reversal are essential for adopting the best approach to frozen starts. The application of standards such as ISO 14687 for hydrogen quality regarding contaminants in inert gases and particles can help maintain a cleaner operating environment, which in turn aids in reducing carbon corrosion. Additional strategies include the optimization of purge and drain procedures and the recirculation of the anode gas, both of which can contribute to mitigating carbon corrosion. The use of a hydrogen reservoir at the anode exit minimizes hydrogen starvation and its associated detrimental effects ([167], [193]).

Lastly, achieving ideal gas diffusion layer, electrode, and flow field qualities is essential for optimal humidity control and gas diffusion properties. This ensures a stable operating environment, reducing the risk of electrochemical carbon corrosion in fuel cells. Collectively, these mitigations form a comprehensive approach to managing carbon corrosion, preserving the performance and longevity of fuel cell systems [167].

4.5.2 Chemical carbon degradation

4.5.2.1 Chemical carbon degradation

Hydrogen peroxide radicals, which can develop at potentials of 0.682 V at the anode or the cathode, attack the carbon material and induce chemical deterioration. As a result, the chemical carbon degradation increases with decreasing voltage at the anode or the cathode, similar to the chemical ionomer degradation, and it has the same underlying influencing factors under fuel cell working

circumstances. Edges and structural flaws are the weak areas of the graphite layers of carbon black or carbon fibers. There, chemical deterioration begins with the creation of carbon radicals, which later create functional groups containing oxygen as a weak spot for more carbon corrosion. The chemical carbon corrosion on pure carbon electrodes in a nitrogen atmosphere does not significantly corrode, in contrast to the electrochemical carbon corrosion, which requires oxygen. Similar to this, platinum's presence speeds up chemical carbon corrosion ([167], [188], [194]).

Electrochemical carbon corrosion in fuel cells presents a significant challenge due to its ability to cause accelerated degradation compared to chemical carbon corrosion. While the ultimate outcome may be similar in both cases, the electrochemical process tends to manifest faster rates of degradation, posing a more immediate concern. Factors such as changes in anode thickness, pore structure, and hydrophobicity can contribute to the increased likelihood of contact resistance, which, in turn, results in elevated electrical overvoltage. Moreover, contact loss between the carbon support and the catalyst, particularly at the anode, can lead to a permanent reduction in catalytic activity and an increase in activation overvoltage. The modification of pore structures and hydrophobicity can exacerbate the problem by promoting the retention of water droplets, ultimately causing localized fuel shortages. Addressing these issues requires a comprehensive understanding of electrochemical carbon corrosion and the implementation of effective mitigation strategies to ensure the long-term performance and durability of fuel cell systems [167].

4.5.2.2 Mitigation Strategies

Mitigations for preventing chemical carbon degradation in proton exchange membrane (PEM) fuel cells involve a multifaceted approach to maintain their long-term efficiency and durability. The central strategy to combat this form of degradation revolves around the avoidance of hydrogen peroxide radical formation, a major driver of fuel cell deterioration. This objective is achieved through several key measures, including minimizing idle load and transient operation, regulating hydrogen pressure and cell temperature to lower levels, and ensuring a consistent and uniform distribution of humidification within the cell. Additionally, safeguarding against the introduction of metal ion contaminants is crucial, as they can exacerbate the degradation process. Furthermore, utilizing high-quality carbon materials in the construction of the fuel cell components, such as the catalyst support, is paramount importance. The use of superior carbon materials can help mitigate the risk of chemical carbon degradation, ensuring the fuel cell operates efficiently and with increased longevity [167].

4.5.3 Supporting materials decomposition

4.5.3.1 Supporting materials decomposition

As the chosen catalyst support, it must possess specified qualities, such as (i) an appropriate porous structure to optimize the specific surface area, (ii) strong electrochemical stability, (iii) fortunate electronic conductivity, (iv) robust chemical bonds at the catalyst-support interface, and (v) good crystallinity. In

this sense, carbon black materials are widely used as supporting materials for Pt nanoparticle catalysts, which can be created by adjusting the synthesis settings, due to their availability and environmental friendliness. Because they have a larger surface area and fewer flaws than ordinary black carbon, graphene and carbon nanotubes in particular are demonstrating improved durability in cell performance. It has been determined that carbon is more likely to corrode when subjected to chemical or electrochemical processes. This is particularly evident at high potentials [195].

CO_2 is a byproduct of carbon oxidation and one of the gases that causes PEMFC poisoning. The catalyst particles' separation from the support will happen more quickly as a result of the carbon support material's breakdown, hastening the decline in performance. For instance, 50% of the Pt surface area was lost during the 50-hour Accelerated Stress Test (AST) of the MEA at 1.3 V, according to an experiment. Reduced gas diffusion may also be caused by the hydrophilic carbon surface species that are created following carbon corrosion. In addition to being correlated with its qualities, the oxidation and decomposition of the carbon support also follow the kind or methods of pretreatment used on the materials. Besides that, non-carbon compounds such metal oxides, nitrides, and carbides have been investigated as catalyst support materials in order to get excellent corrosion resistance supports [195].

