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FUEL CELL ADVANCEMENTS IN THE AUTOMOBILE INDUSTRY
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Υπεβλήθη για την εκπλήρωση μέρους των απαιτήσεων για την απόκτηση του διπλώματος
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ΠΕΡΙΛΗΨΗ

Από τις αρχές του 20^{ου} αιώνα και με την ανάπτυξη και εξάπλωση των κινητήρων εσωτερικής καύσης οι άνθρωποι βασίζονται στα ορυκτά καύσιμα για τις μετακινήσεις τους. Το μεγάλο ενεργειακό περιεχόμενο καθώς και η ευκολία αποθήκευσης και μεταφοράς τους έπαιξαν σημαντικό ρόλο στο να κυριαρχήσουν στην αυτοκινητοβιομηχανία. Τα διαθέσιμα κοιτάσματα υδρογονανθράκων όμως συνεχώς ελαττώνονται με αποτέλεσμα να αυξάνονται οι τιμές τους, ενώ ο τεράστιος αριθμός αυτοκινήτων που κυκλοφορούν, ειδικά στις πόλεις, μολύνει τον αέρα. Επιπλέον, οι κινητήρες εσωτερικής καύσης έχουν αρκετά μικρή απόδοση που αγγίζει το πολύ το 30% και έτσι το μεγαλύτερο ποσό ενέργειας χάνεται με τη μορφή θερμότητας.

Τα καυσαέρια στην ατμόσφαιρα, το φωτοχημικό νέφος και η όξινη βροχή παρατηρούνται έντονα σε μεγάλες πόλεις και το όριο των PM_{2,5}, δηλαδή σωματιδίων διαμέτρου μικρότερης των 2,5μm τα οποία είναι ικανά να διεισδύσουν στα πνευμόνια αλλά και στο αίμα, όπως για παράδειγμα το μονοξείδιο του άνθρακα πολλές φορές ξεπερνιέται βλάπτοντας σημαντικά την υγεία των ανθρώπων. Ταυτόχρονα το φαινόμενο του θερμοκηπίου εντείνεται σε ολόκληρο τον πλανήτη έχοντας ως αποτέλεσμα την αύξηση της θερμοκρασίας. Προκύπτει λοιπόν η ανάγκη για πιο καθαρούς κινητήρες κι έτσι οδηγούμαστε στην ηλεκτροκίνηση. Οι μπαταρίες λιθίου που χρησιμοποιούνται στα αυτοκίνητα όμως έχουν περιορισμένο χρόνο ζωής, χρειάζονται ιδιαίτερη προσοχή για να αποφευχθεί η υπερθέρμανσή τους, απαιτούν αρκετές ώρες για την επαναφόρτισή τους και οι πρώτες ύλες για την παραγωγή τους είναι σχετικά δυσεύρετες. Σαν μια εναλλακτική λύση παρουσιάζονται οι κυψέλες καυσίμου για την παραγωγή ηλεκτρικού ρεύματος με τη χρήση υδρογόνου ως καύσιμο. Οι κυψέλες καυσίμου παράγουν καθαρό νερό αντί για καυσαέρια, ανεφοδιάζονται γρήγορα και έχουν υψηλή απόδοση της τάξης του 56-60%.

Σε αυτή την εργασία αρχικά θα παρουσιαστούν οι βασικές των ηλεκτροχημικών διεργασιών, δηλαδή των χημικών αντιδράσεων που περιλαμβάνουν και την μεταφορά ηλεκτρικού φορτίου. Εξηγείται ο τρόπος λειτουργίας μιας κυψέλης καυσίμου και παρουσιάζεται ο τρόπος κατηγοριοποίησης τους ανάλογα με διάφορα κριτήρια. Στα επόμενα κεφάλαια παρουσιάζονται οι πρόοδοι που έχουν σημειωθεί την τελευταία πενταετία στις κυψέλες καυσίμου τόσο στο εμπορικό όσο και στο τεχνολογικό κομμάτι.

ABSTRACT

Since the beginning of the 20th century and with the development and spread of internal combustion engines, people rely on fossil fuels for their travels. Their high energy content as well as their ease of storage and transport have played a vital role in dominating the automotive industry. The available hydrocarbon deposits, however, are constantly declining, resulting in rising prices, while the vast number of cars circulating, especially in cities, pollutes the air. In addition, internal combustion engines have a fairly small efficiency that reaches a maximum of 30% and so most of the energy is lost in the form of heat.

Exhaust fumes in the atmosphere, photochemical smog and acid rain are strongly observed in large cities and the limit of PM_{2.5}, i.e., particles with a diameter of less than 2.5µm that are able to enter the lungs and bloodstream, such as carbon monoxide is often exceeded, significantly harming people's health. At the same time the greenhouse effect is intensifying all over the planet resulting in an increase in temperature. Therefore, the need arises for cleaner engines and so we are led to electric motors. Lithium batteries used in cars, however, have a limited lifespan, require particular care to prevent overheating, require several hours to recharge, and the raw materials for their production are relatively scarce. Fuel cells are introduced as an alternative, to generate electricity using hydrogen as fuel. Fuel cells produce clean water instead of exhaust gases, refuel quickly and have a high efficiency of 56-60%.

In this thesis we will first present the basic principles of electrochemical processes, that is, chemical reactions involving the transfer of electric charge. Explain how a fuel cell operates and how they are categorized according to various criteria. In the later chapters are presented the advances that have been made in the last five years in fuel cells in both the commercial and the technological part.

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List of abbreviations

AFC= Alkaline fuel cell	PEMFC= Proton Exchange Membrane Fuel Cell
FCEV= Fuel Cell Electric Vehicle	DMFC= Direct Methanol Fuel Cell
PAFC= Phosphoric Acid Fuel Cell	MCFC =Molten Carbonate Fuel Cell
SOFC= Solid Oxide Fuel Cell	FCEB= Fuel cell Electric Buses
DOE= Department of Energy	OEM= Original Equipment Manufacturers
TCO= Total Cost of Ownership	HFS= Hydrogen Fueling Station
ICE= Internal Combustion Engine	R&D= Research & Development
BOP= Balance of Plant	PGM= Platinum Group Members
HOR= Hydrogen Oxidation Reaction	OER= Oxygen Evolution Reaction
HER= Hydrogen Evolution Reaction	ORR= Oxygen Reduction Reaction
EWS= Electrocatalytic Water Splitting	GO= Graphene Oxide
TMOs= Transition Metal RE= Reference Electrode	SE= Sensing Electrode
OCV= Open Circuit Voltage	HEV= Hybrid Electric Vehicle
MEA= Membrane Electrode Assembly	OCV= Open Circuit Voltage

CHAPTER 1

INTRODUCTION

1.1 A brief history of fuel cells

The history of fuel cells can be briefly seen in **Figure 1.1**. The concept of fuel cells was first introduced in the beginning of the eighteenth century by Humphry Davy and was advanced through the work of Christian Friedrich Schönbein to what would become a fuel cell in 1838. In 1839 Sir William Grove, the “Father of the Fuel Cell” experimented with what he called a gas voltaic battery and proved that electricity can be produced from an electrochemical reaction between oxygen and hydrogen and therefore he is credited with inventing the fuel cell. The term ‘fuel cell’ was first used by Charles Langer and Ludwig Mond in 1889 when they tried to use coal gas as a fuel to produce electricity. In 1932 Francis Bacon created the first AFC by modifying Langer’s and Mond’s equipment and in 1959 developed a practical fuel cell system producing 5 kW [1].

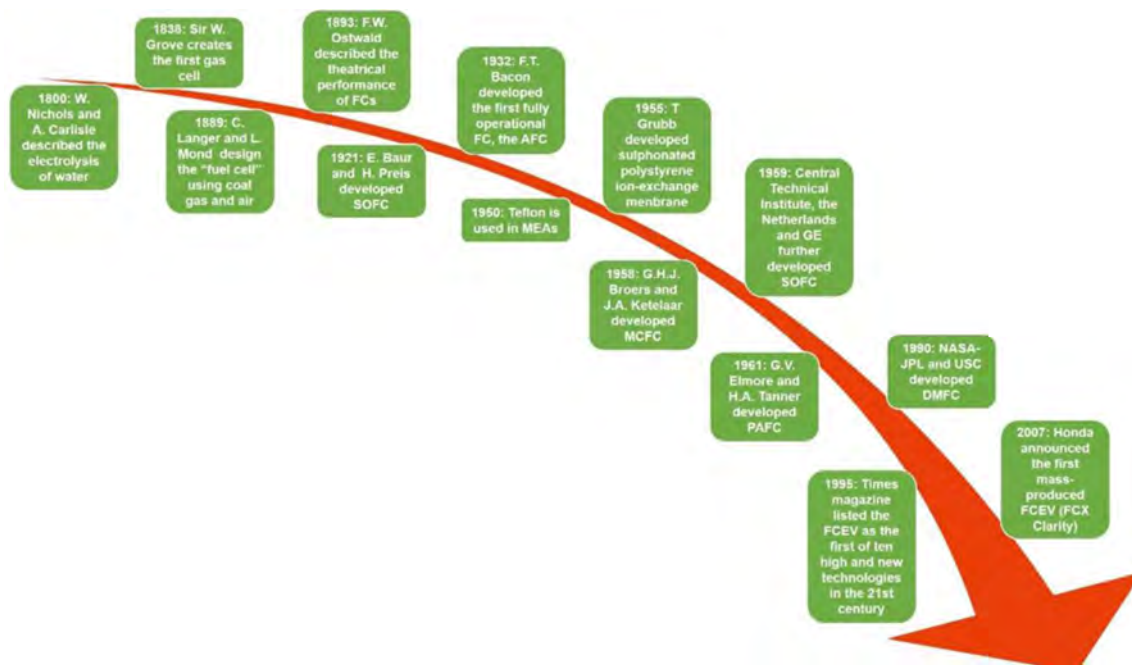


Figure 1.1: A brief history of fuel cells [53].

By the end of 1950s and early 1960s NASA started developing fuel cell generators for manned space flight missions, resulting in the creation of PEMFC (Proton Exchange Membrane Fuel Cell). Over the next

years it kept evolving and was used in the Gemini space program. International Fuel Cells produced an AFC (Alkaline Fuel Cell) for the Apollo space missions that produced both electricity and drinking water for the astronauts. Later the same company produced another more powerful AFC for use on all space shuttle flights. Meanwhile in the Soviet Union fuel cells were mostly developed for military use and ended up being used to power a submarine and the Soviet manned space program [1].

In the 1970s environmental issues as well as oil embargoes made people more concerned about fuel efficiency and cleaner machines, building up to the adoption of fuel cells. General Motors with its Electrovan introduced the first fuel cell electric vehicle (FCEV), although it was only used for demonstrations. Many car makers from all over the world created demonstration-only FCEVs powered by hydrogen or ammonia. This led to the increase of power density for fuel cell stacks as well as the development of methods to store hydrogen fuel. By the end of the century, pure hydrogen was preferred since it produces zero harmful emissions. Concerns for energy shortages led many governments and large companies to start research on more efficient means of producing energy, leading to advances in PAFC technology, mainly in stability and performance. Furthermore, there were many significant field demonstrations with stationary PAFC units. The established natural gas infrastructure also played an important role in developing stationary fuel cells for large power applications and there were advances in MCFC technology, such as the internal reforming of natural gas to hydrogen.

PAFCs continued being developed in the 80s and were expected to provide energy for large-scale power plants and the US Navy funded research for their use in submarines.

PEMFC and SOFC development received the most funding during the 1990s mainly due to their potential as a new market and because of initiatives and regulations to cut down on emissions.

In the new millennium environmental concerns continued to push for low emissions and less consumption of fossil fuels and therefore FCs received even more attention and funding. The HyFleet/CUTE program is worth being mentioned as it deployed Hydrogen buses in Europe, China, and Australia in the mid-2000s. Soon after, FCs started coming with written warranties and complied with markets' codes and standards and their market started being driven by demand. Many fuel cells were installed on boats and the army also took an interest in them. Their reliability was also seen during Hurricane Katrina, where FCs provided power when diesel generators failed [1].

1.2 Benefits and disadvantages of hydrogen fuel cells in the automotive industry

Data gathered in the period 2000-2019 show an increase in consumption of all types of non-renewable fuels. During that time, fossil fuels accounted for a significant 70% of this consumption, with the automotive industry being their main consumer as is also indicated in **Figure 1.2**. This heavy reliance on fossil fuels has created a number of both economic and environmental problems. In an attempt to mitigate these adverse effects, efforts have been made to make internal combustion engines more efficient, but due to their nature, progress is limited and gains in efficiency are small. Hydrogen has also been proposed as an alternative fuel for ICEs, but this endeavor was stopped due to two main reasons. The first one was that with Hydrogen as a fuel, the risk of a backfire was increased, posing concerns about safety. The second reason was that burning Hydrogen in ICEs highly increased the production of Nitrogen Oxides (NO_x) which are harmful pollutants. Hydrogen has therefore only been used in cars powered by fuel cells. Fuel cells produce electricity by combining Hydrogen and Oxygen through an electrochemical process and the only byproducts are heat and water. This method solves the emissions and safety problems of using Hydrogen as a fuel in ICEs and offers an alternative to traditional fossil fuels. Therefore, fuel cells are a much more efficient and environmentally friendly way to produce the energy necessary for automobile applications.

At the moment, fuel cell vehicles (FCEVs) are positioned in the market against the traditional and well-established internal combustion engine vehicles (ICEVs), the emerging battery electric vehicles (BEVs), and the combination of those two that brings the best of both, the hybrid electric vehicles (HEVs), each with their own set of advantages and disadvantages. Production of hydrogen is costly and thus the price is above that of natural gas or diesel. That is only logical, as the methods used to produce hydrogen, like methane steam reforming and water electrolysis require significant amounts of energy input and advanced technologies that greatly increase cost. Fuel cells themselves are also more expensive compared to ICEs. Partly, this is because the production rate is also much smaller for FCVs compared to ICEVs. Additionally, the components used in fuel cells such as the proton exchange membranes and Platinum-based catalysts are costly. These components and materials are also very sensitive to fluctuations in environmental conditions like temperature and humidity, running the risk of drying or freezing, which can have a significant impact on the longevity and performance of the fuel cell. Storing gas and diesel is quite easy as is refueling an ICE-powered car. The power grid is efficient and trustworthy and more and more recharging stations have been built over the recent years, benefiting BEVs and adding to their accessibility and ease of use, as they can be conveniently recharged in various locations, including homes, workplaces, or public charging stations. The infrastructure to supply hydrogen, on the other hand, is almost non-existent in most countries. Moreover, refueling with hydrogen is proven to

be quite difficult, as the fuel must be contaminant-free so as to not damage the cell. The process of achieving and maintaining this level of purity further adds to complexity and cost. The existing ways to store hydrogen are either too power-consuming, not power-dense enough, or the special tanks that are needed are too heavy and expensive. Ongoing research and development as well as the expanse of infrastructure though are expected to solve those problems. Innovations in hydrogen production methods such as the use of renewable energy for electrolysis are expected to reduce costs and improve sustainability. Advances in technology are expected to bring the cost of components down and enhance their durability under all environmental conditions. Efforts are also being made to devise better hydrogen storage solutions, such as more efficient tank designs that will make storing hydrogen more cost-effective and practical, while with the support of government incentives and industry investments, the hydrogen-refueling infrastructure is gradually expanding.

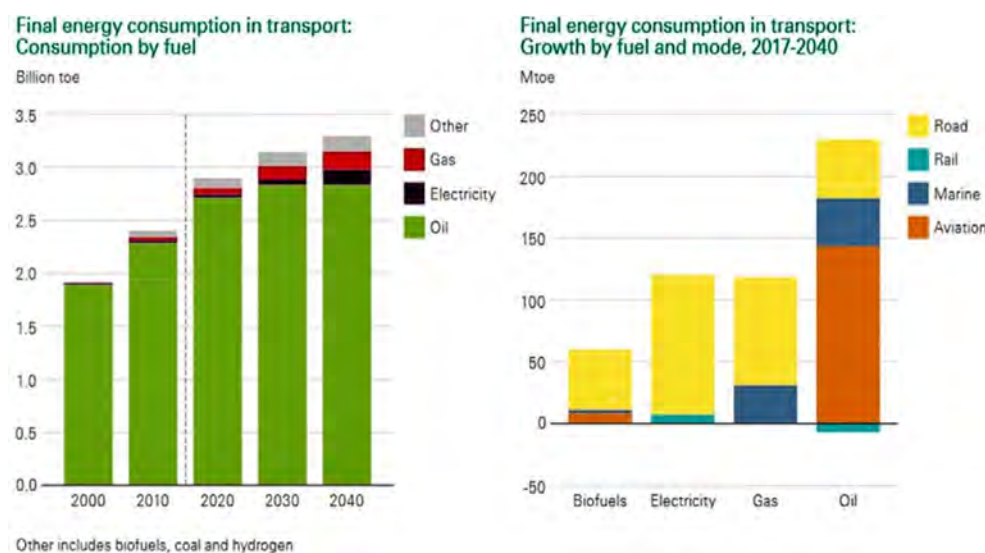


Figure 1.2: Fuel consumption in the period 2000-2040 [51]

On the other hand, fuel cells present many advantages as a means of producing power. Their efficiency is much higher than that of ICEs, meaning that they produce more power per unit of fuel. This translates into fewer refueling stops and better fuel economy, thus making fuel cells an attractive option for long-distance travel and commercial transportation. Fuel cells operate silently which is a major benefit for areas suffering from noise pollution like big cities. This contributes to a more pleasant and less stressful urban environment that benefits all citizens alike and also offers a more silent and relaxing trip to the driver. The only byproduct of fuel cell operation is water and heat, making them emission-free. This characteristic is of high importance as many countries are imposing stricter control and more restrictions on carbon emissions in their effort to combat climate change and improve air quality. Their emission-free operation is aligned with the global effort to transition to cleaner energy sources and reduce greenhouse

emissions and this gives them the edge as a technology that will take the lead in the future. Furthermore, fuel cells are much more compact and smaller than internal combustion engines or battery stacks used in BEVs. This characteristic allows for greater flexibility in car design. Manufacturers can therefore either design smaller cars with increased mobility and more practical for use inside cities, but also featuring the same internal space for passengers as traditional vehicles or utilize the available room in vehicles of the usual size to offer more comfort, cargo space, and safety features. A big advantage against batteries is the refueling time which is much shorter than that of recharging. Refueling an FCEV takes only a few minutes, just like refueling a gasoline or diesel car while recharging a BEV takes a significant amount of time. This is appealing to the everyday driver but is also a significant advantage for users who are short on time, like emergency or commercial transport vehicles. Unlike batteries whose lifespan is limited, and their performance diminishes over time, fuel cells are known to be reliable and maintain their efficiency and output over extended periods of time. This longevity reduces the need for replacements and maintenance and brings down the overall cost of ownership. Finally, spatial orientation does not affect their operation and they do not cause vibrations, nor are they affected by them, making them ideal for use in moving platforms. This further contributes to their reliability and versatility as they ensure a consistent performance regardless of the orientation or the movement of the platform [57].

In **Figure 1.3** a comparison between FCVs and their ICEV counterparts is listed. The result that FCVs outperform internal combustion engine vehicles is clear, as the vehicles powered by FCs have a much better performance in energy efficiency, drivability, and mileage while also requiring less maintenance, being silent, and not polluting the air. However, fuel cell-powered vehicles still lack in terms of power-to-weight ratio and their initial purchase cost is much higher, these problems are expected to be solved with the introduction of new technologies and the increase in production.

Characteristics of vehicle	F CV performance vs. ICEV
Emissions	Much better (zero?)
Noise/smoothness	Better
Energy efficiency	Better/much better
Power: Weight ratio	Worse
Driveability	Better
Range/refuelling	Similar
Running cost	Better
Maintenance	Better
First cost	Worse

Figure 1.3: FCEV vs ICEV [54].

CHAPTER 2

FUNDAMENTALS OF CATALYSIS & ELECTROCHEMISTRY ELECTROCHEMICAL DEVICES FOR ENERGY CONVERSION AND STORAGE

2.1 The electrochemical phenomenon

Every element consists of similar atoms, unique to this element, each possessing unique characteristics. One of those fundamental characteristics that differentiate atoms of one element from another is the number of electrons surrounding the nucleus. These electrons are not distributed randomly but instead can only exist in defined layers or shells with a predetermined distance from the core. Each layer has a maximum capacity of electrons. Namely, the first shell can hold up to two electrons, the second can hold up to eight, and the third and fourth shells can hold up to 18 and 32 electrons, respectively. As a general rule, close to the nucleus, there is a stronger electrostatic attraction between the positively charged nucleus and the negatively charged electrons. Consequently, the further a layer is from the nucleus, the more energetic the electrons that occupy it.