Let's discuss about the decomposition. Certain carbons have flawed surfaces and rich organic surface groups, such as CO, COOH, and CN, when they are utilized as support materials. By spreading the particles, surface flaws can boost activity, but they also make catalysts more susceptible to severe corrosion problems and ultimately inadequate thermochemical stability. Generally, there are two ways that electrons transfer during carbon oxidation: (i) incomplete oxidation, which produces different groups; and (ii) complete oxidation, which breaks down the graphitic plane and produces gaseous CO_2 from CO (Equations (1) – (3)) [195].

$$\mathbf{C \longrightarrow C^{+} + e^{-}} \quad \mathbf{(1)}$$

$$\mathbf{2C^{+} + H_2O \longrightarrow 2CO + 2H^{+}} \quad \mathbf{(2)}$$

$$\mathbf{CO + H_2O \longrightarrow CO_2 + 2H^{+} + 2e^{-}} \quad \mathbf{(3)}$$

WO_3, a common transition metal oxide material, can serve as a support material in acidic environments since it is not prone to corrosion. The average size of Pt on WO_3 changed from 3 nm uniformly deposited Pt clusters to 20–50 nm big clusters, according to the transmission electron microscopy (TEM) observations after 300 cycles at a potential range of 0.0–1.4 V, which was accompanied by a considerable drop in electrochemical activity. Studies on its electrochemical

process revealed that, in accordance with Equations. (4) - (6), WO_3 may react with hydrogen to create stable hydrogen tungsten bronze (H_xWO_3) and substoichiometric oxide WO_{3-y} [195].

$xH^+ + xe^- + WO_3 \rightarrow H_xWO_3$ (4)

$2yH^+ + 2ye^- + WO_3 \rightarrow WO_{3-y} + yH_2O$ (5)

$PtH_{ads} + WO_3 \rightarrow Pt + H_xWO_3$ (6)

The slow dissolving rate of tungsten bronze in acidic solutions could cause Pt clusters to escape the surface and undermine the stability of the Pt/WO_3 catalyst, leading to a decrease in performance. The dissolution was comparable when WC served as the support. One argument was that when E>0.8 V, WC might oxidize to WOx [195].

Extensive research was also conducted on the stability and performance of Pt/indium tin oxide in MEA during conventional fuel cell operation. During the testing process to evaluate the Pt/ITO electrode's deterioration, the indium oxide surface was seen to exhibit prominent hydroxyl groups. Compared to ITO, this hydroxide layer had weak conductivity, which raised the electrode resistance and reduced the MEA's performance. Under severe acidic circumstances, the indium in the hydroxide layer could dissolve and allow In^{3+} to pass through the membrane [195].

These would lower the mass activity (MA) and the electrochemical surface area (ECSA), further increasing cell resistance. It was discovered that because of the strong metal-support connection, a thin (partial) oxide layer that was impermeable to oxygen and could poison the Pt catalyst, could form on top of the atomically built catalyst from Pt nanoparticles on the ruthenium-titanium mixed oxide (RTO) support [195].

4.5.3.2 Mitigation Strategies

Searches have been made for a synergistic combination of carbon-carbon support materials to build the optimal scaffold support in order to achieve both activity and stability of carbon supports. CNT-graphene composite materials have so far been created via partially exfoliated nanotubes, chemical vapor deposition (CVD), and electrostatic self-assembly. It was discovered that the mass transfer of a hybrid single-wall nanotube-multiwall nanotube (SMWNT-MCNT) structure was enhanced. To create a catalyst, scientists added Pt to nitrogen-doped graphene after inserting carbon nanoparticles into it. Retrieving the shed Pt particles was impeded by the graphene. During the 5000 cycles of accelerated durability tests (ADT), the MA of the produced Pt deposited nanocarbon wedged structure was able to retain 76.9%, whilst commercial Pt/C could only manage 32.3% [195].

Others took off the TiO_{2-x} covering on Pt with HF and reopened the active sites of the activated Pt to achieve an appropriate metal-support interaction. They could raise the MA from 1.83 to 4.23 mA/mg Pt in this method. Adding heteroatoms to TMOs typically results in stronger M-Pt interactions and an increase in conductivity. The Ti_3O_5−Mo support was first created by adding Mo to commercial anatase TiO_2, resulting in Ti_3O_5−Mo suboxide. Another researcher created $Ti_3O_5Mo0.2Si_{0.4}$ (TOMS) as a novel catalytic support by dissolving Mo and Si in titanium suboxide. The custom catalyst lost only 10% of its starting value over the 5000-cycle AST, in contrast to commercial Pt/C, which lost more than 81% of its ECSA. By lowering TiO_2's bandgap and stoichiometrically converting Ti^{4+} to Ti^{3+}, the synergistic effect of Si and Mo significantly increased TiO_2's electrical conductivity [195].

Noncarbonaceous supports often have better metal-support interactions and excellent corrosion resistance, but they also confront the following difficulties: (i) Their low conductivity hinders electron conduction, and (ii) their small specific surface area makes it hard to load catalysts like Pt evenly, which leaves them with few active sites and low activity [195].

Generally, it can meet both the stability and activity needs when carbonaceous and noncarbonaceous hybrid support are combined. One the one hand, the highly reactive oxygen species can be efficiently cleaved by the exophilic MO_x phase, shielding the carbon substrates and active sites from damage. On the other hand, by limiting Pt ion migration and/or Pt particle detachment from the support, Pt nucleation on MO_x/junctions of carbon and metal (oxide) results in better corrosion resistance. Consequently, heterogeneous nanohybrids, which combine carbon with WO_3, TiO_2, and MnO_2 metal oxides, have demonstrated special promise in achieving excellent corrosion resistance as well as acceptable conductivity. In a different situation, TiO_2 nanosheets were grafted onto the CNT backbone using solvothermal and then calcination to produce a Pt/CNT@TiO_2 structure. Their chronoamperometric studies verified a more gradual decrease in the current density when the TiO_2 support, which had a feather-like structure and good hydrophilicity, closely encircled the CNTs. Air annealing PtSn alloy nanoparticles on carbon black was used to create platinum-tin oxide hybrids supported on carbon black (Pt-SnO_2/C), as opposed to the conventional two-step loading procedure that preloads MO_x on carbon support and then deposits Pt nanoparticles. The Pt and SnO_2 planes' lattice fringes were observed to clearly overlap in the vertical direction, and the strong interfacial interaction causes SnO_2's lattice distortion. Because of the charge redistribution between C and the valence and conduction bands in SnO_2, the created SnO_2 acts as a binder to both prevent Pt from coalescing and to form a strong contact with support [195].

In summary, lowering the pace at which Pt-based catalysts deteriorate in PEMFCs is largely dependent on the production of important catalytic supports. Further research is required to comprehend the process of corrosion resistance and create more appropriate catalysts [195].

4.5.4 Catalyst Poisoning by CO

4.5.4.1 Catalyst Poisoning by CO

These days, coal, oil, and natural gas are the primary sources of H_2. Depending on how it is produced, the formed H_2 may contain CO_2, CO, H_2S and NH_3, so it is not pure. The established Pt catalysts are very weak against CO. CO binds tightly to anode catalytic sites at PEMFC working temperatures, blocking the catalytically active surface area needed for H_2 adsorption and oxidation. CO poisoning of the catalyst can significantly affect low-temperature PEMFC performance and the impact of CO on these devices' functioning is crucial ([196], [197]).

4.5.4.2 Mitigation Strategies

Firstly, various chemical purification procedures can be carried out prior to the H_2 being fed into the PEMFC. A purer H_2-fuel is produced as a result, but the overall cost and energy footprint increase. Secondly, a second metal can be added to the Pt catalyst to make it more tolerant against CO. Studies have shown that specifically the adding of metals Ir or Pd can has a significant impact on the strength against CO of the Pt catalyst. **Fig. 4.13** shows how this is happens. Even more, these metals can increase the electrocatalytic activity and durability. Also, because of their helpful properties, advanced carbonaceous materials or metal oxides and carbides, such as Mo and W oxides and carbides, can be used as substitute catalyst supports to assist reduce the need for corrosive carbon and improve CO tolerance ([196], [197]).

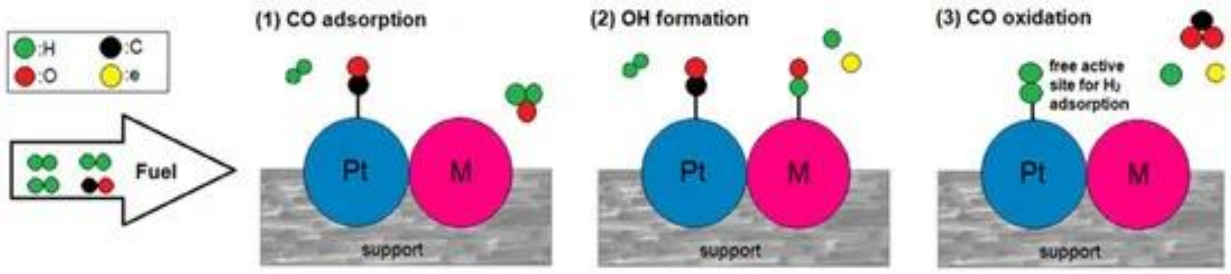

Figure 4.13: The mechanism in a CO-tolerant Pt-M electrocatalyst [197]

4.5.5 Platinum catalyst dissolution and redeposition

4.5.5.1 Platinum catalyst dissolution and redeposition

In an acidic environment, platinum is stable at potentials lower than 1.188 V. As a result, under high cell voltage or OCV circumstances, direct electrochemical platinum dissolution at the cathode or, in the event of cell reversal at the anode, may be feasible. Platinum is oxidized at potentials greater than 0.98 V (Eq. 2), and the resulting platinum oxide can be dissolved by protons at decreasing potentials (Eq. 3). Therefore, the direct electrochemical dissolution at very high potentials is less likely to occur

under fuel cell operating conditions than the dissolution via oxides by load variations. The likelihood that the platinum oxides may dissolve increases with decreasing potential at the electrode declines during a voltage cycling step ([167], [198]).

$Pt \longrightarrow Pt^{2+} + 2e^-$, (Eq. 1)

$Pt + H_2O + 2e^- \longrightarrow PtO + 2H^+$ (Eq. 2)

$PtO + 2H^+ \longrightarrow Pt^{2+} + H_2O$, (Eq.3)

Platinum can be dissolved chemically by chlorides, by the formation of complexes (Eq. (4) and Eq. (5)). The complexity of lifetime and exposure to favorable circumstances for dissolution determine how much dissolving occurs, whereas stable platinum oxides on the surface prevent further dissolution. By suppressing platinum re-deposition, chlorides cause the balance between platinum oxidation and reduction to change, resulting in increased dissolving rates. Platinum dissolution by chloride has the greatest effect at potentials between 0.9 and 1.1 V under fuel cell-relevant circumstances ([167], [199]).