In nature, things tend to expel excess energy and move to a more stable state. For atoms, the most stable state is when the outer layer is filled with electrons to its maximum capacity. This need drives elements to create connections in order to share or expel/take electrons and have their outer layer full. For example, a Hydrogen (H) atom that has one electron in its outer layer, but it needs two to be filled will seek other atoms to connect and either take one more electron or expel the one it has. An Oxygen (O) atom that has six electrons in its outer layer and requires another two to be filled will interact with two Hydrogen atoms in order to fill its outer layer and achieve stability. When two H atoms and one O atom interact and form a chemical bond, they share one electron each, so that the O now has eight electrons in its outer layer, and H atoms have two each, making them all have their outer layers filled to capacity. This bond creates a stable molecule of water (H₂O).

The question posed now is, what keeps the atoms bonded together? Oxygen is more electronegative, which means that it has a stronger pull on bonding electrons and ends up taking the shared electrons closer to it and thus has a double negative partial charge (O^{2-}), while Hydrogen has a positive partial charge (H^+). The positive atoms are then attracted by the negative ones and therefore a stable bond is made between the Oxygen and the two Hydrogen atoms. When a chemical reaction is driven by a difference in electrical potential between two atoms it is called an electrochemical reaction. This means that during the reaction there is an electric charge being transferred in the form of ions or electrons and we can use that charge in various devices. The simplest such device is the electrochemical cell which consists of a porous membrane or diaphragm, two electrodes, an electrolytic medium, and two electrodes as well as an external circuit. The electrolytic medium allows for the movement of ions between the two electrodes, named anode and cathode, and are conductors or semiconductors and the membrane stops the electrons from passing through while still allowing passage to the ions. Finally, the external circuit facilitates the transfer of electrons that gives the desired electric current. The reactions taking place are redox (reduction-oxidation) reactions, meaning that there is an oxidant and a reductant and that electrons are transferred from the reductant to the oxidant. A redox reaction requires an oxidizing and a reducing agent. The reducing agent is a substance that donates electrons (in our case Hydrogen) and the oxidizing agent accepts those electrons (Oxygen in our case). The electrochemical cell can be either a galvanic cell, producing electricity, or an electrolytic cell that consumes electricity. The galvanic cell combines the reductant and the oxidant in a spontaneous redox reaction to form a new substance and produce electricity while the electrolytic one consumes electricity to drive a non-spontaneous reaction and separate the reactants and form new substances. In the case of water for example, O_2 and H_2 are fed to the galvanic cell to produce electricity and H_2O , while water is fed to the electrolytic cell, and it uses up electricity to separate the water in H_2 and O_2 .

When doing a thermodynamic examination of an electrochemical system we tend to consider it at constant pressure (P) and temperature (T). This approach is particularly effective in understanding the behavior and efficiency of various electrochemical devices. The most useful thermodynamic functions that are used are the Gibbs Energy and Enthalpy given by the equations:

$$G = U + PV - TS \quad (2.1)$$

$$H = U + PV \quad (2.2)$$

Where U is the internal energy, V is the product volume and S is its entropy. The Gibbs Energy is a function that indicates the state of a system by determining its spontaneity, while when talking about the transition of a system between two states the change in Gibbs energy is used to find the energy difference between those two states regardless of the way or the speed of the transition. This difference is calculated as

$$\Delta G = Q - W_u \quad (2.3)$$

where Q is the heat exchanged with the environment and W_u is the work done by the system or to the system. An equilibrium is characterized by $\Delta G = 0$ and is where the Gibbs energy is at its minimum. For a system with only pure components, meaning components that form phases that are separate and with constant composition the Gibbs energy is

$$G = \sum N_k * G_k \quad (2.4)$$

Where G_k is the specific molar Gibbs energy of a component k in J/mol and N_k is the number of moles of k present in the system.

For a system with variable components that form phases with variable compositions, the same equation is

$$G = N_k * \mu_k \quad (2.5)$$

$$\mu_k = dG/dN_k = \mu_k^0 + RT \ln(p_k) = \mu_k^0 + RT \ln(c_k) \quad (2.6)$$

Where p_k is the partial pressure, c_k is the molarity and μ_k is the chemical potential of k in J/mol.

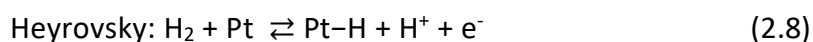
Before moving on to examining the advancements of fuel cells in the automotive industry it is worth mentioning some of the main areas that electrochemical reactors are being used today. Namely: Fuel cells, electrolysis, photoelectrochemical splitting, carbon reduction, batteries, and electrochemical sensors.

2.2 Fuel cells

Fuel cells are placed among the most promising electrochemical devices for energy production. Their versatility and robustness have been tested extensively in a variety of applications, including use in extreme conditions such as space missions and submarine operations. Their usage over the years has demonstrated their potential for a wide range of applications, demonstrating their adaptability and efficiency in producing clean energy.

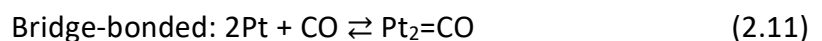
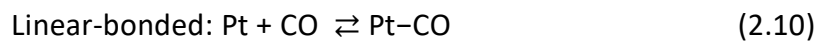
The way FCs work will be explained in the next chapter. Since this study is mostly focused on PEMFCs they will be the ones discussed here. PEMFCs are highly regarded for their various advantages against other types of fuel cells. However, they also come with one major disadvantage and that is their inability to tolerate Carbon monoxide (CO). Currently, the most efficient way to produce Hydrogen (H₂) is methane steam reforming and therefore this H₂ comes along with impurities such as CO [27]. There have been tried some ways to further purify H₂, but they are not highly efficient and greatly increase the cost. As a result, the scientific community has focused its efforts on developing CO-resistant anode electrocatalysts [27]. Most commonly platinum (Pt) is used on catalysts as it is highly active but has a few drawbacks, the chief of which is the high cost and minimal CO tolerance. To address these issues, efforts are being made to create more durable Pt-based catalysts by alloying Pt with other metals [25],[33]. Among these alloys, Pt-Ru seems to be the most feasible [27] while Pt-Ni is the most competitive [30],[33]. Pt-Ni catalysts still suffer from CO poisoning, prompting further investigation to mitigate this problem. It is found that adding Rh, Ru or Pd greatly helps alleviate this problem, although more research needs to be done on that [33]. Alloys not only increase activity by exposing a greater number of active sites but also decrease the amount of Pt used and thus decrease the overall cost [30]. Generally, adding Au or Ni can seal the catalysts' surface from coming in contact with toxic substances and thus increase its durability [30]. Other strategies that are under survey include morphing the catalyst in different structures [25],[30],[33] such as Pt-Pb/Pt core-shell nanoplates, nanocubes of excavated Pt₃Co, Pt-Pd nanodendrites, Pt-Ni nanoframes [23] and Pt-Cu-Rh heterogenous nanocages [29]. Finally, exchanging carbon support with transition metal carbides and oxides is another way to optimize catalyst performance and durability[27].

CO blocks the active surface of the anode responsible for the catalysis and results in decreased activity. To understand this, we must explain the way Hydrogen Oxidation Reaction (HOR) works. HOR reaction can follow either the Tafel–Volmer or Heyrovsky–Volmer reactions [27]. Those are:



For the Tafel-Volmer reaction, first is the Tafel step during which one H₂ molecule, composed of two hydrogen atoms, is adsorbed by two Platinum particles, that act as a catalyst, resulting in two bonded pairs of Pt-H. Then, for the Volmer step, the Hydrogen atom is dissociated from the catalyst, which remains as is, and loses an electron (e⁻), thus becoming a positively charged ion (H⁺). For the Heyrovsky-Volmer reaction, first come the Heyrovsky step which sees an H₂ molecule come in contact with an atom of Platinum. The molecule of Hydrogen is then broken, and one of the two H atoms is adsorbed onto the catalyst surface while the other Hydrogen atom loses an electron and becomes an H⁺ ion. Then comes the Volmer step that was described earlier to break the Pt-H bond.

At the usual temperatures a PEMFC operates the Carbon monoxide rivals H₂ for adsorption onto the anode surface. However, CO has a more negative Gibbs free energy value for adsorption and is, therefore, more strongly adsorbed. As a result, CO molecules preferentially replace hydrogen molecules on the catalyst's active sites, effectively blocking them and prohibiting Hydrogen from undergoing the necessary reactions for the fuel cell operation. The two types of CO adsorption are [27]:



Luckily, as indicated by the double arrow, this process is reversible, meaning that the carbon monoxide can be desorbed, and the catalyst surface can be cleared and regain its functionality.

Efforts have also been made to create Pt-free [32] catalysts and bifunctional catalysts that promote both the Hydrogen Oxidation Reaction (HOR) and HER (Hydrogen Evolution Reaction). However, Pt-free bifunctional catalysts have encountered challenges, particularly with excessive Hydrogen ions (OH) adsorption that leads the HOR region to stop working [28]. Ni-Ru alloys have been found to be good catalysts for both reactions end even more when minimal quantities of Co, Ni, or Fe along with N [32] are added to the alloy [28]. This type of catalyst helps both reactions, but great care must be placed on the structure of the catalyst [28]. Despite advancements in Pt-free catalysts, unfortunately, most studies examine catalysts operating in a basic environment, therefore excluding PEMFCs that by nature are an acidic environment [31]. The most important factors when operating in acidic media are the chemical composition and microstructure that determine the lifetime and efficient active sites of the catalyst and pore structure and specific area, which determine how accessible the active sites are, as well as the transport properties [31].

Iron-based catalysts are prone to oxidation when operating in acidic environments, while Co-N-C catalysts have exhibited a performance below expectations [32].

2.3 Batteries - energy conversion and storage

Ensuring sustainability for clean energy goes beyond just producing it. It is also very important to be able to effectively store and conserve it for future utilization. Among the many different types of batteries that are found in most appliances used worldwide, lithium-ion (Li-ion) batteries stand out as being the most promising due to their lightweight nature and good energy density. However, non-aqueous, rechargeable Li-O₂ batteries appear as strong candidates for commercial use in the automotive industry. These batteries present an energy density as much as ten times higher than that of simple Li-ion batteries and are almost comparable to the energy density of gasoline [49,50,53]. A typical Li-O₂ battery is composed of three based components, namely a Li anode, an organic electrolyte, and an air cathode [49,50]. Its function is described by the equation $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ (2.12) with the forward reaction being the discharge and the backward reaction being the charging of the battery [45]. The main problem here is the slow Kinetics of the cathode, where both the Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) take place [50,51,52]. Noble metals have been historically used as catalysts in batteries and as mentioned before their high cost prohibits their commercial use. Thus, the option of more economical bifunctional catalysts must be explored [45],[46]. Transition metal oxides (TMOs), also discussed in 2.3, have been used as catalysts for the ORR/OER reactions in other types of batteries, including Zn-air and Li-O₂ batteries. However, they continue to suffer from the problems already discussed previously [45],[47]. Selenium (Se) with its distinctively large atomic radius and smaller ionization energy presents an interesting case. Transition metal selenides seem to be more electrophilic and therefore they are good candidates to promote the OER [45]. Moreover, when a Li-O₂ battery is discharged, byproducts that cannot be further solved are accumulating on the cathode. These accumulated byproducts hinder the transport channels and prematurely end the discharge [52,53]. To address this issue, it is therefore necessary to develop cathodes with optimized structures that will facilitate the proper decomposition of these byproducts during the charging phase, resulting in the battery's sustained health and performance [47].

Additionally hindering the widespread commercialization of Li-O₂ batteries is the high expense associated with current collectors [45]. These collectors which are crucial components of the battery are typically made of materials such as carbon paper or cloth alongside metal foam. Acting both as a medium for O₂ to pass through and as a support for the catalyst at the cathode they are crucial to the performance

of the battery [45]. Addressing this challenge to reduce cost, researchers have proposed an interesting solution, biomass-derived materials. Biomass is abundant and has the preferred 3D structure without needing any extra preparation and can easily be doped [49,50]. Wood, in particular, presents a compelling option, featuring an open and vertical channel structure. This structure enhances conductivity, facilitating the diffusion of materials and their transmission throughout the battery system, surpassing other biomass-derived materials in both performance and efficiency [46].

A typical BEV battery stack can be seen in **Figure 2.1**. It is worth noting that the lack of a main engine frees up much space that can be used to store cargo or make a more relaxing passenger space, while the motors placed between each set of wheels offer a variable power output that makes the ride safer and more relaxing. On the other hand, the battery stack takes up all the space under the car, translating to an enormous weight, a huge expense in case of replacement, and a safety risk in case of damage to the batteries due to objects on the road surface.



Figure 2.1: A typical BEV battery stack [55].

2.3.1 Comparison of fuel cells and batteries

Fuel cells are quite similar to batteries in many aspects, particularly in their fundamental operation of producing electrical energy by converting chemical energy. Both devices are based on the same principle of transferring electrons from the anode to the cathode, they require an electrolyte, a catalyst, and an external circuit in order to produce voltage and power [51].

Despite their similarities, there are key distinctions between the two technologies. Their main difference is that while batteries utilize metallic anodes (usually Zinc or Lithium) and cathodes made of metal oxides, which are consumed during operation in order to produce a current, fuel cells are powered by an external fuel supply. This distinction has significant implications for their maintenance needs and costs as well as their expected operating lifespan. Batteries are degraded over time due to

the consumption of their electrode materials, leading to the need for periodic recharging or replacement of the electrodes. Fuel cells on the other hand maintain their components intact as they consume externally supplied fuels, leading to a longer operational lifespan and also a non-stop function for as long as fuel is supplied [51].

Both batteries and fuel cells produce relatively low voltages but can be stacked to produce a greater output. However, since fuel cells can retain their functionality and a steady output for as long as there is a fuel supply, they are preferred for sustained power-generating applications.

2.4 Electrolysis – Hydrogen production - Electrolyzers

H₂ can be produced in many different ways, each with its own advantages, disadvantages, and limitations. Methane steam reforming is considered the dominant production method at present, but definitely not the most environmentally friendly. Other examples of sources of Hydrogen are biological sources, biomass, and coal reforming [44]. However, one of the most straightforward, efficient, and clean ways of producing Hydrogen is electrocatalytic water splitting (EWS) [37],[43].



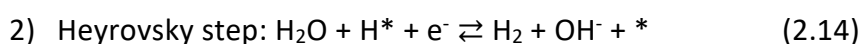
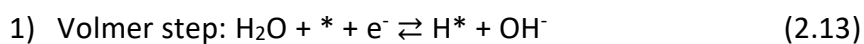
Figure 2.2: An electrolysis device [61].

During this process, a voltage is applied, facilitating the splitting of water into Oxygen and Hydrogen gasses. More specifically, H₂ is produced at the cathode and O₂ at the anode [42]. Because of the inherently slow nature of this reaction, electrolyzers are used to catalyze and accelerate the process [42]. However, the high cost and scarcity of electrolyzers is an obstacle to the widespread adoption of electrolysis, leading to a minimum amount (less than 5%) of H₂ being produced that way [41],[44]. Both in electrolysis and in batteries the oxygen evolution reaction (OER) is of high importance [36][37]. Unfortunately, this reaction also requires a huge amount of

power to be provided, so good catalysts need to be found or developed [36],[37],[43]. Above, in **Figure 2.2**, a simple electrolysis machine can be seen. It consists of a simple cylindrical container, the external circuit that provides electric power, and the electrodes that are encased in glass tubes. Water is contained inside the cylindrical container. Then an electric current is applied through the red and black cables that are seen connected to the electrodes leading water to be split. As mentioned before, Hydrogen is produced in gaseous form at the cathode side and Oxygen at the anode. Both these gases are then collected inside the glass tubes and can be extracted and used.

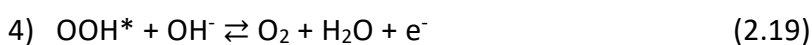
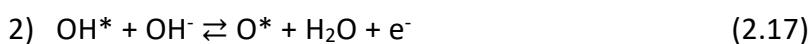
In an alkaline environment, the EWS proceeds as follows:

HER can follow one of the three different paths:



Here, * represents an active site and H* represents a H atom adsorbed at an active site [37]. First is the Volmer step, where a molecule of water comes into contact with an active site of the catalyst and is charged with an electron supplied by the power source. The water is split and an OH⁻ ion is formed while another H atom is adsorbed onto the catalyst's active site. For the Heyrovsky step, a molecule of water comes into contact with an adsorbed Hydrogen atom in the presence of a free electron. Water is again split into an OH⁻ ion that remains as is and a Hydrogen atom that bonds with the adsorbed one, leading the active site to be freed and an H₂ molecule to be formed. Last is the Tafel step which shows two adsorbed Hydrogen atoms being desorbed and bonded with one another, giving an H₂ molecule and two free active sites.

While OER proceeds as:



First, an OH⁻ ion comes in contact with an active site of the catalyst and is adsorbed there, giving off a free electron. Then the adsorbed OH ion comes in contact with another OH⁻ ion. The

Hydrogen breaks off from the adsorbed ion and is desorbed and bonded with the OH^- to form water and release another free electron while an adsorbed O atom is left behind. For the third step, the adsorbed O atom comes into contact with another OH^- ion and is bonded to form an adsorbed OOH ion and release another electron. Finally, another OH^- ion comes into contact with the adsorbed OOH. The OOH is desorbed and split into a molecule of O_2 and a H^+ ion that bonds with the OH^- ion to create water.

Currently, commercially available electrocatalysts predominately rely on noble metals like Pt something that makes them extremely expensive [36], [42]. This prohibiting cost has led studies to focus more on developing non-noble metal-based catalysts [43]. Among the alternatives, considerable attention is focused on Cobalt-based ones, even though they lack in terms of electrical conductivity [36]. To overcome this limitation carbon nanomaterials are used, chief of which is Graphene oxide (GO). Graphene oxide has some advantageous properties, such as that the size of its particles can be controlled, while its chemical bonds help in the transfer of charge. Additionally, it can also be reduced to restore its conductive properties [36]. Since GO is inert during the electrocatalytic process, nonmetallic elements are also used, such as Nitrogen (N), Boron (B), or Phosphorus (P) [36]. Another strategy is to create bifunctional catalysts that promote both the Oxygen Evolution Reaction and the Hydrogen Oxidation Reaction [38]. A variety of materials is researched that are more easily available and so are their oxides, such as nitrides, selenides, and carbides. Moreover, different structures with high specific area are investigated that are able to increase the exposed active sites and increase catalytic activity [37], [38].

The catalysts mentioned above exhibit optimal performance in acidic or alkaline environments, meaning that they are most effective under non-neutral conditions. However, since the creation of such conditions and their byproducts are not environmentally friendly, it is necessary to create electrolyzers that operate in neutral conditions [39]. Catalysts that operate under such conditions are rare and require a high voltage in order to split water [39],[40]. Transition metal oxides (TMOs) have shown great potential in this regard, but they still suffer from poor electric conductivity [40]. Luckily though, Copper (Cu), an abundant and cheap transition metal has gathered significant attention. Cu-doped materials have been under much study as they promote many reactions such as Hydrogen Evolution Reaction, Oxygen Evolution Reaction, Oxygen Reduction Reaction, and CO_2 reduction [39]. Introducing oxygen vacancies through doping has been found to help enhance the performance of TMOs. Unfortunately, synthesizing these materials still comes associated with a high cost, thus limiting their applications [40].

Ruthenium (Ru) represents another interesting case. Ruthenium forms a very strong bond with Hydrogen. So strong that it is comparable to that of Pt, making it a promising catalyst. However, Ru catalysts have no simple and environmentally friendly way of being mass-produced and therefore their widespread use still remains a problem to be solved [40].

2.5 Photoelectrochemical splitting

Photocatalysts are another environmentally friendly way that has been used in the production of Hydrogen [35], and in the latest years, organic ones have been in the spotlight, as they are cheap, easy to synthesize, and free of toxic metals [34],[35]. Despite those advantages, photocatalysts are still not widespread enough. Many photocatalysts are not particularly good at utilizing light in the visible spectrum [34] and are only good in the ultraviolet spectrum [35]. The requirements for a good photocatalyst are many, such as a suitable band gap and efficient transport and separation of electrons and holes created by the irradiating light, just to name two [34], [35]. Many types of organic polymer photocatalysts have undergone thorough investigation. Two great examples are graphitic carbon nitride and covalent organic frameworks [34]. It is also worth mentioning conjugated polymers that contain pyrenes as they show great efficiency under visible light [34], [35]. Additionally, conjugated polymers featuring micropores, covalent organic frameworks, and covalent triazine frameworks have also been under the microscope and studied extensively [35]. Among these, covalent triazine frameworks have shown great potential to be candidates in creating photocatalysts, as their nitrogen atoms accelerate the redox reaction by acting as active sites [34]. However, despite their potential, those organic photocatalysts often require the presence of Platinum (PT) in order to achieve optimal effectiveness and thus their commercial availability is limited [34]. This dependency underscores the importance of developing catalysts that are free of precious metals which has already been discussed.

2.6 Electrochemical sensors

Given that the focus of this paper is on FCs operating with hydrogen in a safety-critical environment, it is worth mentioning that in case of a leak, Hydrogen is very flammable and easily ignited, making its immediate detection critical for the automotive industry [48],[49]. It is also needed to be able to measure Hydrogen content during its production and transportation as PEM fuel cells require Hydrogen without any impurities. Electrochemical sensors are often used to solve these problems, offering the ability to quickly detect Hydrogen, a gas that has no specific color, taste, or odor [48]. Electrochemical sensors, utilizing oxygen-anion and solid electrolytes capable

of conducting protons, have been in use for a long time to detect hydrogen in hot environments and have a great share in the overall sensors market [48]. The reason for their dominance in the market is the solid electrolytes. Solid electrolytes are stable, not easily damaged in harsh environments, and have high ionic conductivity, characteristics that collectively enhance their reliability [48]. The principles on which they operate, determine their categorization as potentiometric, amperometric, or combined amperometric-potentiometric sensors [48], [49].

Potentiometric sensors use the potential between the electrodes to calculate the concentration of hydrogen. Potentiometric sensors are categorized into two main groups, the Nernst type (equilibrium) and mixed potential sensors (non-equilibrium) [48]. Among the solid Oxygen-conducting electrolytes used in those sensors, the most common one is Yttria stabilized Zirconia (YSZ) [48], [49]. YSZ shows great oxygen ion conductivity and durability in time, making it a preferable choice for sensor applications. It is also noteworthy that YSZ base sensors can be in either tubular or planar shape, something that is considered an advantage for application in the automotive industry [49]. These sensors however face the problem of selecting the correct reference electrode, since they operate in hot environments that exceed 600°C [48]. Lately, proton-conducting electrolytes have been gaining ground as they seem to have the desired properties to be used in many industries [48].



Figure 2.3: A tubular potentiometric sensor [60]

Nernst sensors, integral to various electrochemical applications, operate on the principle of detecting and calculating an electric voltage caused by the different gas concentrations on the reference electrode (RE) and the sensing electrode (SE) [48]. Above, in **Figure 2.3** a tubular potentiometric sensor can be seen. The reference electrode is contained inside the sealed cylindrical shell so as to maintain its stable conditions, while the sensing electrode is prolonged outside, in contact with the environment whose gas concentration needs to be measured. The

different concentrations of gas ions creates an electromotive force that is the sensor's voltage when the circuit is open (OCV). The mathematical expression used to determine this voltage is called the Nernst equation and is written as

$$E = -\frac{RT}{2F} \ln \left(\frac{P'_{H_2}}{P''_{H_2}} \right) \quad (2.20),$$

where F and R are the Faraday and ideal gas constants respectively, T is the absolute temperature and P'_{H_2} and P''_{H_2} are the gas partial pressures in SE and RE respectively [48]. In non-equilibrium sensors, there are competing reactions happening on the electrodes, and therefore an equilibrium potential cannot be established. Consequently, an alternative potential is formed between the equilibrium potentials of the two electrodes. This distinct potential is then utilized to calculate the concentration of the target substance [48].

Amperometric sensors operate by applying an external voltage and then measuring the resulting output current in order to determine the percentage of a specific gas in the gas mixture that is being analyzed [48], [49]. This process is grounded in the fundamental principle that a linear relationship can be established between the concentration of hydrogen and the resulting electrical current that can be then used to calculate the concentration of hydrogen by measuring this electrical current. This simple principle of operation makes amperometric sensors useful in analyzing gas mixtures [48]. Furthermore, they do not need a RE, and in many cases that can be considered an advantage [48], [49].

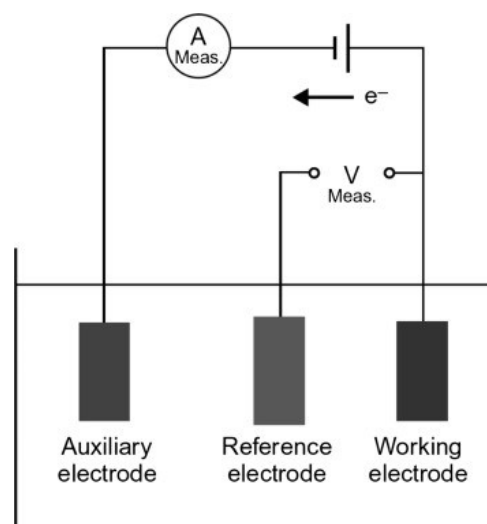


Figure 2.4: Schematics of an amperometric sensor [62].

Amperometric sensors utilize a diffusion barrier, a physical barrier through which gases permeate, to achieve contact between the gas being analyzed and the inner electrode [50]. When the

sensor is placed in the measured atmosphere, it gradually becomes saturated with the gas mixture of this environment. When a voltage is applied, a process is initiated where the gas surrounding the outer electrode is displaced from the sensor. This displacement allows the gas from the inner electrode, which is separated from the diffusion barrier, to fill the sensor. According to Faraday's law which governs electrochemical reactions, the Hydrogen concentration is directly proportional to the current generated by the sensor. This relationship is expressed as

$$J(\text{H}_2) = I/(nF) \quad (2.21),$$

where n represents the number of electrons involved, I is the current and F is the Faraday's constant [50]. The schematics of an amperometric sensor can be seen in **Figure 2.4**. A voltage applied to the reference electrode forces the gas to move to the working electrode and then to the auxiliary electrode, thus creating a current that is measured on the auxiliary electrode in order to calculate the concentration of Hydrogen in the gas mixture.

Finally, in combined potentiometric-amperometric sensors, a dual-cell configuration is employed, featuring two distinct cells. Each cell operates either based on the amperometric or the potentiometric principle. This configuration adds to the system's complexity, as the two cells must be properly coordinated to work together. However, this complexity leads to a greater accuracy in the measurement of hydrogen concentration [48].

CHAPTER 3

FUEL CELLS TECHNOLOGY

3.1 Structure of a fuel cell

Fuel cells are electrochemical, galvanic cells, meaning that they convert chemical power and produce electric current by utilizing an electrochemical reaction, like a battery. However, contrary to batteries, fuel cells require a steady supply of fuel (usually Hydrogen) and oxidant (usually Oxygen from the atmosphere). In the automotive industry, PEM fuel cells have been found to be the most suitable among the other types of fuel cells and the reaction used is the one described before, between Oxygen, as it is free from the atmosphere, and Hydrogen, that is proven to be the most efficient fuel for fuel cells. The process within a fuel cell does not involve any moving parts or heat exchange, contributing to its high efficiency and reliability. A very simple schematic of a typical fuel cell is illustrated in **Figure 3.1**. The flow of fuel to the anode and oxidant to the cathode can be seen as clearly as the flow of electrons through the external circuit that ends up being the produced current. Byproducts, namely water and heat can also be seen exiting the cell from the cathode side. This assembly illustrated here consisting of the electrodes, the electrolyte, and the external circuit is called the Membrane Electrode Assembly (MEA)

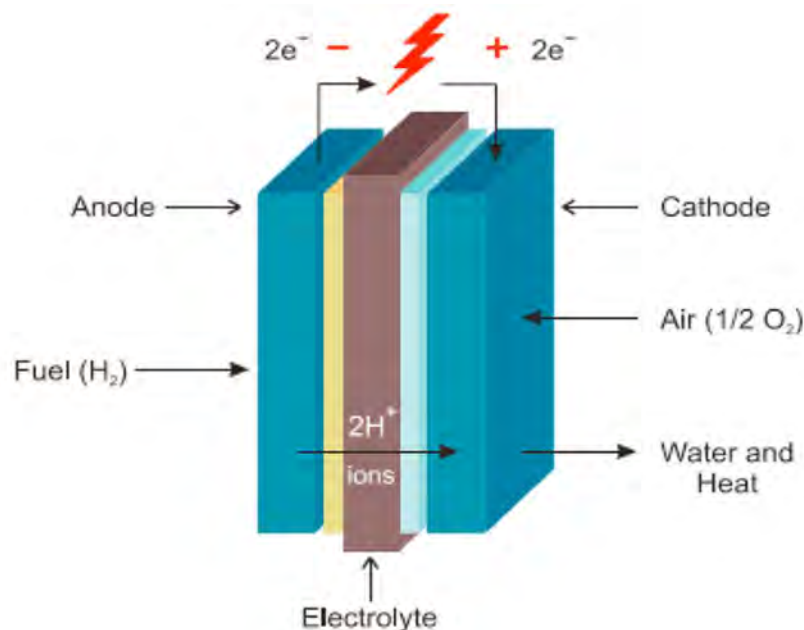


Figure 3.1 A typical fuel cell [51].

3.1.1 Membrane Electrode Assembly (MEA)

In their core, fuel cells consist of two electrodes, connected via an external circuit, that encase an electrolyte. This is called the Membrane Electrode Assembly or MEA and is the most important part of the fuel cell [51]. The MEA is so important as it is there that the reactants come into contact and produce current. The efficiency of a fuel cell heavily depends on the design and material of the MEA. A well-designed one can significantly improve the energy conversion efficiency and durability of the cell. The MEA is composed of two electrodes, the anode and the cathode, that enclose an electrolyte. This assembly is intricately designed to maximize the contact surface area and thus maximize the efficiency of the chemical reactions. A noteworthy part of the MEA is the three-phase boundary layer. This is the zone where the reactant gasses, the catalyst, and the solid electrolyte membrane interact. At this interface, the Hydrogen molecules coming in contact with the catalyst are separated into electrons that are then collected and travel through the external circuit and protons that travel through the membrane to reach the cathode.

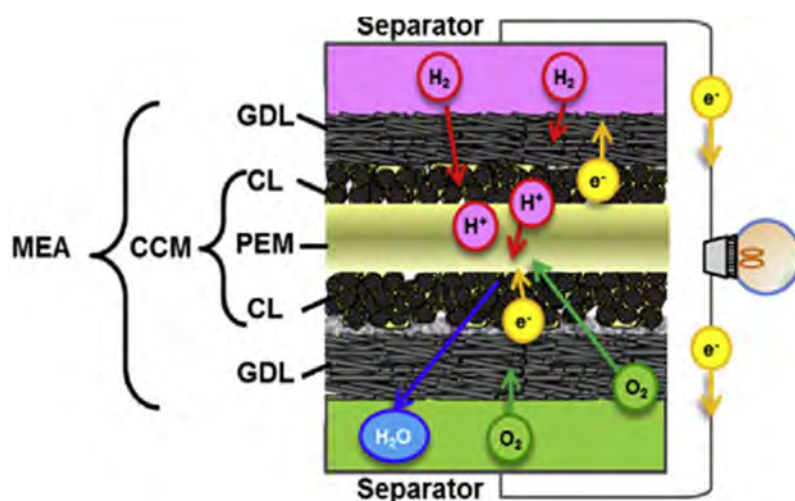


Figure 3.2: Schematics of a fuel cell [52].

Other than being the most important, this is also a very delicate area of the cell. Its intricate structure means that it requires a manufacturing process of high precision as well as delicate maintenance to ensure optimal performance. Even so, small imperfections that are caused by the manufacturing process or occur later due to usage and the passage of time can cause the different layers (membrane, catalyst, and electrodes) to separate and highly increase power losses or stop the cell's function altogether. A typical MEA assembly together with the separators and an electric consumer can be seen in **Figure 3.2**, where CL stands for catalyst, GDL is the Gas Diffusion Layer and CCM is the catalyst-coated membrane. The role of the Gas Diffusion Layer is to ensure that the reactant gasses are evenly distributed across the whole surface of the

catalyst. This layer is also designed to manage the flow of water produced during operation of the cell in order to prevent a flooding of the membrane in case the water flow to the outside is not enough, or a drying of the membrane if too much water is removed. In **Figure 3.3** an exploded image of the GDL and catalyst layer can be seen. Readers can see how the gases permeate through the GDL and reach the catalyst layer where the electrochemical reactions occur. This layer's porosity allows for efficient gas diffusion, ensuring the effective transfer of the reactants to the catalyst sites. The interaction at the catalyst layer involves the adsorption of reactant molecules, their dissociation, and subsequent electrochemical reactions facilitated by the catalyst. The two electrodes are specifically designed to only allow electrons to pass through them. Those electrons are the anode where the oxidation reaction occurs and the cathode where the reduction reaction takes place. It is especially important to choose the correct materials for both electrodes as this will improve both the performance by minimizing losses and increasing efficiency by enhancing the electrical conductivity and the life expectancy of the cell, by adapting better to temperature fluctuations and changes in the load condition. These materials are also less prone to degradation over time, maintaining their structural integrity and operational effectiveness. Moreover, the right materials can make the electrodes less vulnerable to common issues like poisoning, where impurities bind to the catalyst, and flooding, where excess water blocks the gas pathways. Since PEMFCs operate in low temperatures, catalysts are strategically placed between each electrode and the membrane. These catalysts are crucial for enhancing the reactivity at the anodes and speeding up the chemical reactions that occur within the cell [51].

The electrolyte is non-metallic and only allows ions to pass through it. This selective ion permeability is essential for maintaining the separation of the electrochemical reactions that occur at each electrode. The electrolyte can be either in a solid or a liquid state, depending on the specific type of fuel cell. To achieve this selective permeability, a chemical process called chemical doping is employed. During chemical doping, atoms of another substance are added to the crystalline structure of the electrolyte, resulting in the creation of holes through which only the preferred ions can pass. Finally, the external circuit is used to transfer electrons between the electrodes. In a typical fuel cell setup, like the one seen in **Figure 3.1**, approximately 1V of direct current (DC) is generated. Since a bigger power output is needed for most applications, multiple cells are often stacked together in a series, so as to achieve it [51].

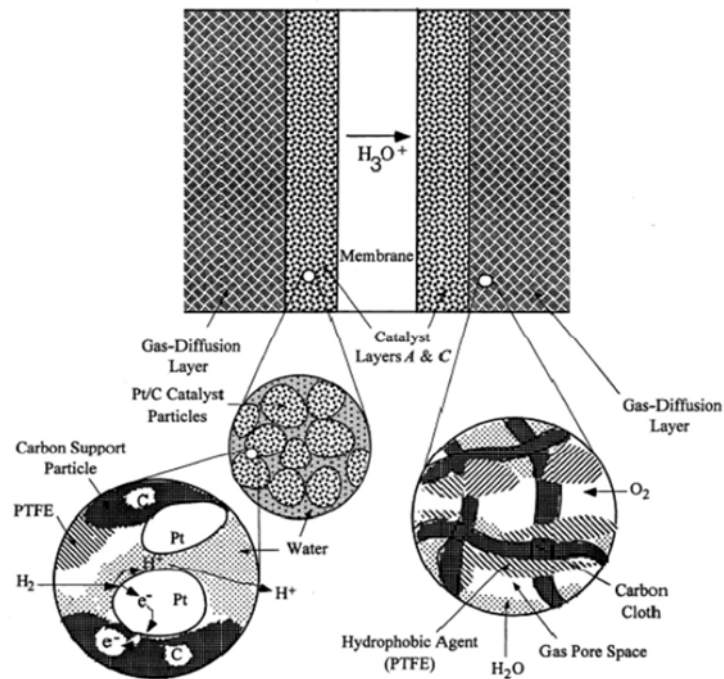


Figure 3.3: Exploded section of the GDL and catalyst diffusion layer [57].

3.1.2 Flow field plates

The Membrane Electrode Assembly is sandwiched between flow field plates. These plates, usually made of graphite, serve the purpose of providing the oxidant gas and fuel to the electrodes through specially designed channels. The channels are designed with extra care to maximize the surface area where the reactants come in contact with the Membrane Electrode Assembly, thus enhancing the efficiency of the electrochemical reactions. A good plate design helps the creation of a homogenous and stable power output through the whole area of the cell and manages the exhaust water, in order to avoid flooding. Plates are also used to conduct electricity, facilitating the transfer of electrical current from each cell to the outer boundaries of the stack. Last but not least, around each cell are the coolant flow channels. They are similar in their design to flow field plates and act to maintain optimal operating temperatures by efficiently dissipating excess heat [51]. The interaction between the MEA, the surrounding flow field plates, and the supporting infrastructure of coolant channels ensures the steady performance and longevity of the fuel cell system.

3.1.3 Overall stack design

To summarize, a complete fuel cell stack must be described in order to have a better picture of it. As already mentioned, its heart and most important component, the MEA, is placed between two flow field plates that provide channels for the reactant gasses to travel to their corresponding place. A byproduct of fuel cell operation is heat and when many cells are placed in a stack this heat can cause

problems. Therefore, between each stacked fuel cell, cooling plates are added allowing for the flow of coolant that regulates the temperature by either increasing or decreasing it as needed. For safety reasons as well as for the function of the fuel cell stack, the flows of fuel, oxidant, and coolant must never come in contact with each other and for that reason, the cell alignment, and tolerances between parts and seals must be under constant observation. At the very ends of the stack, electrical plates are fitted to collect the produced current and lead it to the external circuit. The whole stack is then secured in place by mechanical means. Its design must be one that maximizes output for a given electrolyte membrane, making it as power-dense and compact as possible. This optimization is vital, considering that the intended environment in which the fuel cell stack will be used, cars and other moving platforms, offers only a limited space, making efficiency and power density paramount [51].

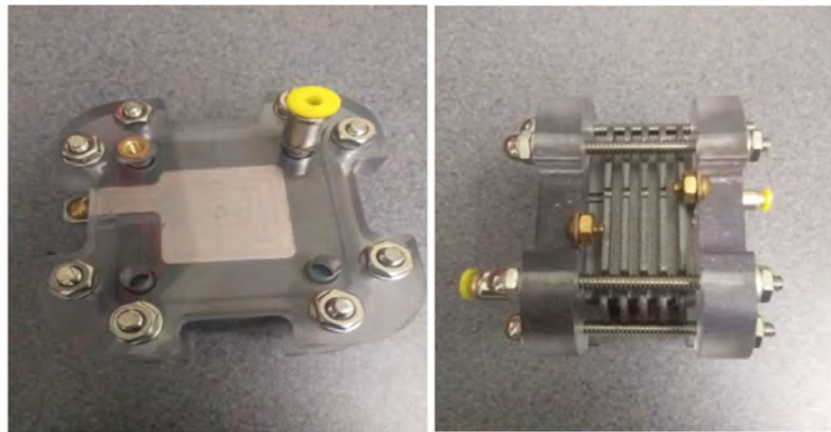


Figure 3.4: two real fuel cell stacks [51].

In **Figure 3.5** the exploded design of such a stack can be seen in its entirety, providing a comprehensive view of the arrangement of its various components. This illustration depicts the sequential placement of the parts inside the stack assembly. Meanwhile, **Figure 3.4** offers a tangible representation with images of two actual stacks that serve as examples of the completed system.

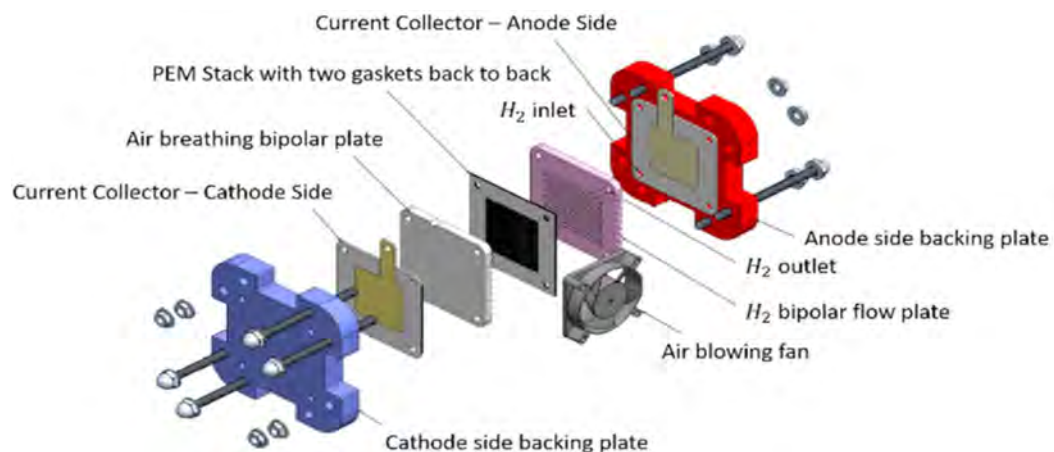


Figure 3.5: An exploded fuel cell stack design [51]

Finally, in **Figure 3.6** a complete fuel cell system is presented. Seen in this picture is not only the fuel cell stack itself but also other components essential for its operation. These include fuel storage facilities from which the fuel is provided, as well as Balance of Plant (BoP) components like the coolant circulation pump, responsible for the flow of coolant through the flow field plates, a DC/DC converter that converts the output current in a voltage suitable for the various consumers and the system load. Together, these elements constitute a fully functional FC system, demonstrating the integration of various subsystems in order to achieve efficient energy conversion.