$Pt + 4Cl^- \rightleftharpoons [PtCl_4]^{2+} + 2e^-$ (Eq. 4)

$Pt + 6Cl^- \rightleftharpoons [PtCl_6]^{2+} + 4e^-$ (Ep. 5)

Platinum catalyst dissolution and redeposition within proton exchange membrane (PEM) fuel cells have substantial consequences on the performance and durability of these electrochemical systems. The reduction of platinum ions at the interface of the cathodic high potential and the anodic low potential leads to the formation of a "platinum band" within the membrane. This phenomenon is accompanied by platinum dissolution and particle growth, which result in the irreversible reduction of the active catalyst surface. The implications of this reduction are significant, leading to an increase in the activation overvoltage, particularly pronounced at the cathode due to the underlying high potential. These effects of platinum catalyst dissolution and redeposition underscore the necessity for careful management of catalyst materials and operating conditions in PEM fuel cells, as they directly impact the efficiency and longevity of these energy conversion devices ([167], [200], [201]).

4.5.5.2 Mitigations Strategies

Mitigations to address platinum catalyst dissolution and redeposition in proton exchange membrane (PEM) fuel cells are crucial for ensuring the longevity and performance of these energy conversion systems. Several key strategies play a significant role in mitigating the effects of platinum catalyst dissolution and redeposition. It is essential to avoid operations characterized by frequent and highly transitory load changes, which can lead to increased mechanical stress and potential catalyst loss. Additionally, preventing excessive cell voltage and refraining from using cell reversal as a freeze start

technique are essential to minimize the dissolution of platinum catalyst particles. Reducing the frequency of start-up and shut-down events and start/stop operations can alleviate the impact of redeposition. Maintaining a lower cell temperature and ideal ionomer humidity helps mitigate platinum catalyst degradation. Furthermore, preventing the introduction of chloride contaminants into the fuel cell system is vital, as chloride ions can accelerate catalyst dissolution. Adhering to the ISO 14687 standard, which addresses chloride contaminants in hydrogen, can assist in maintaining a cleaner operating environment. Moreover, the stability of platinum catalysts supported by carbon is enhanced when the platinum particles are small, evenly dispersed, and similar in size and shape. These combined mitigations are essential for preserving the integrity of platinum catalysts and, by extension, the efficiency and durability of PEM fuel cells ([167], [198], [202], [203], [204]).

4.5.6 Platinum catalyst detachment and coalescence

4.5.6.1 Platinum catalyst detachment and coalescence

The detachment and coalescence of platinum catalyst particles within proton exchange membrane (PEM) fuel cells are phenomena that can significantly affect their performance and longevity. Several primary factors contribute to these processes. Particle development through coalescence, without first undergoing dissolution, is one cause. This entails the merging of smaller platinum particles into larger ones, altering their distribution and activity. Additionally, the detachment of platinum particles can occur due to various factors, including mechanical impacts within the fuel cell, degradation of the carbon support material, and a lack of robust attachment of platinum particles to the carbon support surfaces. These combined factors can lead to the displacement and aggregation of platinum catalyst particles, potentially compromising their efficiency in catalyzing electrochemical reactions within the fuel cell. Understanding and addressing the causes of platinum catalyst detachment and coalescence is essential for maintaining the integrity and effectiveness of PEM fuel cell systems ([167], [205]).

4.5.6.2 Mitigations Strategies

Mitigating the detachment and coalescence of platinum catalyst particles is crucial for maintaining their optimal performance and longevity. To address these challenges effectively, several key mitigation strategies are essential. Avoiding extremely transitory operations helps minimize mechanical stress that can lead to catalyst detachment. Preventing excessive cell voltage and refraining from frequent start-up/shut-down events and start/stop operations is vital in reducing the risk of both catalyst detachment and coalescence. Maintaining standard cell operation temperatures is key to preventing particle detachment and promoting stability. Furthermore, careful management to avoid conditions that encourage chemical and electrochemical corrosion of the active layer's carbon material is essential, as corrosion can weaken the catalyst's bond with the electrode. These mitigation measures collectively contribute to the preservation of platinum catalyst integrity, ensuring the sustained efficiency and reliability of PEM fuel cells [167].

4.5.7 Poisoning or blocking of the platinum catalyst

4.5.7.1 Poisoning or blocking of the platinum catalyst

The adsorption of substances that inhibit the active sites for the oxygen reduction reaction or the hydrogen oxidation reaction is the root cause of platinum catalyst poisoning. Contaminants are brought into the fuel cell system by air pollutants, particularly industrial or traffic emissions, reformate hydrogen impurities or contaminants from the fuel cell system itself. The most significant species that impede the platinum catalyst are Pt-CO, Pt-SH-, Pt-SO2, Pt-SO_4, and Pt-S. Furthermore, silicone fragments produced by gasket corrosion or other system parts, particularly from the cooling liquid, that can form crystalline or amorphous forms, might deposit on the catalyst surface ([167], [206], [207]).