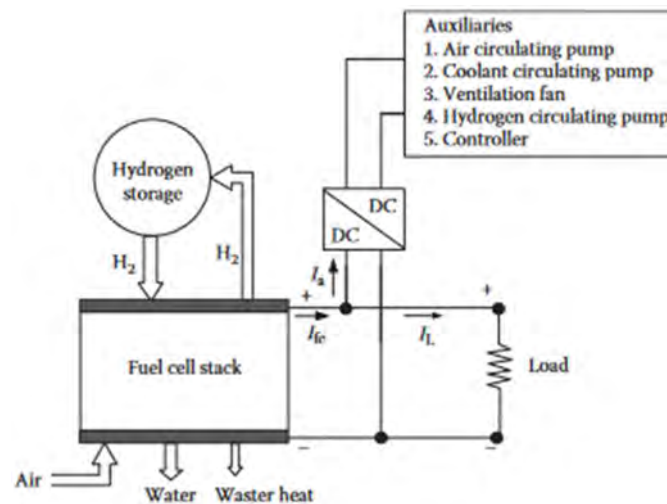


Figure 3.6: A complete fuel cell system [56]

To achieve a fully operational fuel cell system, it is crucial to incorporate Balance of Plant (BoP) components. These components serve a supporting but vital role in the overall system functionality, by providing air and fuel, managing cooling or humidification of the system, or conditioning the generated electricity so as to bring it to a voltage suitable for the various connected devices [57]. In **Figure 3.7** the process flow and key components of a PEMFC system are depicted, offering a visual representation of how these components interact within the system framework.

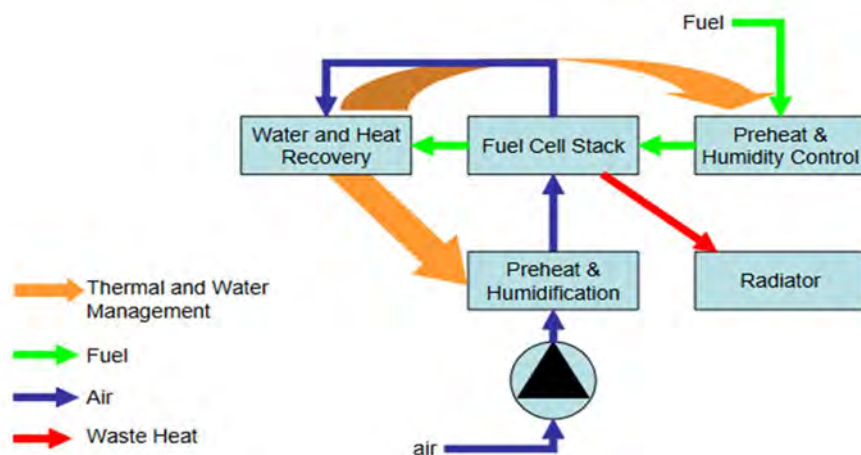


Figure 3.7: Process flow and major components in a PEMFC system [58].

The balance of plant components may have a supporting role, but they are essential components within a fuel cell system. As it will be later discussed, fuel cells must operate under strict conditions of humidity and temperature in order to avoid critical failures. As is depicted in **Figure 3.7**, heaters/coolers and humidifiers/de-humidifiers are needed in order to condition the fuel and air intakes before they reach the cell, ensuring that they meet the requirements that ensure the system's prolonged operation while having optimal performance.

3.2 Electrochemical reactions in a fuel cell

As mentioned above, the steady operation of fuel cells requires a continuous supply of fuel and oxidant, essential for sustaining the electrochemical reaction in order to produce an electric current. Oxygen from the atmospheric air is used as an oxidant, supplied to the cathode electrode, and Hydrogen is most commonly used as fuel, supplied to the anode electrode. At the anode, fuel undergoes oxidation, and in the process, it releases free electrons that then travel to the cathode, where they are consumed, through the external circuit and thus the fuel is ionized and becomes H^+ . The free electrons are taken by the Oxygen molecules in the cathode where they are reduced and ionized in order to become O^{2-} . Hydrogen ions pass through the electrolyte, a solid polymer film that at most times is an acidified Teflon [51], and meet with the Oxygen ions at the cathode where they form a bond as explained earlier and create water and heat, the byproducts of fuel cells. This process takes place in a controlled thermal and pressure environment, where the temperature is relatively low, between $70^{\circ}C$ and $90^{\circ}C$ and the pressure does not exceed the threshold of 2 bar [51]. A change in these conditions significantly affects the components of the cell and may even cause it to stop functioning.

Summarizing, the reactions taking place [3]:



Molecules of H_2 are adsorbed onto the catalyst releasing two electrons and forming two H^+ ions.



Atoms of Oxygen take in free electrons in order to fill their outer shell and O^{2-} ions are formed as a consequence.



The two H^+ ions formed earlier pass through the membrane and come in contact with an O^{2-} ion. Two bonds are created, one between each Hydrogen atom and the Oxygen atom, and a molecule of water is produced along with heat.

As seen in **Figure 3.8**, depending on the type of the electrolyte, different ions are let through, namely PEMFCs as well as PAFCs let Hydrogen ions be transferred from the anode to the cathode through the electrolyte while on AFCs it is the OH^- ions travel the opposite direction.

Anode	Electrolyte	Cathode
$\text{H}_2 \rightarrow$ $\leftarrow \text{H}_2\text{O}$	PEMFC, $\sim 80^\circ\text{C}$ $\text{H}^+ \rightarrow$	$\text{O}_2 \rightarrow$ $\leftarrow \text{H}_2\text{O}$
$\text{H}_2 \rightarrow$ $\leftarrow \text{H}_2\text{O}$	AFC, $\sim 70^\circ\text{C}$ $\text{OH}^- \leftarrow$	$\text{O}_2 \rightarrow$ $\leftarrow$
$\text{H}_2 \rightarrow$ $\leftarrow \text{H}_2\text{O}$	PAFC, $\sim 200^\circ\text{C}$ $\text{H}^+ \rightarrow$	$\text{O}_2 \rightarrow$ $\leftarrow \text{H}_2\text{O}$
$\text{H}_2 \rightarrow$ $\leftarrow \text{H}_2\text{O}, \text{CO}_2$	MCFC, $\sim 650^\circ\text{C}$ $\text{CO}_3^{2-} \leftarrow$	$\text{O}_2, \text{CO}_2 \rightarrow$ $\leftarrow$
$\text{H}_2, \text{CO} \rightarrow$ $\leftarrow \text{H}_2\text{O}, \text{CO}_2$	SOFC, $500\text{--}1000^\circ\text{C}$ $\text{O}^{2-} \leftarrow$	$\text{O}_2 \rightarrow$ $\leftarrow$

Figure 3.8 Most common fuel cell reactions [10]

SOFCs allow for some impurities such as CO to be present in the anode and it is then combined with O^- , which comes to the anode through the membrane, and let in the ambient as CO_2 exhaust gas. MCFCs use CO_2 along with O_2 as a fuel in the cathode and there it synthesizes CO_3^{2-} . The electrolyte used in MCFCs permits CO_3^{2-} to pass through and is then combined with H_2 and carbon monoxide to form water and CO_2 .

3.3 Fuel cell performance

Since the basic principles and chemical reactions behind the function of a fuel cell are already explained, its theoretical and real performance should be also analyzed.

The overall chemical reaction taking place ($\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{heat}$) (3.4) is the same as the combustion of Hydrogen, which is an exothermic reaction. First, we need to calculate the higher heating value (from now on simply called heating value) of hydrogen in order to determine the useful energy provided by its combustion. The heating value, or the enthalpy of hydrogen combustion is the difference between the heat of formation of products and reactants. Therefore, $\Delta H = (h_f)_{\text{H}_2\text{O}} - (h_f)_{\text{H}_2} - 1/2 (h_f)_{\text{O}_2}$ (3.5). At 25°C the heat of formation of water in liquid form is -286 kJ/mol with the negative meaning that energy is released, while by definition the heat of formation for elements is zero [57]. We can now rewrite (3.4) as $\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + 286 \text{ kJ/mol}$ (3.6). Even though there is no combustion involved, the heating value can be used to calculate how

much energy enters the fuel cell, and ideally, this would also be the produced power of the cell. Unfortunately, in every chemical reaction, there is also entropy produced, and only a portion of the heating energy can be converted to useful work. That energy can be calculated as the Gibbs free energy $\Delta G = \Delta H - T\Delta S$ and $\Delta S = (s_f)_{H_2O} - (s_f)_{H_2} - 1/2 (s_f)_{O_2}$ (3.7). From Appendix A of [57] we can extract the needed values and calculate that at 25°C only 237.34 kJ/mol can be converted to useful electrical energy while the other 48.68 kJ/mol are turned into heat [57].

The maximum electrical work (W_{el}) that can be produced by a cell operating in constant conditions is $W_{el} = -nFE$ (3.8), where n is the number of electrons in the reaction, E is the cell's ideal potential and F is Faraday's constant ($F = 96,485$ Coulombs/electron-mol). W_{el} can also be given by the Gibbs free energy equation meaning that the equation can be written as $W_{el} = -(\Delta G)$ (3.9). The theoretical potential of the cell can then be calculated as [57]:

$$E = \frac{-\Delta G}{nF} = \frac{237.340 \text{ J mol}^{-1}}{2 \cdot 96,485 \frac{\text{Coulombs}}{\text{electron-mol}}} = 1.23 \text{ Volts} \quad (3.10)$$

Therefore, we can calculate, that at room temperature the theoretical potential of a hydrogen fuel cell is 1.23Volts.

The efficiency of a device is by definition the amount of energy released from the device relative to the amount of energy that was inserted in the device. In the case of a fuel cell, the useful output is the electrical energy that is produced (ΔG) and the inserted energy is the hydrogen's heating value (ΔH). Therefore, the maximum possible efficiency is $\eta = \frac{\Delta G}{\Delta H} = \frac{237.34}{286.02} = 83\%$ (3.11) [57].

While all of the above are true at atmospheric pressure and at 25°C these are not the conditions in which a fuel cell operates. In true conditions, the pressure is as high as 6-7atm and higher than 25°C. The ideal performance of a cell in such conditions can be calculated as a function of temperature and pressure called the Nernst potential and is as follows [57]:

$$E(T, P) = -\left(\frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right) + \frac{RT}{nF} \ln \left[\frac{P_{H_2}P_{O_2}^{0.5}}{P_{H_2O}}\right] \quad (3.12)$$

From this equation, it is easily deduced that the efficiency is decreased at higher temperatures, but it increases as the fuel and oxidant pressure increases.

If the cell is provided with reactants and the electrical circuit is open, the actual potential, called open circuit voltage (OCV) is decreased, and is most often less than 1V, suggesting that there are losses inside the fuel cell even without any external current being generated [57]. On

the other hand, useful work can only be produced when a current is generated. Even in that case, the real potential is less than the Nernst potential due to irreversible losses. Hydrogen crossover losses may be important at OCV, but at a closed circuit with a current being drawn, they can be neglected. To properly calculate the performance of the cell three main losses must be taken into consideration and deducted from the calculated Nernst potential. These losses, called overpotential, overvoltage, or polarization are concentration polarization, ohmic polarization, and activation polarization [57],[58].

Slow electrode kinetics are associated with activation polarization, as some voltage is necessary to start the electrochemical reaction. These losses depend on the occurring reaction, the catalyst material, and its microstructure [58]. Even though these losses are observed at both electrodes they are much bigger on the oxygen side, as its reduction is much slower and requires a bigger overpotential. The Tafel equation can be used to calculate the activation losses. In the Tafel equation below, i_0 is the exchange current density and α is the electron transfer coefficient of the reaction at each electrode [57].

$$\Delta V_{act} = \frac{RT}{\alpha F} \ln \left(\frac{i}{i_0} \right) \quad (3.13)$$

A resistance in the flow of electrons through the electrodes and the protons through the electrolyte is responsible for the ohmic losses. Both the electrolyte and the electrodes obey Ohm's law and therefore these losses can be calculated by the equation $\Delta V_{ohm} = i \cdot \Omega$ (3.14), where Ω is the total resistance of the cell, including ionic, electronic, and contact resistance and i is the electrical current flowing through the cell [57],[58].

As the reactants are consumed there is a loss of potential as the surrounding materials lose their ability to maintain the concentration of the bulk fluid and therefore a concentration gradient is formed. At current densities that can actually be practical, concentration polarization occurs because of the slow transport of products/reactants from or to the reaction site. This overpotential can be calculated as [57]

$$\Delta V_{conc} = \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i} \right) \quad (3.15)$$

In this equation i_L is the limiting current, indicating the current density that is reached when the reactants are consumed faster than they can reach the catalyst surface. The limiting current cannot be exceeded because there are no reactants at the catalyst surface.

Activation and concentration losses can occur on both electrodes and therefore the actual cell voltage is [57]:

$$V_{cell} = E_{T,P} - (\Delta V_{act} + \Delta V_{conc})_a - (\Delta V_{act} + \Delta V_{conc})_c - \Delta V_{ohm} \quad (3.16)$$

Where $E_{T,P}$ is the ideal performance voltage. Introducing the above equations for ΔV_{ohm} (3.13), ΔV_{conc} (3.14), and ΔV_{act} (3.12) an equation describing the relationship between current density and fuel cell potential is obtained, also called the fuel cell polarization curve, written below [57].

$$V_{cell} = E_{T,P} - \left(\frac{RT}{aF} \ln \left(\frac{i}{i_0} \right) + \frac{RT}{nF} \ln \left(\frac{iL}{iL-i} \right) \right)_a - \left(\frac{RT}{aF} \ln \left(\frac{i}{i_0} \right) + \frac{RT}{nF} \ln \left(\frac{iL}{iL-i} \right) \right)_c - i\Omega \quad (3.17)$$

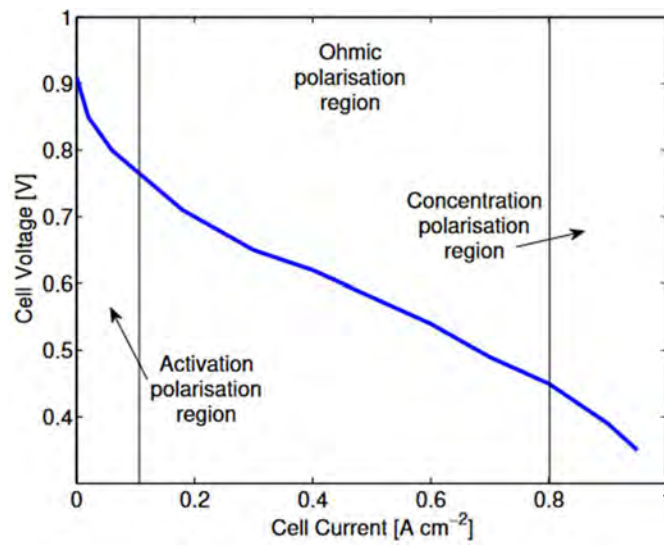


Figure 3.9 PEM fuel cell polarization curve [57]

In **Figure 3.9** the polarization curve of a Proton Exchange Membrane Fuel Cell with 5cm² electrochemical surface area is depicted. In this figure, three distinctive regions can be identified and are clearly marked. These regions of the diagram offer invaluable insights into the underlying electrochemical process governing the fuel cell's performance dynamics. The first is the activation polarization characterized by a steep decline in voltage. In that region, the activation energy barrier is manifested, impeding the progression of all electrochemical reactions. Consequently, the voltage is caused to fall rapidly, something that is attributed to the activation barriers that impede the transfer of electrons across the electrode-electrode interface. Next is the ohmic polarization region, marked by a more gradual and linear descent in voltage. This phenomenon is caused by the membrane and electrode ohmic resistance. The ionic conductivity of the membrane pales in comparison to that of the external circuit, meaning that the membrane resistance is dominant in this region. The final region is the concentration

overpotential. In that region voltage losses are mainly caused by mass transport limitations that exist in high current densities [57],[58].

3.4 Categorization of fuel cells

The categorization of fuel cells depends mostly on the type of electrolyte employed within the cell architecture. This way of classification is attributed to the profound influence exerted by the electrolyte on a spectrum of critical factors. The type of electrolyte determines the kind of electrochemical reactions that take place within the cell, the temperature range of operation, the required fuel, and other factors that end up affecting the selection of material for the electrodes and all other components that are exposed to the reactants are might be affected by temperature. Consequently, each distinct category of fuel cells has a specific profile, making it more or less suited for specific tasks and applications based on its operational attributes and unique performance characteristics.

There are many distinct types of fuel cells, each with its own advantages, disadvantages, and limitations. Some of them are presented here:

Polymer Electrolyte Membrane (PEM) Fuel Cells (FCs): Sometimes called Proton Exchange Membrane Fuel Cells, these fuel cells come with several advantageous characteristics. They possess a compact design, thus occupying less space and are lighter than other types, while despite their small size they can deliver high power density with an efficiency of 40% - 70%. Furthermore, these small-sized fuel cells can deliver significant power outputs of up to 500kW.

The operating temperature varies depending on the type of electrolyte employed. When equipped with a Nafion membrane as an electrolyte, this temperature ranges from 60°C to 120°C. However, if an alternative type of membrane is used, this temperature range extends from 120°C up to 220°C. This operational temperature spectrum renders PEMFCs particularly useful for the automotive industry. Operating at relatively low temperatures translates to them being easier to start as they do not require a warm-up, enhancing operational convenience, but also resulting in better durability due to less wear on components [59].

Despite their numerous advantages, PEMFCs are not without their own limitations. One of the most notable drawbacks is that they need a noble-metal catalyst, usually platinum, to separate the Hydrogen's protons and electrons. With Platinum being even more expensive than gold, this reliance on the precious metal drives the cost of the system upwards. Platinum catalysts are also at considerable risk of carbon monoxide poisoning, thus requiring a special reactor to be integrated

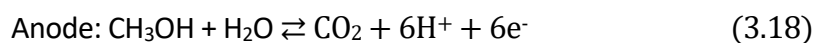
into the system, in order to reduce CO in the fuel when it comes from reformed hydrocarbons. Along with the catalyst, the integration of the reactor adds greatly to the overall cost.

PEM-FCs are ideal for utility in vehicular applications, including cars, heavy trucks, and buses, because of their compact form and high power density. On the other hand, they are rarely utilized in stationary applications mainly due to considerations about their efficiency and high cost.

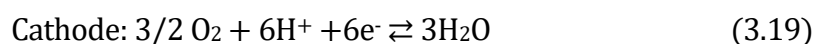
Direct Methanol (DM) Fuel Cells: Distinguished from other fuel cells that typically require to be fed pure hydrogen or reform hydrogen internally from hydrogen-rich fuels such as ethanol, Direct Methanol Fuel Cells operate by utilizing a fuel that consists of pure methanol usually mixed with water and supplied directly to the anode. They produce small amounts of power, from 1mW to 1kW at an efficiency of around 25% and temperatures not higher than 90°C, but they excel in being operational for extended periods of time without stopping.

Just like PEMFCs, DMFCs use a polymer electrolyte with Nafion being the most usual choice and Platinum catalysts positioned at each electrode.

In the presence of water, liquid methanol undergoes oxidation at the anode to produce protons, electrons, and CO₂. Subsequently, the free electrons travel through the external circuit and the protons pass through the electrolyte to reconnect again at the cathode. At the cathode site, they are reduced and produce water. The fundamental electrochemical reactions occurring within a DMFC are described by the following equations:



CH₃OH is broken down to CO that bonds with the Oxygen atom of water to produce Carbon dioxide (CO₂), while the four Hydrogen atoms from the methanol along with the two from water lose their electrons and become H⁺ ions.



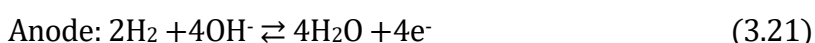
O₂ particles from the atmosphere come in contact with the H⁺ ions that traversed through the electrolyte and the free electrons that come from the external circuit and are bonded to produce molecules of water.

One of the main advantages of DMFCs is that they are easier to supply with fuel compared to other types of cells, as their fuel, methanol is liquid and can be transported and put in storage using existing infrastructure. Furthermore, Methanol exhibits a higher energy density than Hydrogen, but still, its power density is less than that of conventional fuels, like gasoline or diesel.

Primarily, DMFCs are employed to power portable electronic devices like laptops and cell phones, offering a practical and versatile solution for on-the-go energy needs.

Alkaline Fuel Cells (AFCs): AFCs were one of the first types of fuel cells ever developed and have been frequently used by NASA in space missions to produce both electricity and water aboard spacecrafts. Traditionally, an electrolyte of potassium hydroxide dissolved in water is being used, though many modern iterations of AFCs in recent years use a polymer membrane. The latter share many similarities with conventional PEMFCs, with the difference of the electrolyte being alkaline in AFCs and acidic in PEMFCs. A notable characteristic of Alkaline fuel cells is the speed of their reactions. Electrochemical reactions in AFCs happen rapidly, significantly improving performance. The efficiency of AFCs is observed to be above 60% on space applications. They operate in temperatures varying from 50°C up to 100°C while exhibiting the highest productivity at 80°C. AFCs are able to produce up to a few hundred kW.

The reactions happening inside a fuel cell of this type are characterized by the following equations:



Here, Oxygen molecules react with water in the cathode, and hydroxyl ions are produced that then travel through the electrolyte to the anode. There, they react with Hydrogen and produce molecules of water along with electrons. Those electrons are then transferred to the cathode through the external circuit, generating an electrical current.

AFCs, like all other types of fuel cells, face some challenges. One of the most significant ones is that this cell type's performance can be greatly reduced by CO poisoning, so much in fact that even the small amounts of CO in the atmospheric air can hinder their performance because of carbonate formatting on the electrolyte. AFCs that operate by using a liquid electrolyte can be used in recirculating mode, allowing electrolyte regeneration to ease the effects of carbonate formation, but this mode comes with its own problems, such as shunt currents. Some other problems include the difficulty managing differential pressures, their wettability, and increased corrosion of components.

Alkaline Membrane Fuel Cells (AMFCs) have made great strides in tackling those problems faced by traditional AFCs, but still remain susceptible to CO poisoning, while still falling behind PEMFCs in terms of performance and durability. AMFCs are to be used for applications that require a power output on the scale of Watts to kW. The problems that occur with AMFCs are membrane conductivity durability, operation at high temperatures, susceptibility to CO poisoning, water management, power density, and slow anode electrocatalysis.

Phosphoric Acid Fuel Cells (PAFCs): Phosphoric Acid Fuel Cells are characterized by their use of an electrolyte made by a liquid phosphoric acid contained in a Teflon-bonded silicon carbide matrix. The electrodes are porous carbon and within them, a platinum catalyst is contained. PAFCs are among the most mature and commercially available fuel cell types as it was one of the first to be available for commercial usage. They are primarily used for stationary applications but are sometimes used on large vehicles like buses and they can produce around 100MW of power.

One of the significant advantages of PAFCs is their ability to tolerate impurities in Hydrogen derived from reformed hydrocarbons better than PEMFCs. However, PAFCs are still overly sensitive to Sulfur contaminants. Their efficiency is around 40% when producing electricity alone, but it reaches more than 85% when used in combined heat and power (CHP) applications, where both electricity and heat are co-generated.

Type	Common Electrolyte	Temperature	Power Output	Electrical Efficiency	Application	Advantages	Challenges
PEM	Perfluoro-sulfonic acid	<120°C	<1 kW–500 kW	60% direct H ₂ , 40% reformed fuel	Backup power, transportation	High durability, low temperature, quick start-up,	Expensive catalysts, needs pure fuel
AFC	Aqueous potassium hydroxide soaked in a porous matrix, or alkaline polymer membrane	<100°C	1–100 kW	60%	Military, space, transportation	Cheap components, low temperature, quick start-up	Needs pure fuel, water management issues
PAFC	Phosphoric acid soaked in a porous matrix or imbibed in a polymer membrane	150°–200°C	5–400 kW, 100 MW module (liquid PAFC) <10 kW (polymer membrane)	40%	Distributed generation	Suitable for CHP, can handle fuel impurities	Expensive catalysts, long start-up time, sulfur sensitivity
MCFC	Molten lithium, sodium, and/or potassium carbonates, soaked in a porous matrix	600°–700°C	300 kW–100 MW	50%	Electric utility, distributed generation	Efficient, fuel flexible, suitable for CHP, hybrid/gas turbine cycle	Unreliable in high temperatures, long start-up time, net particularly power dense
SOFC	Yttria stabilized zirconia	500°–1,000°C	1 kW–100MW	60%	Auxiliary power, electric utility, distributed generation	Efficient, fuel flexible, solid electrolyte, suitable for CHP, hybrid/gas turbine cycle	High temperature corrosion and breakdown of cell component, long start-up time, limited number of lifecycles

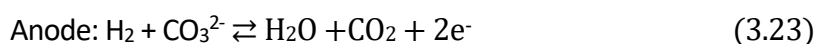
Table 3.1 Categorization of fuel cells [4].

Despite these advantages, Phosphoric Acid Fuel Cells come with their own set of challenges. PAFCs are not very efficient compared to other types of fuel cells, with their efficiency being just above that of internal combustion engines, thus being much heavier and occupying a much larger space than other types of more efficient fuel cells for the same power output. Needing a larger amount of platinum as a catalyst also makes them far more expensive than other types of fuel cells. Finally, the high concentration of phosphoric acid (H₃PO₄) in the electrolyte means that they need a heating auxiliary system to maintain the temperature above 40°C to make sure there is no freezing when the cell is switched off. PAFCs continue to be a viable option for specific applications, particularly where high-efficiency heat and power generation is needed.

Molten Carbonate Fuel Cells (MCFCs): Molten Carbonate Fuel Cells operate at elevated temperatures, around 650°C, utilizing an electrolyte of molten carbonate salts contained in a porous, chemically inert ceramic lithium aluminum oxide matrix. These fuel cells are capable of producing up to 100MW with a median efficiency of 55%. These high operating temperatures mean that less valuable metals can be used as catalysts to speed up the reactions, thus reducing the cost of the cell. The electrochemical reactions taking place in an MCFC are described by the following equations:



Molecules of Oxygen from the air come in contact with CO₂ at the cathode, along with free electrons, and produce CO₃²⁻ that then travels to the anode through the electrolyte.



At the anode, Hydrogen particles interact with CO₃²⁻ ions, and bond to produce water molecules as well as Carbon dioxide and release free electrons.

The high operating temperatures remove the need for an external reformer to convert hydrocarbons to hydrogen, further reducing their cost. At these temperatures, methane and other light hydrocarbons are reformed within the cell by a process that happens at the anode, called internal reforming characterized by the following equations:



This capability of internal reforming fuels allows MCFCs to use various fuel types without any significant issues, enhancing their flexibility and cost-effectiveness.

One of the main advantages of Molten Carbonate Fuel Cells is their efficiency. MCFCs are very efficient, as when coupled with a turbine, their efficiency can be as high as 65%, while if the waste heat is appropriately used, they can reach up to more than 85%.

Molten Carbonate FCs have their own set of disadvantages, namely poor durability, long startup time, and their emissions. Their main challenge is durability, with their current lifetime being around 40.000 hours, or approximately five years, as their lifespan is limited because the high operating temperatures combined with the corrosive electrolyte accelerate component breakdown. Efforts are focused on developing materials more resistant to corrosion, as well as new fuel cell designs that could end up doubling their current lifespan. Another disadvantage is, that operating at such high temperatures means that they need more time to start operation, as they need to reach the target temperature first. Furthermore, with CO₂ being one of their products they are not environmentally friendly like the other types of cells.

Currently, MCFCs are being developed for military and industrial applications, as well as for usage in natural gas and coal power plants. Their ability to reform various hydrocarbon fuels and their high efficiency make them highly suitable for large-scale power generation.

Solid Oxide Fuel Cells (SOFC): Solid Electrolyte Fuel Cells utilize an electrolyte made of a hard non-porous ceramic compound. Working at temperatures ranging from 600°C up to 1.000°C, SOFCs do not require precious metals like Platinum to be used as electrolytes, so Nickel or Nickel oxides are used in their stead. Furthermore, due to high operating temperatures, there is also no need for an external reformer, since the fuels are reformed internally, which allows a wide variety of fuels to be used and greatly reduces cost.

Unlike the types of fuel cells mentioned above, SOFCs are not only invulnerable to CO poisoning, but in fact, they can even use it as fuel. This flexibility also allows the usage of natural gas, biogas, and gasses made from the reformation of coal. Furthermore, they are highly resistant to sulfur, being able to handle a concentration of sulfur that is orders of magnitude higher than what other types are able to, without damage. SOFCs are able to produce power that ranges from tens up to a few hundred MW. In terms of efficiency, they are around 60% efficient when converting fuel to electricity but rise to approximately 85% when the waste heat is captured and used.

SOFCs utilize an electrolyte made of a solid ceramic membrane with a thickness of 0.1mm that carries Oxygen ions (O_2^-) and is usually either Nafion or Yttria (Y_2O_3) stabilized Zirconia (ZrO_2) symbolized as YSZ. The cathode is composed of ceramics with a perovskite structure like Lanthanum Strontium Manganite or Lanthanum Calcium Manganite. These materials facilitate the reduction of Oxygen molecules, allowing them to accept electrons and form Oxygen ions (O^{2-}) that then migrate to the anode through the electrolyte. The anode is a composite material made of a combination of YSZ and Nickel oxides.

Like every other type, though, SOFCs have their own drawbacks. Working at such elevated temperatures creates a need for thermal shielding to protect people around them and retain heat, making them unsuitable for transportation applications, and increasing the start-up time greatly. Another drawback is material durability. At those high operating temperatures and corrosive environment, a threat is posed to the integrity of the system, and its durability is lowered. Consequently, efforts are being made to develop materials that can manage these temperatures but at the same time do not heighten the overall cost. Presently, the potential of SOFCs that operate at lower temperatures, around 700°C, is being explored, something that will bring down costs while at the same time creating fewer issues with durability. Unfortunately, those lower-temperature SOFCs are shown to be less efficient than higher-

temperature ones and the materials needed for them to operate better are still under development. Finally, even though there is no need for expensive materials to be used as catalysts, the overall cost of an SOFC system still remains high as the high temperatures in which it operates create a need for advanced materials to be used along with thermal management systems.

Reversible Fuel Cells: Just like all fuel cells, Reversible Fuel Cells use Hydrogen and Oxygen to produce electricity. What makes them unique is the ability to use electricity to electrolyze water and create Hydrogen and Oxygen, which essentially means that we have both a fuel cell and an electrolyzer in a single device. This function can play a critical role in energy storage, particularly for energy created from renewable sources, such as wind and solar, in the form of hydrogen, helping to further the expansion of technologies that utilize renewable power sources. Power production from these sources is intermittent, meaning that power is only generated when conditions are favorable (e.g. when the wind is blowing, or the sun is shining). By using surplus electricity to produce electricity by means of electrolysis, Reversible Fuel Cells enable the storage of this excess energy. The stored Hydrogen can then be used to generate electricity during periods of low renewable energy production, ensuring a continuous and reliable power supply.

Reversible Fuel Cells help promote sustainability, as by storing renewable energy they promote the use of clean energy sources and reduce reliance on fossil fuels. Their efficiency is high in both modes, either when they produce Hydrogen or electricity, contributing to overall energy system efficiency and they are versatile as they provide both energy production and energy storage in the same device.

On the other hand, Reversible Fuel Cells have some drawbacks. First and foremost is their integration into the existing energy system, as it would require careful planning and adaptation of the system to the newly added cells. Then comes the cost of this whole operation together with the high cost of the cells themselves as the materials and systems needed for efficient operation are costly. Finally, the repeated switching between fuel cell and electrolyzer modes has a heavy toll on the system and can impact and limit the durability and lifespan of the cell. Reversible Fuel Cells can mostly be utilized in the renewable energy production sector as they address one of the main problems of this sector. With their addition to a power-producing system, the variability in power production due to environmental conditions can be eliminated, thus making the energy grid more reliable, and stable, and helping further the adoption of renewable energy technologies. This information about each type is also summarized in **Table 3.1**

Since PEM fuel cells are the most preferable to be used in the automotive, the focus of this study will be placed on those. From now on, when the term “fuel cell” is mentioned it refers only to PEMFCs unless specifically stated otherwise.

CHAPTER 4

ADVANCES OF FUEL CELLS IN THE AUTOMOBILE INDUSTRY

4.1 Commercial advancements

Fuel cell technology has existed for more than a hundred years now, but it is still unknown to lots of people and commercially available to even less, particularly in the context of fuel cell electric vehicles (FCEVs). Despite the long history and many potential benefits of fuel cells, widespread adoption has been slow. However, some car manufacturers are trying to take advantage of that emerging market by being the first to introduce FCEVs to consumers, like Toyota and Honda for example, who have made great investments in research and development to improve fuel cell technology, reduce costs, and increase the efficiency and range of their vehicles. They are also working on developing the necessary hydrogen refueling infrastructure to support their vehicles. Additionally, governments around the world are developing strategies to promote the adoption of fuel cell technology and FCEVs to the general public.

In **Figure 4.1** we can see the powertrain of a standard FCEV. The heart of the vehicle is its fuel cell stack as they are the main power producer for the whole system, responsible for its operation. Next are the Hydrogen tanks that are used to store and supply the fuel needed for the fuel cells to produce power and make the car run or perform other stationary functions. Auxiliary energy units also play a vital role in the powertrain. Such auxiliary systems include supercapacitors or batteries that are used to store excess energy generated in various ways, like energy recuperation while breaking, or provide an extra boost to the system like they do in Hybrid Electric Vehicles (HEVs). The electronic drive & control plays a critical role in managing the flow of current from the fuel cell stacks and auxiliary energy units to the electric motors that give motion to the wheels or other electric devices like the pump of the air-conditioning unit of the car. Finally, the DC-DC converter is a vital component that converts the voltage of the system to meet the specific needs of various consumers. This converter ensures that power is properly distributed to the various subsystems depending on the specific needs at each given moment. For example, when reducing

speed, the power generated by braking must be appropriately conditioned to reach a specific voltage and be stored in the auxiliary units and the opposite must be done when accelerating.

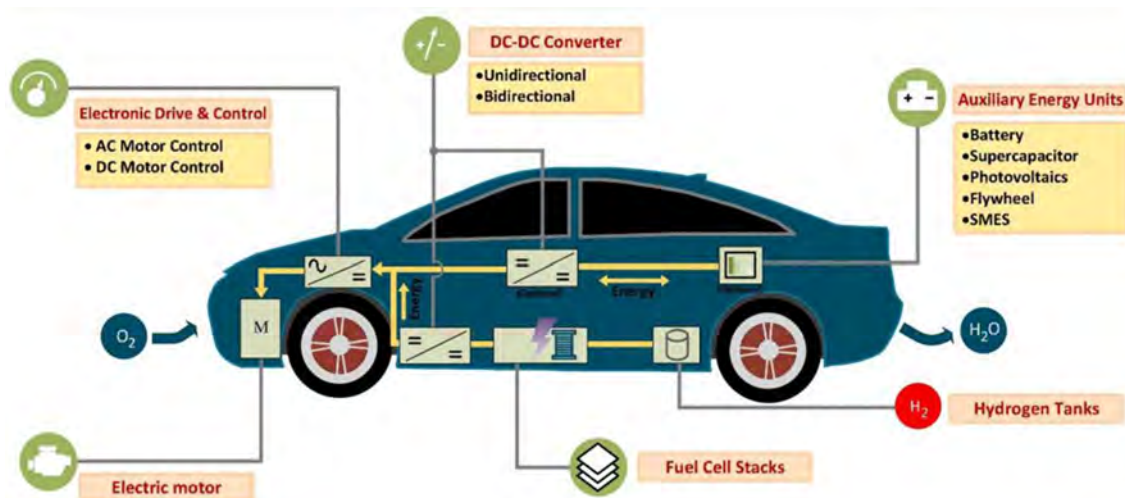


Figure 4.1: FCEV powertrain [53].

4.1.1 Commercial availability

In the realm of fuel cell-powered vehicles, commercial sales remain limited, with only a handful of countries offering them to consumers, and even within these countries, supporting infrastructure is scarce. Let us take the case of FCX Clarity as an example. The FCX Clarity is primarily sold in China and only started being commercially available in California a decade after its initial development highlighting the slow spread of fuel cell technology in automobiles around the globe. Similarly, the Toyota Mirai and Hyundai ix 35 are more common, as common as FCEVs get, but only 15 countries worldwide have stations where these vehicles can be refueled [51]. But before coming to commercial availability, we have to talk about this technology's adoption by the general public and industry.

During the initial stages of adoption, fuel cells are more easily implemented in heavy-duty trucks and buses, where their implementation is not only feasible but also highly demanded. Heavy trucks are vastly used in commerce worldwide with China alone witnessing the sale of approximately 1.2 million annually both in 2019 and 2020. However, the extensive usage of these vehicles that feature big and internal combustion engines that consume lots of fuel, comes at a significant environmental cost. Transportation accounts for more than 50% of all petroleum consumption in China, while truck emissions are responsible for 74 percent of total NO_x emissions and more than 52.4% of overall particle emissions. Given those environmental challenges, it is clear then that there is a pressing need for them to be replaced with a cleaner, more efficient alternative, such as fuel cell-

powered trucks. In spite of this imperative need, the widespread adoption of fuel cell technology in heavy-duty trucks still remains in its infant stages. Currently, they need to be technologically upgraded in order to meet operational requirements and regulatory standards. At the present time, fuel cell-powered vehicles are primarily utilized in small-scale pilot applications, often in urban settings where specific routes and easier refueling options ease their deployment. These applications commonly include city buses and logistic vehicles, where the controlled operational environment and predictable fuel needs align well with the capabilities of fuel cell technology and supporting infrastructure [7].

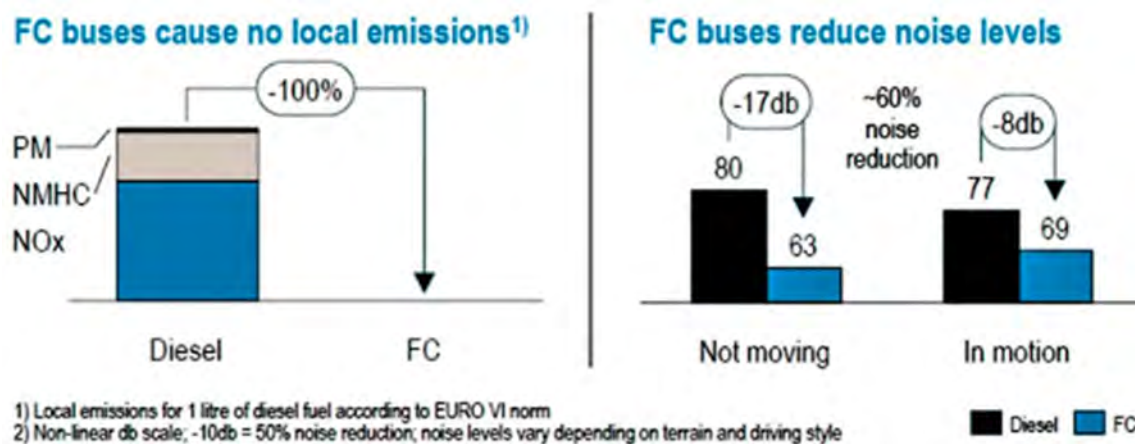


Figure 4.2: Comparison of the noise levels and emissions of diesel and FC buses [51].

As far as 2021 significant application breakthroughs with FC technology in trucks remained elusive. However, noteworthy progress was made in China. In 2017 the China National Heavy Duty Truck Co., Ltd. launched its FC heavy-duty truck, the first of its kind in all of China, designed for port freight applications, marking a significant milestone for the industry. Following this, 2019 also witnessed the release of X5000, a 49-tonne truck by Shaanxi Heavy Duty Truck Co., Ltd., powered by Weichai Power Co., Ltd.'s fuel cell system. Operating primarily in Hebei, China, this vehicle has gathered substantial attention due to its innovative technology and potential for revolutionizing freight transport [8]. Another great platform to display the usefulness of FCs is buses, particularly their benefits in terms of cleanliness and quiet operation. As illustrated in **Figure 4.2**, FC buses significantly outperform their diesel-consuming counterparts in terms of noise levels and polluting emissions. FC buses operate with 60% less noise and produce zero emissions, highlighting the critical need for investment in this technology. A study conducted in 2017 made a comparison between four Hydrogen-powered buses and four diesel ones. This study found that despite the higher cost of fuel per kilometer for FC buses, their fuel economy was more than 80% better than that of diesel-powered ones [51]. It is worth considering that the production price for Hydrogen fuel at the time was \$9.10 per kilogram, but this number is expected to decrease with further investment in

the Hydrogen industry [51]. This study underscores the long-term economic and environmental advantages of adopting FC technology in public transportation.

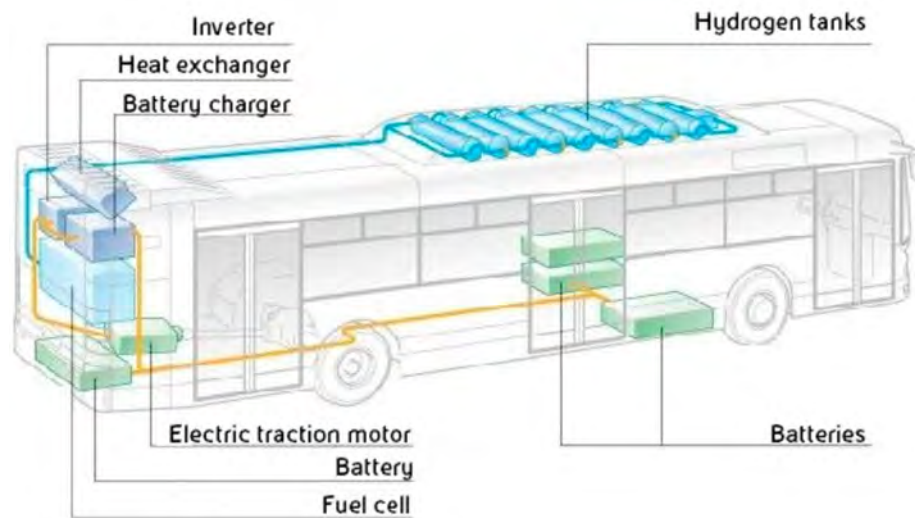


Figure 4.3: Schematics of a standard fuel cell-powered bus [51].