Platinum poisoning leads to reversible or irreversible voltage losses, resulting from a reduction in the active catalyst surface area and an increase in activation overvoltage. One common form of poisoning is caused by carbon monoxide (CO), even at relatively low concentrations, which can completely cover the platinum surface on the anode. The degree of CO poisoning is influenced by both the CO concentration and the duration of exposure. Additionally, even trace levels of sulfur-containing contaminants can lead to severe catalyst poisoning by adhering to the catalyst's active sites. Similarly, mild adsorption of nitrogen oxides (NO_x) on the platinum surface can slightly block oxygen reduction sites, and the extent of poisoning is influenced by exposure time and concentration. Long-term exposure to these contaminants can, in some cases, result in permanent catalyst poisoning, which impairs the overall efficiency and reliability of PEM fuel cells. Thus, mitigating the effects of poisoning is critical to maintaining the long-term functionality of these energy conversion devices ([167], [208]).

4.5.7.2 Mitigations Strategies

Several strategies are instrumental in addressing this challenge. Firstly, the reduction in platinum's CO coverage as cell temperature rises can be leveraged to lessen the impact of carbon monoxide poisoning. The use of air filtration devices at the air intake helps to reduce the ingress of contaminants into the fuel cell system. Adhering to standards such as ISO 14687, which addresses sulfur-containing compounds, organic contaminants, and gases like CO and CO_2, contributes to a cleaner operating environment with lower contamination levels. Furthermore, the adoption of platinum alloy catalysts can enhance CO tolerance, as they have a greater affinity with carbon monoxide compared to pure platinum. These mitigations collectively aid in safeguarding the platinum catalyst's integrity, thus ensuring the sustained efficiency and performance of PEM fuel cells ([167], [209], [210]).

Additionally, the platinum catalyst that has been poisoned can be recovered in some ways. One method involves the addition of hydrogen peroxide to the anodic gas supply, which helps to alleviate CO poisoning and restore the catalyst's activity. Pt-CO oxidation with oxygen or water at potentials

exceeding 0.7 V offers a means of recovery from CO poisoning. For brief exposures to NO_2, a clean air supply can lead to full catalyst recovery. Recovery techniques utilizing current pulsing or anode/cathode reversal operation are also effective in restoring catalyst performance. Pt-S oxidation with oxygen or water at potentials exceeding 0.9 V can result in partial recovery of the catalyst, especially in cases of sulfur dioxide (SO_2) adsorption. Co-adsorption of intermediates O and OH can further weaken SO_2 adsorption, contributing to catalyst recovery. These mitigation strategies collectively offer a path to rejuvenating the platinum catalyst and maintaining the overall effectiveness of PEM fuel cells ([167], [206], [208], [210], [211], [212], [213], [214]).

4.5.8 Catalyst degradation caused by operation conditions

4.5.8.1 Catalyst degradation caused by operation conditions

All of the reactive gas is adequately fed into the anode and cathode during regular operation, resulting in a uniform distribution on the electrode surface. If an uneven gas distribution forms within the fuel cell, a hydrogen-air interface will form at the anode as a result of oxygen or air from the cathode diffusing into the anode due to the concentration difference. Operating conditions such as cold starts, air starvation, and frequent shutdowns and starts can result in uneven gas distribution. Due to brief variations in load and gas feed, starting and stopping the system has a major influence on the durability of the fuel cell in many fuel cell applications. This severely limits the system's lifetime. For instance, the fuel cell's voltage increases when the hydrogen and air supply are cut off, causing an oxidation reaction and an irreversible decline in the cathode catalytic layer's performance [195].

4.5.8.2 Mitigation Strategies

Currently, when a hydrogen-air interface is present, there are three primary methods to prevent or suppress fuel cell performance attenuation: (i) look for catalyst supports that are resistant to corrosion, (ii) prepare catalysts that are highly resistant to corrosion and (iii) implement a control strategy to prevent or limit carbon corrosion on the cathode side. Studies measured the concentrations of gasses such as CO_2, CO, and SO_2 released from the cathode outlet during fuel starvation in a PEM fuel cell cathode to calculate the corrosion rates of various carbon carriers such as Vulcan XC-72, graphite nano powder, and carbon nanotubes. Their findings indicated that the Pt catalyst supported by carbon nanotubes performed the best. According to the research, ordered mesoporous carbon is more resistant to degradation than carbons with low BET surfaces, such as graphite nanoparticles. Additionally, some prepared a membrane electrode assembly to ascertain the impact of electrospraying morphology on the rate of cell degradation and directly electrosprayed cathode CL on the membrane using catalysts with varying Pt/C ratios. Because the electrospraying morphology increases the homogeneity of cell responses, it lessens the harmful effects of localized water accumulation in cells. Furthermore, the catalyst layer's (CL) porous form offers strong hydrophobic

properties, which negatively affects the kinetics of corrosion. Because Pt acts as a catalyst to cause carbon corrosion, the long-term degradation rate in the CL increased as the Pt/C ratio increased. One of the most useful techniques for reducing the amount of time that the hydrogen-air interface is present at the anode, is gas purging. Three procedures are carried out: (i) tensile loading, (ii) stopping air flow through the PEMFC's cathodic compartment and (iii) isolating hydrogen by opening the anodic compartment to the outside atmosphere [195].