Due to their fixed routes and running schedules, it is easier to develop the necessary infrastructure to support buses powered by hydrogen. This logistical predictability simplifies the establishment of refueling stations and maintenance facilities. Additionally, the larger size of busses provides ample space for fuel storage, typically done in tanks mounted on the roof. The schematics of an FCEB are illustrated in **Figure 4.3**. When comparing this layout to that of an internal combustion engine-powered bus, the main difference is the placement of the fuel tanks. In Fuel Cell Electric Buses (FCEBs) these tanks are strategically located in a more secure place on the roof, protecting them from hazards that can be found on the surface of the road. Moreover, the placement of fuel tanks on the roof also optimizes the distribution of weight along the whole body of the vehicle adding stability and bettering the handling of the vehicle. This design also allows for easy access during maintenance and refueling operations, reducing downtime and improving operational efficiency. The average FC stack used in these buses produces up to 200kW which is sufficient for vehicles that are typically around 9 meters in length.

With more than 60 hydrogen-powered buses operating in Europe for longer than 15 years under the Clean Urban Transport for Europe (CUTE) program, China has also recognized their potential. Thus, with support from the Chinese new energy vehicle program, around 30 hydrogen buses have been in operation since 2017. Notably, the largest hydrogen bus project around the world has been underway in Foshan, with an annual production capacity of 5000 FC electric buses (FCEBs) [2]. On the other side of the Atlantic, about 50 such buses are operational in California, including one on the campus of the

University of California. As an achievement of this technology, these buses have met the U.S. Department of Energy's durability target of 25,000 hours under real-world driving conditions. The visibility of buses in daily transit makes them an excellent platform for promoting hydrogen technology, as people get to experience first-hand their many advantages, clearly showing the support of public authorities for this transition [9]. More than 10 companies, including some notable ones like Volvo and Daimler-Chrysler, have already developed their own FCEB models [51]. The active involvement of these prominent manufacturers highlights the industry's commitment to advancing hydrogen fuel cell technology as a suitable alternative for public transportation.

One great example of a project aspiring to integrate FCEBs is London's "Transport of London" initiative. The city has allocated 13.8€ million to buy twenty double-decker buses, that will conduct routes inside the city's "Ultra Low Emission Zone", and at the same time build the necessary infrastructure to support them [51]. This significant investment highlights London's commitment to more sustainable and emission-free urban transport. Liverpool has set an ambitious goal to be carbon-neutral by 2040. As part of this objective, the city has come to an agreement with Bus Alliance to commence trials with new fuel cell buses in 2020. This move positions Liverpool at the forefront of innovation in public transportation. Another joint venture between Frundenberg Sealing Technologies and Flixbus (one of Europe's largest operators for long-distance bus travel) is also making strides in the development of hydrogen-powered buses in the next few years. This project is also expected to be funded by the German government through the "National Innovation Program – Hydrogen and Fuel Cell Technology". Although the exact number of buses is not yet known, some of the technical characteristics have been revealed. The upcoming buses are expected to have a minimum driving range of 500km, require less than 20 minutes for refueling, and offer an acceleration performance that will be at least the same as the acceleration performance of currently used diesel buses [51].

In **Figure 4.4** an initial design of Flixbus' new hydrogen fuel cell buses is depicted. The layout shows a well-thought-out arrangement aimed at maximizing efficiency, safety, and performance. The fuel cell module is located in the back right next to the fuel cell control module and its associated thermal management system. This placement ensures efficient operation and at the same time aids in effective thermal regulation that is crucial for maintaining optimal performance and longevity of the system. The electric motor is strategically located just behind the back wheels where it can directly drive them minimizing energy loss through transmission.

This configuration is typical in modern electric vehicles as it simplifies the drivetrain and increases overall efficiency. Towards the front, beneath the baggage compartment are the auxiliary batteries. These batteries play a critical role in storing excess energy, which can be generated through regenerative braking or during periods of low demand. They also regulate the flow of current throughout the whole system, ensuring a stable and reliable power supply for all the bus's electrical components. Unlike the conventional ICE buses, in Flixbus' design, the fuel tanks are placed on the roof, offering a significant advantage. This placement is particularly beneficial for buses that are used for long-distance travel, as it is more likely that they have to deal with some type of road hazard like rocks on the road surface for example. By positioning the fuel tanks on the roof, they are less susceptible to ground-level impacts or a collision with another car. This design choice enhances the safety of the vehicle by reducing the risk of fuel leaks, which can occur if the tanks are punctured.

What about commercial cars though? The commercial car market presents the greatest potential for the widespread adoption of fuel cell technology. As the global number of cars continues to rise [51], automotive manufacturers are increasingly keen to secure a share of this growing market. Honda, a pioneer in fuel cell technology, started research as early as the late 1980s and made history when it was the first manufacturer to release an FCEV back in 2002 [52]. Other major players are also deeply invested in the development and production of FCEVs. General Motors (GM) and DaimlerChrysler have entered into a collaboration to produce fuel cell vehicles, leveraging their combined expertise to accelerate advancements in this field. Meanwhile, Toyota and Hyundai, are releasing their own innovative prototypes, the Mirai and NEXO respectively, both with a driving range averaging 360 miles. These models really showcase the strides made towards making FCEVs more practical and commercially viable. In addition to these notable examples, China's automotive market is also moving forward with the Saic MAXUS FCV80 [8], [9], [12]. This vehicle represents China's commitment to advancing fuel cell technology and integrating it into its automotive offerings. The competitive landscape for FCEVs is becoming increasingly vibrant, with multiple companies striving to refine and perfect their technologies. As these vehicles become more accessible and infrastructure for refueling with hydrogen continuously expands, the commercial viability of FCEVs is expected to grow substantially, potentially transforming the automotive industry.

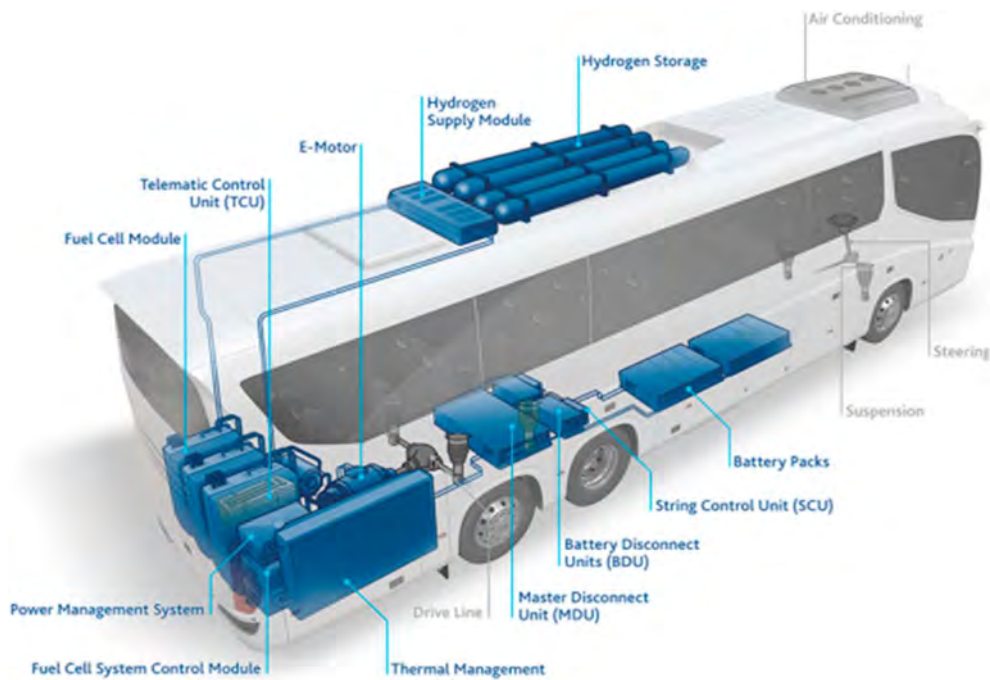


Figure 4.4: Flixbus FC composition [51].

A survey prior to 2021 among around 1000 senior executives from automotive original equipment manufacturers (OEMs) revealed that almost 80 percent of them agree that PEMFC EVs represent the future of passenger vehicles. This consensus among industry leaders underscores the significant potential seen in fuel cell technology for transforming the automotive sector. Studies conducted in South Korea further increase this optimism, highlighting the substantial role that FCEVs can play in reducing pollution. In turn, the promise of cleaner air and reduced greenhouse gas emissions is a compelling factor that could drive the market success of FCEVs, especially in regions grappling with severe air quality issues. Furthermore, in Spain, the feasibility of transitioning to hydrogen-powered vehicles has also been studied. It was estimated that an initial investment of 25 million euros would be enough to set up the infrastructure needed to render hydrogen competitive with gasoline. This estimate takes into account the supportive government policies that are crucial for fostering the growth of hydrogen infrastructure and making it economically viable [2],[6]. These insights reflect a growing recognition of the benefits and potential of fuel cell technology in the automotive industry. The combination of industry support, environmental benefits, and feasible economic investments presents FCEVs as a promising solution for the future of the transportation industry.

For a technology taking its first steps in the commercial world, sales of fuel cell electric vehicles are showing promising growth. In Japan, more than 3,521 FCEVs and 22 fuel cell-powered

buses were sold by September 2019. By September 2020 a number greater than 8,573 FCEVs were sold or leased in the U.S. [9]. Additionally, more than 30,000 fuel cell forklifts were operational in the U.S. as of 2019. In China, more than 3,000 commercial FCEVs were sold from 2017 to 2019. Hyundai reported impressive sales of 10,000 NEXO models in Korea since its debut in 2018 [9]. What seems like an obstacle to more widespread sales is the inflated cost of fuel cell electric vehicles. For example, the Toyota Mirai cost 58,000 dollars before 2020, a price that dropped to 49,500\$ in 2021. Similarly, the price for a single FCEB in 2016 ranged from 1 to 1.5 million dollars, more than two times the DOE's target value of 600,000\$ [9]. However, the Total Cost of Ownership (TCO) is expected to drop below that of battery electric vehicles by 2026 and will be less than that of ICEVs by 2027. Overall, Deloitte estimates that both TCO and the purchase of FCEV's cost will be halved in the next ten years. Government subsidies play a crucial role in accelerating the adoption of fuel cell electric vehicles and supporting the development of hydrogen infrastructure. In China, these subsidies are structured to address various aspects of the FCEV ecosystem, aiming to make FCEVs more affordable and attractive to consumers. These subsidies are typically implemented as follows:

- Subsidies on each FCEV sold. The government provides subsidies to consumers for each FCEV sold, effectively lowering the price of purchase of these vehicles., incentivizing consumers to choose FCEVs over more traditional ICEVs. These subsidies are expected to last until 2025, though experts anticipate that they will be gradually reduced as the years pass and the market matures leading to production costs to decrease. This gradual reduction encourages OEMs to improve efficiency and lower production costs.
- Subsidies on the construction of Hydrogen Fueling Stations (HFS). These subsidies are allocated to support the construction and expansion of hydrogen fueling infrastructure. This is essential for creating an extended network of refueling stations, making hydrogen refueling more accessible to FCEV owners and consequently making FCEVs more practical to use. This investment gives private companies the incentive to invest in building and operating hydrogen stations.
- Subsidies on the cost of hydrogen refueling. To further incentivize FCEV usage, subsidies are provided to reduce the cost of hydrogen refueling. This helps bring down the Overall Cost of Ownership, making FCEVs competitive with conventional ICE vehicles. The ultimate goal of these subsidies will be to bring the cost per 100km on par or even less than that of ICE vehicles [11].

Overall, government subsidies play a significant role in driving FCEV adoption forward by addressing cost barriers and supporting infrastructure development. These subsidies create a favorable environment for FCEV manufacturers, hydrogen infrastructure developers, and consumers, thus helping the transition of the automotive industry to a sustainable and low-emission transportation future.

It would be interesting now to take a look at some of the upcoming FCEV concepts, or at vehicles that are already in circulation.

4.1.1.1 Overall comparison

Table 4.1 provides valuable insights into the characteristics and performance of a select few FCEVs that are currently available in the market. Toyota was the first to enter the market of FCEVs with Mirai and only two years later Honda followed with the Clarity Fuel Cell, with Hyundai making its entry to the market only in 2018. It is also noteworthy that even though Europe is home to some of the first and most prestigious car manufacturers all three of the above-mentioned OEMs are from Asia. All three cars have similar weight, a little less than 1.9 tons with Mirai being the lightest at 1850kg. The power density of all three cars is a bit over 3kW/L of fuel with Honda's model taking the lead by a small margin of 0.02kW/L more than its competitors. Their acceleration time from stationary to 100km/h is a little less than 10s. The Toyota Mirai achieves the fastest acceleration at 9s while Hyundai's Nexo is the slowest at 9.5s. All vehicles store fuel at a pressure of 70 MPa, ensuring efficient storage and utilization of hydrogen. The Nexo has a distinctive fuel capacity, as it can store 1 kg of fuel more than its adversaries. Despite its smaller fuel capacity, The Honda Clarity Fuel Cell can drive for a longer distance of 598km, under ideal conditions, compared to the 595km of the Nexo, while the Toyota Mirai demonstrates the lowest fuel consumption of the three, consuming only 0.76kg of fuel per 100km.

FCEV	Launch date	Mass (kg)	Fuel cell/ motor power (kW)	Power density (kW/L)	Acceleration time (0-100km/h)(s)	Fuel tank capacity (kg)	Fuel Pressure (MPa) (gas)	Driving range (km)	Fuel consumption (kg fuel/100km)	Drag coefficient
Toyota Mirai	2014	1850	90/114	3.10	9	5.0	70	312-502	0.76	0.29
Hyundai Nexo	2018	1873	95/120	3.10	9.5	6.33	70	370-595	0.94	0.329
Honda Clarity Fuel Cell	2016	1875	103/130	3.12	9.2	5.46	70	366-598	0.97	0.32

Table 4.1: Comparison of Toyota Mirai, Hyundai Nexo, and Honda Clarity Fuel Cell [51].

4.1.1.2 Audi concept

The Audi h-tron quattro concept is a representation of Audi's advancements in fuel cell technology, showcasing a fuel cell stack that is the company's fifth generation of improvement on its fuel cell stacks [51]. This advanced stack consists of 330 cells that are operated from 220V to 280V at a temperature a little below 100°C. It is complemented by a 1.8kW battery stack, weighing 60kg, and a 100kW motor, creating a powerful and efficient system. The hydrogen fuel required for this system is stored in tanks at a pressure of 700 bar, enabling quick refueling times of only four minutes and offering an impressive range of approximately 600km. The vehicle's energy efficiency is further enhanced through regenerative braking, which recovers energy during deceleration [51]. Below, in **Figure 4.5** the basic components of the car can be seen, highlighting the innovative distribution of a fuel cell system. The fuel tanks are placed in the back of the car, while the traction battery is located under the floor, optimizing weight distribution and lowering the car's center of gravity for improved handling. The fuel cell stack and DC/DC converter are located below the hood and the two motors can be found between the front and back wheels each, ensuring balanced power delivery and traction. This thoughtful arrangement of components comes in contrast with the traditional layout of ICE vehicles, where major components are typically concentrated in a single area, whether it is a front-, mid- or rear-engine layout. In the h-tron quattro, the components are evenly distributed throughout the vehicle, providing several advantages. Not only is the weight distribution and handling improved, but space is also freed within the vehicle that can be used for reinforcing the exterior, enhancing overall safety. The Balance Of Plant components, such as the air compressor and hydrogen recirculation blower are crucial for maintaining optimal operating conditions. These components ensure that the system operates efficiently and reliably under varying driving conditions by conditioning the air pressure, humidity, and temperature of the fuel cell stack.

4.1.1.3 Toyota Mirai

The Mirai is Toyota's entry into the market for passenger FCEVs. It is a mid-sized car first revealed to the public at the 2014 Los Angeles Auto Show by Toyota and since then it has seen big success in Japan, the U.S., and Europe [53]. The main system that runs the car consists of the fuel cell stack, which is called the Toyota FC Stack (TFCS) [53] and is combined with a battery as well as the supporting components such as the power control unit that dictates the proper use of power by each component, and it can be seen on **Figure 4.7**. The layout indicates better weight distribution and a lower gravity center that leads to a better and safer driving experience that cannot be achieved in ICE vehicles due to space limitations. The FC stack

with BOP components can be seen in **Figure 4.6**. The same stack can be seen in the center of the car floor highlighting again how much smaller and compact it is compared to an internal combustion engine.

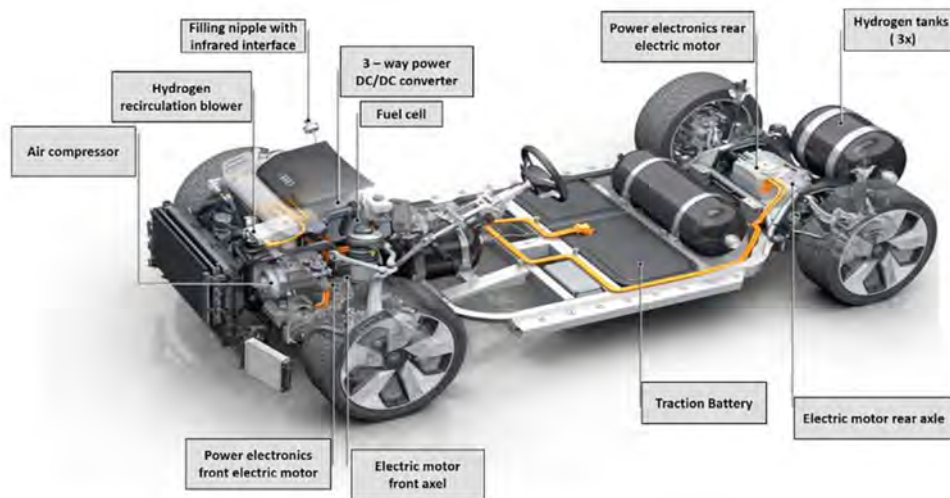


Figure 4.5: Basic components of the Audi concept car [51]

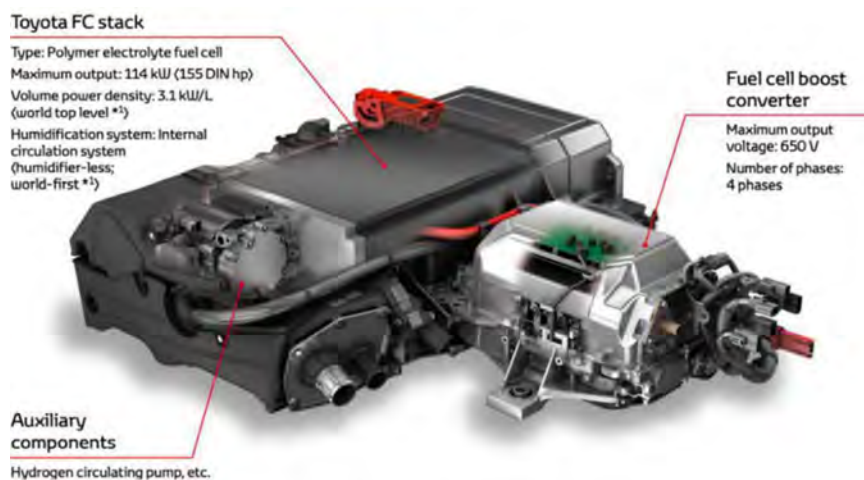


Figure 4.6 Toyota Mirai FC stack with BOP components [9]

The TFCS itself is a marvel of efficiency and power. It is capable of producing up to 114 kW of power, with a power density of 3.1 kW per liter of fuel, and boasts a fuel consumption rate of just 0.8kg of fuel per 100km. These attributes earned the Mirai the title of the most fuel-efficient FCEV in 2016 by the US Environmental Protection Agency [53]. The Mirai delivers a good performance with an acceleration from 0 to 100 km/h in ten seconds and a driving range of 644km it can satisfy every need of somebody who drives it daily [53].

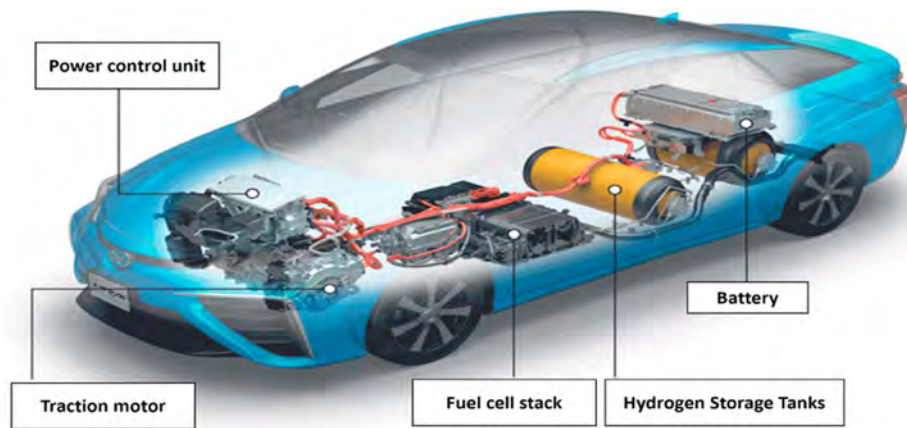


Figure 4.7: Components of the Toyota Mirai [51]

Commercially, Toyota Mirai has already proven itself, as more than 10 thousand units have been manufactured. However, that number would be even greater according to the Japanese OEM's plans, if the slow growth rate of the supporting infrastructure were not limiting the number of FCEVs that can be supported for use on the road [51], [53]. Another significant barrier to the wider adoption is the Mirai's prohibiting price starting at \$59,500. This cost is considerably higher than that of other Hybrid or electric models made by Toyota, which can deter potential buyers [51]. This elevated price is inevitable due to the fact that all components used in the Mirai are fitting for high-end vehicles, while some more exotic materials are used, like hydrogen tanks made of carbon-fiber for example, that are essential for ensuring safety and performance but add significantly to the overall cost [51].