4.6 Failure of Gas Diffusion Layer

4.6.1 Mechanical degradation of the active layer and the gas diffusion layer

Factors such as thermal and humidity cycling can lead to interfacial delamination between the active layer and the ionomer, driven by issues like surface cracks, buckling deformations, and ionomer swelling and shrinking. Freeze starts can inflict damage by disrupting pore structures due to rapid enthalpy changes. Low stiffness or deformation resistance in the gas diffusion layer can result in surface damage, active layer heaves, and interfacial delamination, particularly impacting regions beneath the gas pathways in the bipolar plate. Pressure cycling, overpressure, and pressure gradients can lead to damage, especially in electrodes with high platinum loading, causing elastic and plastic deformation, crack development, and delamination. Additionally, non-uniform contact pressure within the stack can trigger mechanical tension, favoring delamination, deformation, and crack formation in both the gas diffusion layer and the active layer. Managing and mitigating these factors is essential to ensure the reliable and sustained operation of PEM fuel cells for various applications ([167], [182], [214], [215], [216], [217], [218], [219], [178]).

The mechanical deterioration of carbon materials within proton exchange membrane (PEM) fuel cells can have profound consequences on their overall performance. This degradation manifests in the form of cracks appearing within the electrodes, as well as the delamination of the active layer from the membrane, notably beneath the channels of the bipolar plate, particularly when early cracks are present. These developments result in the loss of uniform pressure distribution from the gas diffusion layer to the catalytic layer surface. These mechanical issues can trigger several potential effects, including an increase in contact resistance, which subsequently leads to elevated electrical overvoltage. Furthermore, variations in humidity uptake and product water removal become problematic, potentially resulting in cell flooding and subsequent carbon corrosion due to fuel shortage or a voltage drop due to an inadequate air supply. The degradation of gas diffusion characteristics contributes to an increase in diffusion overvoltage, further underscoring the importance of addressing and mitigating mechanical deterioration in carbon materials to maintain the efficiency and reliability of PEM fuel cells ([167], [218]).

4.6.2 Mitigation Strategies

Mitigations aimed at addressing the mechanical degradation of the active layer and the gas diffusion layer in proton exchange membrane (PEM) fuel cells are crucial for sustaining their long-term efficiency and reliability. To combat these issues, several strategic measures are paramount. Avoiding excessive pressure cycling, overpressure, pressure gradients, and thermal and humidity cycling can minimize mechanical stress on these layers. An effective shutdown plan is essential for removing any remaining liquid water and preventing the formation of ice particles within the stack during shutdown procedures. Implementing optimal frozen-start management, including measures to avoid cell reversal as a freeze start tactic, significantly aids in mitigating mechanical degradation. Resisting vibrations ensures the structural integrity of these layers. Employing high deformation-resistant and high-quality gas diffusion layer materials with an ideal active layer further minimizes surface deterioration and mitigates catalyst layer delamination triggered by freeze/thaw cycling. Lastly, achieving perfect stack assembly with precise contact pressure is instrumental in reducing mechanical degradation and prolonging the operational life of PEM fuel cells. These mitigation strategies collectively play a vital role in preserving the integrity and performance of fuel cell systems ([167], [218]).

4.7 Bipolar Plates' Failure

4.7.1 Bipolar plate degradation

Bipolar plate degradation in proton exchange membrane (PEM) fuel cells can result from a combination of factors related to the challenging operating conditions within the cell. Under these conditions, electrochemical metal bipolar plate corrosion can occur when the current potential reaches or exceeds the standard potential of the metal material. The presence of humidity in the fuel cell serves as the corrosion medium between the bipolar plate and the gas diffusion layer. Additionally, the material of the metal bipolar plate can dissolve chemically when exposed to fluoride or chloride ions, which may be present in the fuel cell environment. Moreover, bipolar plates constructed from carbon materials are susceptible to both chemical and electrochemical deterioration, particularly under the harsh conditions of a fuel cell. Mechanical stress, often experienced within the fuel cell, can further exacerbate the degradation process by initiating or hastening deformations, crack development, or the separation of protective layers. These multiple factors collectively contribute to the degradation of bipolar plates in PEM fuel cells, highlighting the need for careful material selection and operating conditions to ensure their longevity and reliable performance ([167], [220]).

The degradation of bipolar plates can lead to a range of harsh effects on the performance and longevity of the cells' system. Pinholes or cracks in the bipolar plate can result in coolant liquid and gas crossover, ultimately shortening the stack's operational lifetime. Corrosion of the bipolar plate coating

raises contact resistance, causing electrical overvoltage and hindering efficient electrical conduction. Local variations in the bipolar plate's thickness, shape, and wetting behavior can disrupt gas flow characteristics, potentially leading to cell flooding and fuel starvation. Additionally, the emergence of local temperature peaks within the cell is a consequence of elevated electrical resistance in these areas. The release of metal ions as a result of degradation can contaminate the ionomer, promote chemical membrane deterioration, and encourage the formation of pinholes, further undermining the functionality and durability of the PEM fuel cell. Managing and mitigating these effects is essential to ensure the sustained and efficient operation of the fuel cell system [167].