Figure 4.8: Fuel tanks of a Hyundai Nexo [51]

The name "Mirai" which translates to "future" in Japanese, encapsulated Toyota's vision for the future of the automotive industry. This entry into the market signifies the OEM's dedication to advancing FCEV technology and promoting a future characterized by environmental friendliness and zero emissions.

4.1.1.4 Hyundai 2019 Nexo

The Hyundai Nexo is an SUV of medium size and was first introduced to the market in 2018, representing the manufacturer's Eco Series[53]. It represents Hyundai's commitment to sustainable and environmentally friendly transportation solutions. The Nexo's design was modeled after the "sandwich" principle, which maximizes space utilization. This innovative layout ensures ample room for both the passengers on board and the propulsion mechanism, which is able to deliver up to 120kW of power [53]. The efficient use of space in the Nexo not only enhances passenger comfort but also contributes to the vehicle's overall performance and handling. However, Hyundai, like other FCEV manufacturers faces significant challenges related to the limited hydrogen refueling infrastructure. To address this issue, Hyundai has focused on enhancing the Nexo's fuel storage capacity. A unique selling proposition for the Hyundai 2019 Nexo is its high fuel storage capacity, achieved through a triple-tank system, as seen in **Figure 4.8**. This system has a combined storage volume of 59L and can carry up to 6.4 kg of Hydrogen (in comparison, the Toyota Mirai can carry only four kg of fuel), offering a driving range of 612 km, making it one of the most efficient FCEVs on the market in terms of fuel storage and range [51]. Fuel storage is a well-known issue that plagues the FCEV industry. Hydrogen has to either be liquified under very low temperatures or be stored under very high pressure. Both these methods require lots of energy to either freeze or pressurize it and also create the need for special tanks to store it as they have to either maintain ultra-freezing temperatures or be able to tolerate extreme pressures. Furthermore, storing so much hydrogen in a tank placed inside, or most usually under the car poses a safety concern as a hydrogen leak in case of a crash or damage to the tank can be disastrous. While Nexo's triple-tank system is a notable advancement, it also highlights the inefficiencies currently inherent in hydrogen storage solutions. For comparison, an ICE vehicle would require only a single fuel tank to store the same volume of energy and would occupy much less space while also costing a lot less to manufacture. This underscores the need for continued research and development in hydrogen storage technology to make FCEVs more competitive with traditional ICE vehicles.

4.1.1.5 Honda Clarity Fuel Cell

Marketing of the sedan FCX Clarity began in 2008 and Clarity Fuel Cell entered the market in March 2016. Honda Clarity Fuel cell has an impressive power density of 3.1 kW/L of fuel, which is 60% more dense than previously used cells [52]. This significant improvement in power density

allows for the cell stack to be smaller in size, reducing its size by 33% and utilizing 30% fewer cells [52]. This compact design not only makes the stack more resilient to collisions but also results in a powertrain comprised of the FC stack, the fuel supply system, the air supply system, the motor, and the voltage converter, whose whole size is comparable to only on V6 engine [52]. The advantage here is that this compatibility means that the powertrain can fit in an already existing five-seat car chassis, facilitating integration into traditional vehicle designs without major alterations. The Clarity Fuel Cell's fuel storage system, which maintains a pressure of 70 MPa, promises an impressive driving range of almost 750 kilometers with refueling taking around three minutes [52].

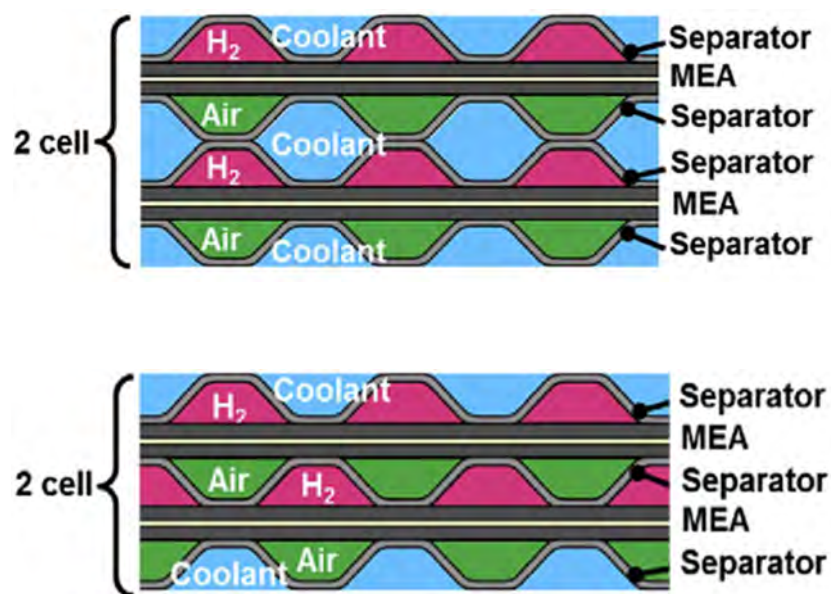


Figure 4.9: (Above) a normal fuel cell with two separators, (below) the cell used in Clarity Fuel Cell [52]

Honda has also innovated in the design of the fuel cells themselves. In other stacks, a cell consists of the MEA and two adjacent separators. Honda in its effort to decrease size used a wave-like configuration which eliminated the need for the fourth separator while simultaneously increasing the gas diffusion performance of gas channels [52]. This configuration as well as a normal one can be seen in **Figure 4.9**. It is noteworthy that other than saving space, the design of the fuel cell for Clarity Fuel Cell features interlocking flow channels that add to robustness. Moreover, the usage of fewer separators brings the stack's price a little down and the elimination of the extra coolant flow channel reduces the load of the coolant pump and the overall cooling system, allowing for more energy to be conserved and used to drive the car further or power other devices onboard. For the Clarity Fuel Cell, a thinner MEA is also used, and a humidity feedback control combined

with counter flows of water and hydrogen, and air achieves an optimized water content control. The gas channels can therefore be reduced by 20% in depth, reaching down to 1mm [52].

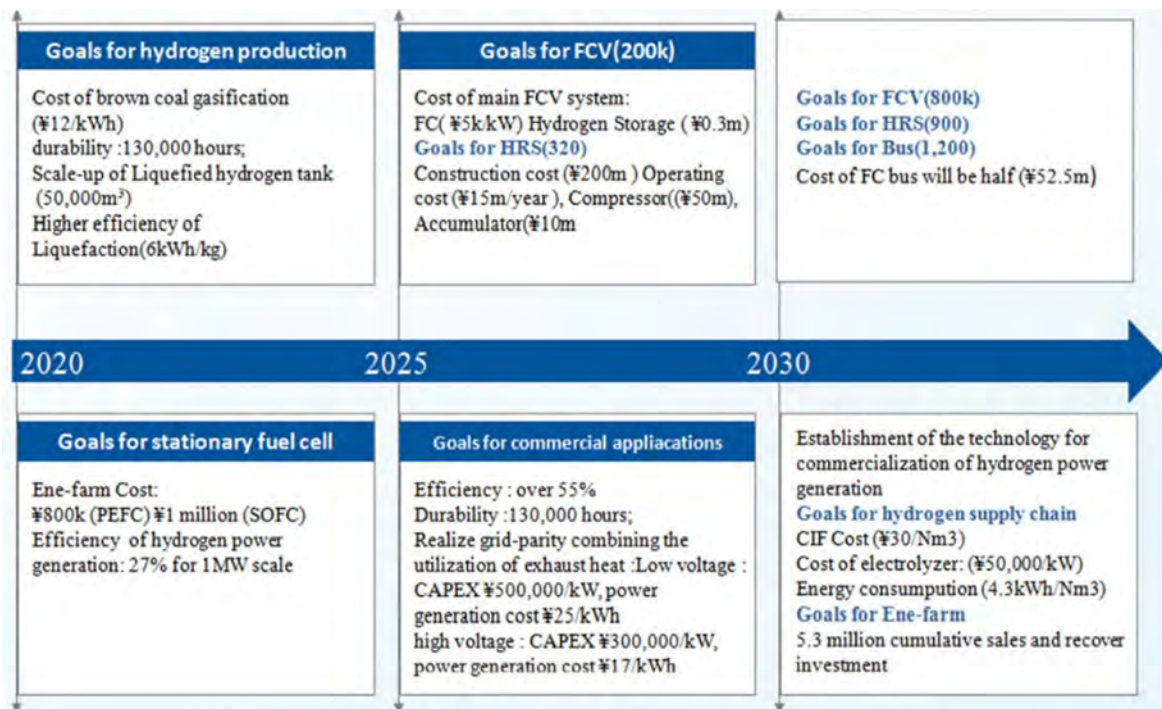


Figure 4.10: Strategy of Japan for fuel cells and hydrogen 2020-2030 [2].

4.1.2 Future commercialization plans

Future decarbonization of the power sector would require the advancement of technologies to capture, store, and utilize carbon. Additionally, there will need to be an increase in the usage of renewable energy. Fuel cell technology can play a crucial role in this transition by providing a clean and efficient alternative to traditional combustion-based energy generation [51]. As mentioned before, many governments around the globe have seen the potential benefits of FCEVs and are actively planning to promote their use. Various plans and roadmaps have been made for the upcoming years, aiming to boost research on new, more durable, and more affordable fuel cell technologies. These initiatives also aim to commercially promote FCEVs, thus accelerating the transition to a more sustainable energy future.

By early 2021 more than 30 countries had announced their hydrogen roadmaps, collectively committing a sum greater than \$70 billion in investments. Estimates predict a fleet of 350 million units of electric means of transportation in the near future, most of which will be passenger cars and half of them will be powered by Hydrogen fuel cells [51]. Below, are the roadmaps and strategies already made by countries that are actively developing and selling or utilizing FCEVs either as a way to commute or for vehicles used in the industry, like forklifts. Japan, being the birthplace of

manufacturers like Toyota and Honda, is one of the leading nations in the adoption of FCEVs. Japan boasts a production capacity exceeding 10,000 units of Toyota Mirai and has established more than 100 Hydrogen Fueling Stations (HFS) [2]. The Japanese government had also aimed to have more than 100 FCEBs operational by the 2020 Olympics, highlighting its commitment to hydrogen-powered transportation. The Japanese Ministry of Economy, Trade, and Industry (METI) provided a sum of 260 million dollars in 2018, aimed at research and development of hydrogen and fuel cell technology. Japan's dedication to hydrogen energy is evident in its national strategy, which was formalized in the "Basic Strategy of Hydrogen Energy" released in 2017. This strategy describes a planned, step-by-step course of action for hydrogen production, FCEVs, and general FC commercial applications from 2020 to 2030.

As seen in **Figure 4.10**, Japan's hydrogen strategy for 2020 aimed to promote hydrogen production and stationary fuel cells by setting specific targets. These targets included reducing the cost of coal gasification (12yen/kWh), scaling up the liquefied hydrogen tanks (50.000m³), and setting the target for the efficiency of power generation by Hydrogen to 27% for 1MW plants. By establishing these goals, Japan intended to create a foundation for widespread hydrogen adoption and lay the groundwork for future advancements in fuel cell technology. Looking ahead to 2025, the strategy aims at significant cost reductions and infrastructure expansion. It is expected that the cost of FC-powered vehicle systems will drop to 5 yen/kW. Furthermore, there are plans for 300 HRSs to be established, with their construction costing around 200 million Yen. These stations will be crucial in supporting the growing fleet of fuel cell electric vehicles. The efficiency of commercial applications is expected to be above the 55% threshold, while the power generation cost for these applications is anticipated to decrease to 17 Yen/ kWh. These improvements aim to make hydrogen more economically competitive with conventional energy sources, facilitating broader adoption in various sectors. The plans for 2030 are even more ambitious, predicting substantial growth in the FCEV fleet. By this time, it is expected that there will be 800 thousand FCEVs and 1200 FCBs roaming the roads. This greatly expanded fleet will be supported by a network of 900 Hydrogen Refueling Stations. This extensive infrastructure will be essential in ensuring the practicality and convenience of hydrogen-powered transportation. The plan for 2030 reflects Japan's commitment to making hydrogen a central component of its energy and transportation systems as it will be in the heart of the country's overall plan to have an economy fully independent from fossil fuels.

South Korea has outlined a comprehensive plan for hydrogen development and adoption, shown in **Figure 4.11**. The country's roadmap is ambitious, focusing on achieving significant milestones in hydrogen production, fuel cell technology, and vehicle deployment over the next two decades. According to the plan, by 2025 it is expected that Korea will achieve up to 78% efficiency in hydrogen reforming processes at medium-sized plants, with the capability to export hydrogen. This efficiency target will be extended to smaller reforming plants by 2030. Korea's strategy also includes substantial investments in renewable energy to support these hydrogen production goals. From 2020 through 2028, the emphasis will also be on developing water electrolysis methods to produce hydrogen and ensuring that fuel cell systems achieve high efficiency and stability by 2030. In terms of fuel cell electric vehicles, The Republic of Korea has set ambitious production targets. By 2022, the country aims to produce 35,000 units of FCEVs and have 65,000 such vehicles in use. The plan for 2025 is even more ambitious, targeting a production of 100,000 units with 40 thousand of them intended for export. This scale of production is expected to bring the cost of FCEV production down to a level rivaling that of ICE vehicles. By 2030 it is expected that one in every three cars sold inside Korea's borders will be powered by hydrogen. To support this transition, the South Korean government is providing substantial subsidies for the purchase of hydrogen vehicles. In 2020, the government allocated 34,715 dollars for every hydrogen vehicle purchase, alongside nearly 35 thousand dollars on Research and Development in hydrogen-related technologies. These subsidies are designed to decrease gradually as the cost of hydrogen vehicles drops due to increased production and technological advancements. Looking further ahead, the government's plans for 2040 include the deployment of 80 thousand hydrogen taxis, 40 thousand FCEBs, and 30.000 hydrogen-powered trucks [17]. Overall, South Korea's hydrogen strategy demonstrates a strong commitment to advancing hydrogen technology and integrating it into the nation's energy and transportation system. By setting clear targets and providing financial support, the government is fostering an environment that promotes innovation and growth in the hydrogen sector.

In the private sector, The Hyundai Motors Group and its affiliates are at the forefront of South Korea's hydrogen initiatives. Since launching its first hydrogen car in 2013, the Tucson iX35, Hyundai has made great strides in the hydrogen vehicle market. Despite initially trailing behind Toyota, Hyundai has emerged as the global leader in FCEV sales. In 2018 Hyundai announced its ambitious "FCEV Vision 2030" plan, which outlines its strategy for research, development, and facility expansion in the hydrogen sector. Under this vision, Hyundai intends to invest \$6.7 billion, with the ultimate goal being the production of 700 thousand FC systems annually by 2032. Of these,

500,000 will be dedicated to powering hydrogen vehicles. Hyundai's sales target under the "FCEV Vision 2030" is equally ambitious. The company aims to sell 40,000 FCEVs in 2022, ramping up to 130,000 units in 2025, and almost four times that, at 500,000 units by 2030. These targets reflect the giant OEM's confidence in the growing demand for hydrogen vehicles and its readiness to meet this demand with substantial production capacity. In 2019 Hyundai took a significant step towards expanding its hydrogen vehicles operations by partnering with H2 Energy in Switzerland and forming a joint venture. This collaboration led to the formation of Hyundai Hydrogen Mobility, aimed at providing 1600 heavy-duty trucks for leasing by 2025. This initiative not only focuses on the Swiss market but also plans to extend its reach beyond the borders of Switzerland. Furthermore, Hyundai announced plans to begin production in China by 2023 [17]. This move is part of a broader strategy to tap into the rapidly growing Chinese market, which is seen as a critical region for the expansion of hydrogen vehicle technology. Both those moves show Hyundai's goals in establishing a production presence in Europe and China, leveraging local market dynamics, and strengthening its position as a global leader in the FCEV market.

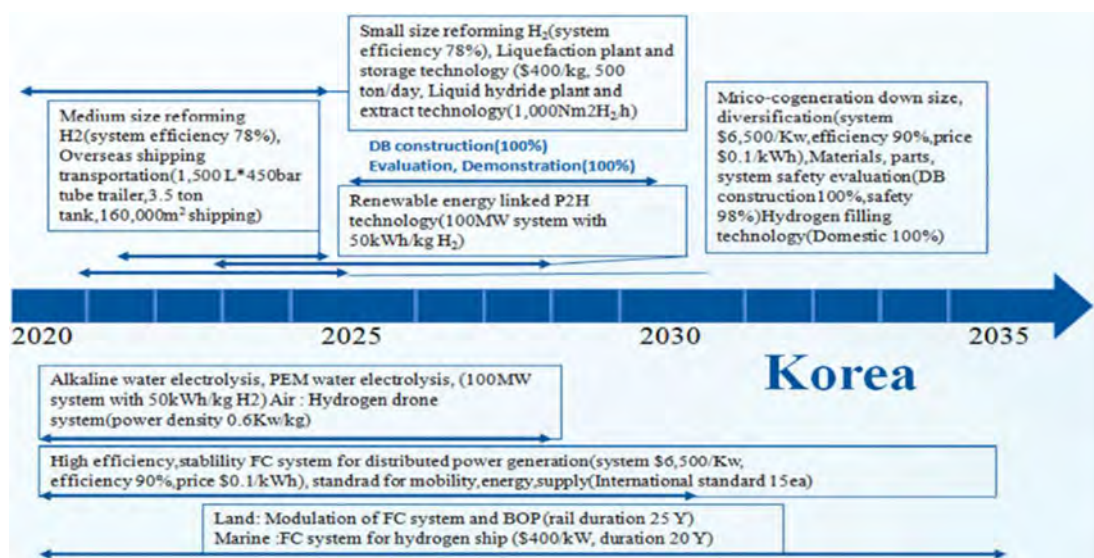


Figure 4.11: Strategy of South Korea for hydrogen and fuel cells from 2020 to 2035 [2].

Developing nations can significantly benefit from the usage of hydrogen energy as it provides them with a sustainable and safe energy source essential for their growth and environmental goals. One prominent example is China, which has an ambitious goal of achieving carbon neutrality by 2060. In line with this objective, the Chinese government unveiled the "New Energy Automobile Industry Development Plan (2021-2035)" in November 2020, stating that a sustained effort over the next 15 years will result in the full commercialization of fuel cell vehicles and the continuous development of hydrogen supply infrastructure.

The “New Energy Automobile Industry Development Plan” is depicted in **Figure 4.12** and consists of three five-year parts. The first and most expensive part (2020-2025) is projected to cost 1.5 million Chinese Yuan (CNY).

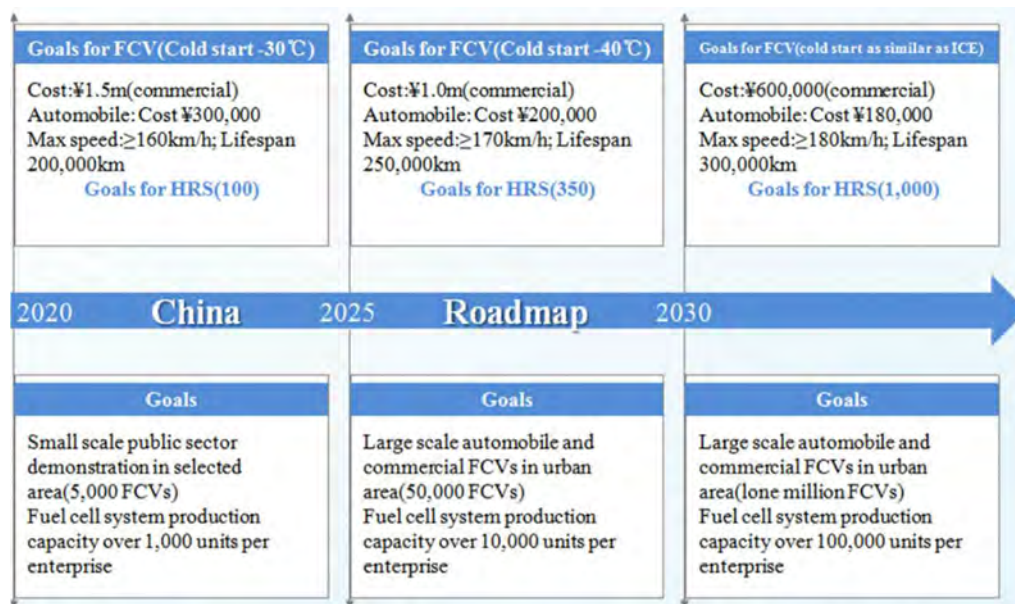


Figure 4.12: China’s roadmap for hydrogen and FCEVs 2020-2030 [2]

This part of the plan will see a small-scale private sector demonstration of around 5 thousand FCEVs operating in a selected area. These early models are expected to cost approximately 300.000 CNY each and will feature a cold start capability down to minus 30°C, albeit with performance metrics that are somewhat lower compared to ICE vehicles. The second part (2025-2030) will see an increase in the overall FCEV fleet accompanied by lower costs and better performance. The cost of this step is expected to be one million CNY and will bring the cost for a single FCEV car down to 200 thousand CNY by increasing the output capacity of enterprises to 10,000 FCEV units each. At that time the top speed of FCEVs is targeted to be at least 170 km/h with a lifespan of 250,000km. The total fleet of FCEVs in urban areas is targeted to grow to 50 thousand units, supported by a network of 350 Hydrogen Fueling Stations, which is 250 more than the initial 100 developed in the first part of the plan. As the plan progresses to its last phase, significant advancements are anticipated. The cost is expected to decrease to 180 thousand CNY per car, making them economically viable, and will see FCEVs be used on a large scale in urban areas. The cars are expected to endure more than 300 thousand kilometers, be able to reach speeds greater than 180 km/h, and have a cold start ability similar to that of ICEs. Refueling infrastructure is critical to support the growing hydrogen vehicle fleet and so the network that will already be developed from the previous stages of the plan is expected to expand to one thousand fueling stations by 2030. Additionally, the “Energy Saving and New Energy

Vehicle Technology Roadmap 2.0” released by the China Society of Automotive Engineers in 2020 complements this development plan. It sets forth its own optimistic targets, proposing to have 100,000 FCEVs in operation by 2025 and scaling up to 1.000.000 by 2035 [15].