4.7.2 Mitigation Strategies

To counteract the degradation of bipolar plates in proton exchange membrane (PEM) fuel cells, a range of effective countermeasures can be implemented. Avoiding frequent start-up and shut-down events, as well as transient operations that cause voltage peaks, is essential to reduce mechanical and thermal strains on the bipolar plates. Local hydrogen deficiency, which can result in a very high cathodic potential, should also be prevented to maintain the integrity of the plates. Additionally, extreme mechanical and thermal strains should be minimized to avoid detrimental effects on the bipolar plates. Care should be taken to prevent local temperature peaks and excessively high cell temperatures, which can accelerate plate degradation. Ensuring adequate membrane humidification is crucial to prevent fluoride ion leakage and chemical breakdown of the ionomer. Lastly, for coated bipolar plates, strong and full adherence of the coating to the base material is necessary to protect against corrosion and ensure the long-term performance of the fuel cell system. By implementing these countermeasures, the degradation of bipolar plates in PEM fuel cells can be effectively mitigated, leading to improved durability and reliability of the system [167].

4.8 Additional Failures

4.8.1 Degradation of silicone or polytetrafluoroethylene gaskets

4.8.1.1 Degradation of silicone or polytetrafluoroethylene gaskets

Under operational circumstances for fuel cells, silicone rubber can break down. The presence of fluoride ions, temperature, the high acidic environment, and added mechanical stress are the key contributing elements. The rate of breakdown increases with increasing environmental acidity. With rising fluoride concentration, silicone breakdown is accelerated by fluoride ions. There hasn't been any silicone abrasion reported. Additionally, silicone elastomers have a high level of resilience against coolant liquids. Under operating circumstances that are relevant to PEM fuel cells, polytetrafluoroethylene (PTFE) has a high level of corrosion resistance ([167], [221], [222], [223]).

The degradation of silicone or polytetrafluoroethylene (PTFE) gaskets can yield a range of adverse effects on the system's performance and longevity. Severe gasket deterioration, often more pronounced near the membrane electrode assembly's (MEA) edges, increases the risk of gas leaks. These leaks can impact safety, potentially leading to local fuel or air starvation, which, in turn, affects fuel efficiency and stack performance. Additionally, carbon corrosion may occur as a result of these issues. The breakdown fragments of silicone, driven either by preferential deterioration on the cathode side or the electrical field direction, exhibit high mobility and are prone to redepositing on both crystalline and amorphous forms, particularly on the cathode side. Their accumulation on the platinum catalyst raises the activation overvoltage, thereby impairing the fuel cell's efficiency ([167], [224], [222]).

Moreover, polymer or elastomer fragments that have been redeposited in the pores of the active layer or the gas diffusion layer can alter the porosity and wetting behavior, leading to an increase in diffusion overvoltage. The occlusion of these pores can cause fuel or air starvation, which, in turn, contributes to carbon corrosion. Lastly, ions released from the gasket filler, such as Mg^{2+} and Ca^{2+}, may inhibit the proton-conducting sites of the ionomer. Overall, the degradation of silicone or PTFE gaskets can have a multifaceted impact on the performance and durability of PEM fuel cells, necessitating careful management and maintenance to address these challenges effectively ([167], [224]).

4.8.1.2 Mitigation Strategies

Mitigating the degradation of silicone or polytetrafluoroethylene (PTFE) gaskets is essential to maintain the system's performance and longevity. To address this challenge effectively, several mitigation strategies are instrumental. Ensuring that no operational situations induce ionomer decomposition and fluoride ion emission is crucial to preserving gasket integrity. Avoiding localized heat spots and excessively high cell temperatures helps reduce gasket deterioration. Preventing direct contact between highly acidic membranes and the gaskets is essential to protect their structural integrity. Additionally, minimizing mechanical stress on the gaskets is crucial for preventing accelerated degradation. Regular stack maintenance is vital to ensure the stack maintains optimal compression force and gas tightness, particularly in cases of deteriorated gaskets. These mitigation measures collectively play a crucial role in safeguarding the gaskets' performance and the overall efficiency of PEM fuel cells, extending their operational life and reliability ([167], [222]).

4.8.2 Failure of Direct Ethanol Fuel Cells

4.8.2.1 Failure of Direct Ethanol Fuel Cells

Depending on the kind and structure of the catalyst employed, the temperature field set etc., the electro-oxidation of ethanol in DEFCs below 100 °C does not progress all the way to carbon dioxide (CO_2), but rather to acetaldehyde (CH_3CHO), acetic acid (CH_3COOH), and CO_2. Due to the presence of heavily

adsorbed intermediates, pure Pt is not a particularly effective anode catalyst for ethanol electro-oxidation at room temperature or moderate temperature. Adsorbed carbon monoxide, CO, is constantly present in the anodic reaction mechanism and causes anode poisoning, which in turn causes significant anodic overpotentials in comparison to the theoretically achievable fuel cell voltages [225].

4.8.2.2 Mitigation Strategies

One practical method of preventing poisoning from electro-oxidation process intermediates, particularly the adsorbed CO, is to make platinum alloys with a second or third metal, such as ruthenium, Ru. Ru activates water molecules and gives favorable sites for –OH adsorption at lower potentials than Pt, based on the bi-functional method for electro-oxidation. For the poisoning intermediates to fully oxidize to CO_2, a sufficient number of -OH species are required. It has been established that adding tin (Sn) can significantly increase the electrocatalytic activity of Pt for ethanol oxidation. The shape and nature of the anode catalysts influence the ethanol's adsorption and electro-oxidation, while raising the PEMFCs' operating temperature range when they are directly fed liquid ethanol can speed up the electro-oxidation reaction and lower the anode overpotential [225].

CHAPTER 5

Conclusions

In conclusion, the commercialization of Proton Exchange Membrane (PEM) fuel cells holds immense importance in the realm of sustainable energy solutions. These fuel cells offer a clean and efficient alternative to traditional fossil fuel combustion, with the potential to revolutionize various sectors including transportation, stationary power generation, and portable electronics. PEM fuel cells operate at high efficiency, converting chemical energy directly into electrical energy with minimal emissions, thus mitigating environmental pollution and reducing greenhouse gas emissions. Their modular design, compact size, and rapid start-up make them suitable for a wide range of applications, from powering vehicles to providing backup power for residential and commercial buildings. Moreover, PEM fuel cells facilitate the integration of renewable energy sources such as hydrogen and biomass, offering a pathway towards a greener and more sustainable energy future. The commercialization of PEM fuel cells not only fosters technological innovation and economic growth but also contributes to addressing global energy challenges and achieving a cleaner and more resilient energy infrastructure.

While these fuel cells exhibit significant advantages, the path to widespread commercial usage is laden with hurdles. Drawbacks such as mechanical degradation, platinum catalyst poisoning, and issues related to membrane integrity have hindered seamless integration into various applications. However, these setbacks serve as catalysts for ongoing research and innovation. The exploration of failures and mitigations in PEM Fuel Cells underscores both the potential and challenges in the quest for sustainable energy solutions. New techniques were born, a lot of obstacles were surpassed while persistent concerns still exist until today. The need for new green technologies has never been more critical, and PEM Fuel Cells emerge as a promising candidate on this transformative journey.

In the pursuit of addressing the failures and challenges inherent in PEM fuel cells, researchers and engineers are actively exploring various avenues and strategies. These efforts encompass a broad spectrum of approaches, including material innovations, system optimizations, and advanced manufacturing techniques. One key focus area involves the development of novel catalyst materials with enhanced durability, activity, and resistance to poisoning. Additionally, improvements in membrane design and electrode architecture are being pursued to mitigate issues such as water

management, gas crossover, and membrane degradation. System-level optimizations, such as better thermal management, more efficient gas distribution, and enhanced control algorithms, are also being investigated to improve overall performance and reliability. Furthermore, efforts are underway to streamline manufacturing processes, reduce costs, and scale up production to make PEM fuel cell technology more accessible and commercially viable. Through collaborative research, innovation, and continuous improvement, the quest for overcoming the obstacles facing PEM fuel cells remains a dynamic and multifaceted endeavor, driving towards a future of cleaner, more efficient energy technologies.

The identified failures in PEM Fuel Cells not only highlight current limitations but also emphasize the urgency of finding robust solutions. As the world pivots towards clean energy, PEM Fuel Cells must overcome these challenges to emerge as reliable, efficient, and economically viable alternatives. The ongoing research and development efforts are pivotal in addressing these failures, ensuring the technology's resilience and adaptability. In recent years massive technology steps have been gained at the PEM Fuel Cells section both in terms of research and implementation. The commitment to overcoming these obstacles reflects a broader dedication to shaping a sustainable energy future. PEM Fuel Cells, with their potential to produce clean energy and reduce dependency on fossil fuels, stand at the forefront of this endeavor.

In this context, the necessity for commercially viable PEM Fuel Cell technology becomes evident. Its successful integration into various sectors, from transportation to stationary power generation, relies on the collective efforts of researchers, engineers, and policymakers. The commercialization of PEM Fuel Cells is not merely a technological milestone, it's a key enabler for a greener and more resilient energy landscape.

Today, because of the difficulty producing and providing clean hydrogen as fuel, ethanol and methanol PEM fuel cells represent promising alternatives in the quest for sustainable energy solutions. These fuel cells utilize ethanol or methanol as fuel sources, offering advantages such as high energy density, ease of transport, and compatibility with existing infrastructure. Ethanol and methanol fuel cells have made significant strides in recent years, with ongoing research focusing on improving their efficiency, durability, and cost-effectiveness. Despite their potential, challenges such as fuel crossover, catalyst poisoning, and system complexity remain hurdles to widespread adoption. However, advancements in materials science, catalyst development, and system engineering are driving huge progress towards overcoming these challenges. Today, ethanol and methanol PEM fuel cells are finding applications in portable electronics, backup power systems, and even transportation, with efforts underway to enhance their performance, reliability, and affordability for broader

commercialization. As research continues to refine these technologies, ethanol and methanol PEM fuel cells hold promise as viable alternatives for clean and sustainable energy generation.

In summary, understanding and addressing failures in PEM Fuel Cells are integral to advancing this technology. The ongoing research initiatives and mitigation strategies underscore a commitment to overcoming challenges and unleashing the full potential of PEM Fuel Cells. As we navigate the complexities of energy transitions, the journey towards a sustainable future demands perseverance, collaboration, and the relentless pursuit of technological excellence.

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