Overall, China has taken many steps to reduce its carbon footprint which is much bigger than that of many other countries combined, mainly due to the country’s heavy industry and currently more relaxed regulations concerning emissions. These steps include a transition to renewable energy sources, better regulation, and research in new more efficient, and clean technologies. The commitment of China to integrating hydrogen energy into its transportation sector is clearly highlighted by these plans. This integration will help the nation achieve a more sustainable and eco-friendly future by achieving the goal of carbon neutrality by 2060.

The United States is also making significant strides in the development and deployment of hydrogen energy infrastructure and the adoption of fuel cell electric vehicles. In March 2021, the H2@scale1 initiative was announced, focusing on developing infrastructure for hydrogen production, transportation, and utilization technologies. As illustrated in **Figure 4.13**, the U.S. Department of Energy (DOE) has set targets for the future aiming to integrate hydrogen power into its transportation network. These targets include a decrease in the cost of automotive fuel cell stacks from more than 120US\$/ kW down to a point where the whole FCEV will cost approximately \$72 thousand by 2030, while by 2050 there is no specific estimate, but expectations are that a single car will cost less than \$60 thousand [51].

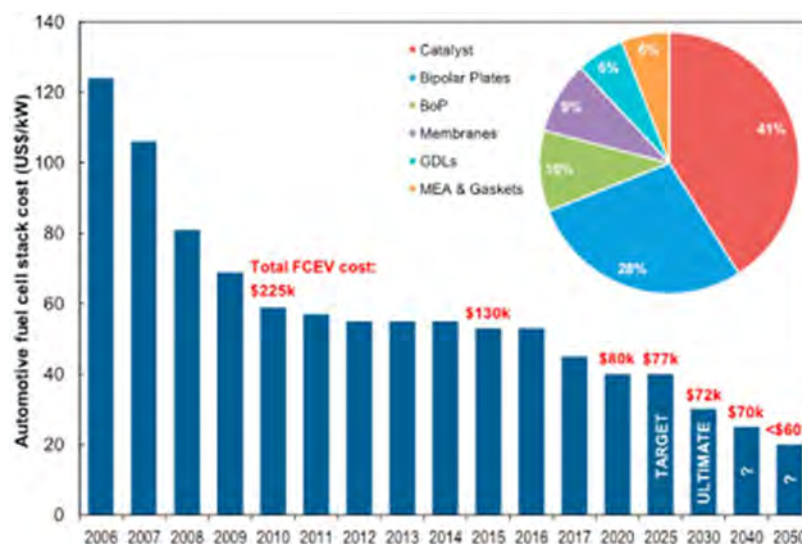


Figure 4.13: Projected system cost by US DOE [51].

In **Figure 4.13** is also evident that the highest cost of the system is found at the catalyst, which makes up 41% of the total expense, due to precious metals that are needed for its production. This cost reduction will make FCEVs more competitive in the automotive market. To further support the development of

infrastructure, H2USA, a public-private partnership with FCEV OEMs has been established. This partnership is aimed at further expanding the availability of hydrogen options to the public. Their plan consists of four steps. The first one is the introduction phase, planned to continue up to 2023. This phase focuses on introducing fuel cell technologies to the public, raising awareness, and demonstrating the viability of hydrogen as a transportation fuel. The expansion Phase, from 2023 to 2025, will witness large-scale production and demand of hydrogen that will bring its cost down. Another goal of this phase is to have 125,000 material-handling FCEVs and 150,000 light and heavy-duty trucks in operation, supported by a network of 1,000 Hydrogen Fueling Stations that will be developed.

The third step is from 2026 to 2030 and it is the growth phase. By 2030 17 million metric tons of hydrogen will be consumed annually as fuel, used at 4,300 stations that will refuel the aimed 1.2 million FCEVs that will be sold next to 300 thousand material handling hydrogen vehicles. The production volume is aimed to be 1.5 million vehicles per year and attracted investments will be around \$8 billion. Finally, the maturation phase starts in 2030 and aims for the future. By 2050 it is anticipated that almost one in three cars on the road will run on hydrogen, reflecting the full integration of hydrogen vehicles into the mainstream automotive market. The State of California is leading the way in this transition. With a target of establishing 1,000 HFS by 2030, California aims to provide adequate refueling options for the one million fuel cell vehicles that are planned to roam the streets. The state's proactive "planning-subsidiary evaluation" system has turned it into the most active and demonstrative market for FC development and deployment in the US. [18].

Finally, Europe, a continent with a rich history of car manufacturers, could not have been absent from the adoption of FCEVs by its many automotive manufacturers and car enthusiasts. Not surprisingly, the highest number of projects is found there. The European Union's commitment to the adoption of hydrogen energy is encapsulated in its Hydrogen Strategy, which is a detailed plan aimed at developing renewable hydrogen across the member states. As seen in **Figure 4.14**, by the year 2030, one-third of H₂ production is expected to be almost zero-emission and produced in industrial applications, including refineries and ammonia production. At the same time, renewable hydrogen generation plants will be developed, while surplus energy produced from renewable sources will also be directly converted into hydrogen and stored for future use. The strategy also has a target of 3700 Hydrogen Fueling Stations that will supply fuel for a fleet consisting of more than 3.5 million hydrogen-powered passenger cars. The commercial transportation sector will also see significant changes, with plans to replace 570 diesel trains with hydrogen-powered ones and to

use 45,000 fuel cell trucks for the transport of both goods and people. Finally, a most optimistic target for 2030 is to have 500,000 fuel cell light commercial vehicles operating across all of Europe.



Figure 4.14: Roadmap for Europe by the year 2030

To achieve these ambitious goals, the EU has outlined specific targets. More specifically, by 2025, Europe must have over 747 HFSs and 291 FCEBs in operation. Additionally, individual countries have set their own benchmarks. For instance, by the year 2025, France aims to have 5,000 passenger vehicles, 200 buses and trucks, and 100 HFSs. By 2030, these numbers are expected to increase dramatically, with France targeting 20,000 to 50,000 passenger cars, 800 to 2,000 trucks, and around 700 Hydrogen Fueling Stations. The Netherlands is also setting its own goals. This country is aiming for 15,000 cars and 3,000 heavy-duty trucks by 2025, with an ultimate target of 300,000 cars by 2030. Spain plans for 5,000 to 7,000 light and heavy-duty vehicles and 100 to 150 HFSs by 2030, while Switzerland targets 1,600 heavy-duty trucks. Italy's ambitious targets include nearly 300,000 passenger cars, 3,600 buses, and 200 thousand trucks by 2030. Finally, on the same time horizon, the UK aims for 1.6 million hydrogen-powered cars to roam its roads [12].

The Fuel Cells and Hydrogen Joint Undertaking (FCH JU) issued the "Hydrogen Map Europe" setting some more long-term targets for hydrogen mobility. According to this map, by 2030, the goal is for one out of twelve passenger vehicles, one out of twelve light commercial vehicles, and 45 thousand trucks and buses to be powered by fuel cells. By 2040 these ratios are expected to improve significantly, with one out of seven passenger vehicles and one out of five light

commercial vehicles being hydrogen-powered, and 450,000 trucks and busses supported by 15,000 HFSs. The ambitious scenario for 2050 envisions 45 million passenger cars, 6,5 million light commercial vehicles, and 250 thousand buses powered by fuel cells. In the less ambitious scenario, which is characterized by inconsistent or inadequate efforts by the member states, there will be only 700,000 light commercial vehicles, 60,000 buses, 380,000 trucks, and 1.4 million passenger cars by 2050. This scenario though, fails to achieve the EU's climate targets [16]. These plans and roadmaps show that just like the rest of the countries that were discussed, the European Union envisions a green and eco-friendly future that is characterized by emission-free transportation and is dedicated to achieving it.

Hydrogen technology is gaining global traction, with more than 30 countries setting targets for its development and application. The Hydrogen Council's 2017 report projected that by 2030 there will be between 10 to 15 million hydrogen-powered cars and 500 thousand hydrogen trucks globally. This projection includes significant adoption rates in regions such as Germany, Japan, South Korea, and California, where one out of every twelve cars is expected to be hydrogen-powered. Looking further ahead to 2050, the estimates become even more ambitious. The Hydrogen Council anticipates that more than 400 million FCEVs will be used commercially. This fleet will also include another 15-20 million trucks and 5 million buses, all powered by fuel cells [16].

Summing up, **Figure 4.15** gives a rough estimation of the numbers and types (both current and expected) of FCEVs in four key regions, namely the US, Europe, Japan, and China.

						
		Passenger vehicles	Buses and coaches	Trucks**	Forklifts	Refueling stations
US	Current	7,271 ⁴⁴	35 active, 39 in development	prototype test	>30,000 ³³⁵	~42 online ³⁷
	Target		5,300,000 FCEVs on US roads by 2030 ³³⁷		300,000 by 2030 ³³⁷	7,100 by 2030 ³³⁷
China	Current	0	2,000+ ^{64 83 84 85}	1,500+ ⁹⁴	2	23 ⁸⁹
	Target	3,000 by 2020 ⁸⁷ 1,000,000 by 2030 ³³⁶	11,600 commercial vehicles by 2020 ⁸⁷			100 by 2020 500 by 2030
Europe	Current	~1000+ ⁴²	~76 ^{42 73 86}	~100 ⁸⁸	~300 ⁴²	~152 ⁷¹
	Target	3,700,000 by 2030 ³⁴	45,000 fuel cell trucks and buses by 2030 ³⁴			~3,700 by 2030 ³⁴
Japan	Current	3,219 ⁴⁴	18	N/A	160	127; 10 in progress
	Target	40,000 by 2020	100 by 2020		500 by 2020	160 by 2020
		200,000 by 2025	1,200 by 2030 ²⁴		10,000 by 2030 ²⁴	900 by 2030 ²⁴
		800,000 by 2030 ²⁴				

Figure 4.15: Global targets for the number of FC vehicles

The United States has taken the lead in the number of buses and coaches powered by FCs and is expecting to keep that lead until 2030 with an estimated fleet of just under 5.5 million FCEBs. Europe follows with an expected fleet of 3.7 million FCEBs by the same year. In terms of supporting infrastructure though, the U.S. has fallen behind both Europe and Japan who have 152 and 127 HFSs in operation compared to 42 in the United States. In the future though this picture is expected to change, with the U.S. planning to construct and operate 7,100 Hydrogen Fueling Stations by 2030 while Europe is expected to have only 3,700 and Japan a meager 900 followed by China's 500 HFSs.

4.2 Technological advancements

Although fuel cells have been in use for many decades now there are still improvements needed to render them competitive against internal combustion engines. One of the primary challenges is the cost of manufacturing fuel cells. Currently, fuel cells are more expensive to produce than ICEs, largely due to the materials and technologies involved in their construction. Reducing their cost is essential in making them a viable alternative for mainstream automotive use. Another critical area for improvement is the power output of fuel cells. FCs must be able to provide adequate power to propel a car efficiently under various driving conditions while also providing power to other onboard systems like the air-conditioning for example. This includes that fuel cells can perform well during a cold start, which is crucial, especially in countries with colder climates, where the ability of a vehicle to start reliably in low temperatures is essential for consumer acceptance. Moreover, the longevity of fuel cells needs to match or exceed that of ICEs. Consumers rely on their cars and expect them to have a long operational life with minimal performance degradation over time. Fuel consumption is another area where fuel cells need to improve. Efficient fuel usage is necessary, particularly considering that the infrastructure for hydrogen refueling is still underdeveloped [5].

4.2.1 Cost reduction

Battery Electric Vehicles are currently in a rapidly growing phase and tend to dominate the market for passenger cars in the upcoming years especially for short distances and urban use [51]. BEVs offer a convenient solution for city driving, with their increasing range and the expanding network of charging stations making them an attractive option for many consumers. FCEVs consequently aim to take the lead in long-distance and/or heavy transport applications, areas that are still predominantly served by internal combustion engine vehicles. FCEVs offer several advantages in these sectors, including faster refueling times and greater range compared to BEVs. However, ICE vehicles currently have a significant cost advantage, being almost 50% cheaper than

FCEVs [51]. To effectively compete with ICEVs and be a viable option in the market, the cost of fuel cells used in the automotive industry needs to be significantly reduced. According to the Carbon Trust, the cost must drop down to \$36 per kilowatt (kW).

Manufacturing costs can be easily categorized as 1) capital cost of manufacturing equipment, 2) raw material and component cost, and 3) labor cost. In the initial stages of production, all three categories contribute significantly to the overall cost. However, as production scales up and moves towards mass production, economies of scale come into play. The capital and labor costs of a product tend to decrease as the production process becomes more efficient and streamlined [5]. What remains as a significant cost factor, even in mass production, is the cost of raw materials and components. Efforts to reduce the cost of materials and components can involve several strategies. One approach is to invest in research and development to find cheaper alternative materials or more efficient ways to utilize the existing materials. Another approach is to improve supply chain management to reduce the cost of sourcing and transporting materials. Additionally, fostering partnerships with suppliers to secure better pricing through bulk purchasing agreements can also help lower costs.

In an FCEV the most important and also costly component is the fuel cell stack which can amount to half the cost of the whole system., The high cost of the stack is primarily due to the catalyst, which makes up more than half of the stack's cost, or 25% of the cost of the whole vehicle [14]. **Figure 4.16.** illustrates the cost distribution for each part of an 80 kW proton exchange membrane fuel cell stack. This figure provides a detailed breakdown of the costs associated with the various components that make up the fuel cell stack system, highlighting the significant contribution of the catalyst to the overall cost.

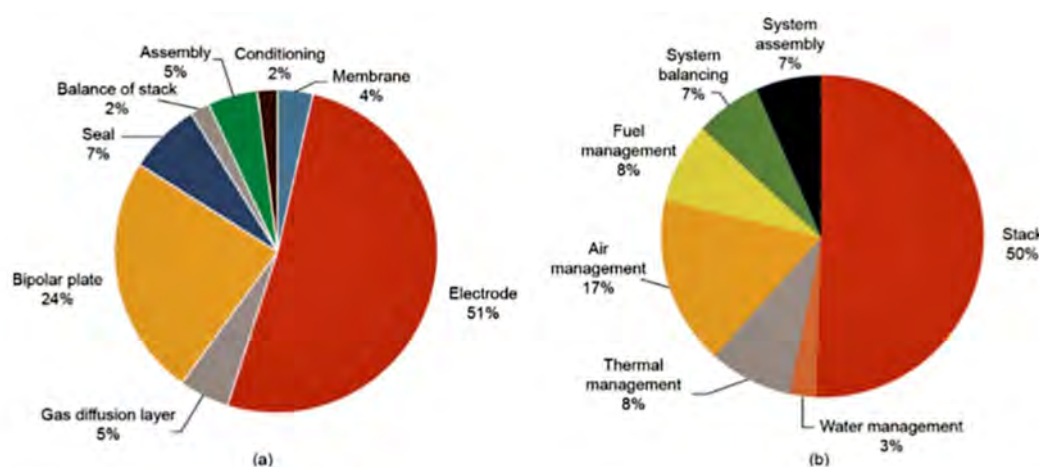


Figure 4.16: Component cost percentage of an 80kW FC stack. Stack cost (left) and stack system cost (right) [51].

The material best suited for catalysts is Platinum (Pt), but it is also precious and rare with its global reserves being estimated at >30.000 tons. Most of this Platinum is being mined in Russia, South Africa, and North America at a rate of 250 tons/year [5]. Given its limited availability and high cost, it is evident, that the usage of Pt must be limited, while the Pt used must be recycled. In the Toyota Mirai, before 2020, the Pt loading was 0.05 mg/cm² in the anode and 0.315 mg/cm² in the cathode, while the target set by the US Department of Energy (DOE) is 0.1 mg/cm² for cars and less than 0.2mg/cm² for heavy-duty vehicles such as trucks by 2025, as well as a durability of over 25,000 hours [9].

One of the most straightforward ways to reduce Pt usage is to alloy it with other less precious metals. Common examples are alloys with Chromium (Cr) and Ruthenium (Ru) [5]. Alloys like Pt-Ni/C and Pt-Co/C can significantly enhance the catalytic process, increasing its efficiency by ten to one hundred times compared to commercial Pt catalysts in rotating disk electrodes (RDEs). However, a notable limitation is that those RDE tests cannot be conducted on fuel cells, and furthermore, all these Pt alloys tend to disintegrate quickly, reducing their effectiveness and longevity of the cell [9]. An innovative approach to mitigate this issue is the use of core-shell catalysts. In this design, a nanoscopic core made of a cheap metal such as Copper (Cu) is covered by a shell of Pt. This configuration reduces the amount of Platinum required while maintaining high catalytic activity. It is worth mentioning that at Brown University scientists managed to create a catalyst using this method, that greatly outperforms traditional Pt ones and managed to hit the targets set by the U.S. DOE [13].

The Department of Energy has established strict performance criteria for fuel cell catalysts to promote the viability and longevity of FCEVs. Specifically, the DOE set the bar at an initial activity of 0.44 amps/mg of Pt and a retention of at least 0.26 amps/mg of Pt after 30,000 voltage cycles (roughly the equivalent of five years of fuel cell usage). A breakthrough new catalyst managed to achieve an initial 0.56 amps/mg of Pt and a final of 0.45 amps/mg Pt after 30,000 cycles, surpassing both these benchmarks. This impressive performance is mainly due to its innovative design, which involves alloying Pt with Cobalt in nanoparticles with a specialized structure critical for the catalyst's performance and durability. These special nanoparticles have an outer layer of pure Platinum coating over a core consisting of layers of Platinum and Cobalt atoms alternatively [13]. By optimizing the atomic arrangement, the catalyst can effectively utilize the properties of both Platinum and Cobalt, leading to a significant improvement in both efficiency and durability.

Another promising alternative for reducing the cost and thus increasing sustainability is the development of catalysts that do not rely on PGMs (Platinum Group Members). Such catalysts use

cheaper, more abundant, and highly active metals such as Fe, Ni, Co, and Mn. Highly advanced PGM-free catalysts are almost equal to Pt/C catalysts in terms of performance. A notable example of such a catalyst comes from researchers from the University of California- Riverside. This new catalyst consists of porous carbon nanofibers embedded with another reactive metal that is more abundant and less expensive than Pt, like Co. This type of catalyst shows great potential for use with PEMFCs [13]. Another innovative approach is FlowCath[®], a technology patented by ACAL Energy. This system is noteworthy as it works in an innovative way, deviating from the conventional design. Instead of the usual Pt-based cathode, it utilizes a liquid polymer solution. In the anode, things work as usual, but then the electrons and protons are absorbed by a continuous flow of a solution containing redox catalyst systems and go from the stack to an external regeneration vessel. This design offers several advantages. Not only does it reduce the usage of Pt by eliminating the need for a platinum-based cathode, but also simplifies the system by decreasing the number of components as it avoids the need for water recovery and fuel humidification. Finally, it increases durability because there is no solid cathode, which degrades and limits the system's lifespan. The projected cost for a fuel cell working according to this patent is 36\$/kW [5].

Finally, another patent that greatly reduces cost was developed by Imperial College & University College London. A unique design called "Flexi-Planar" represents another significant deviation from conventional fuel cell architectures. The Flexi-Planar design consists of layers of laminated, printed circuit board materials, stacked on top of each other. This layered structure creates channels for air, water, and fuel throughout the whole fuel cell system. By consolidating these functions into the core design, the need for additional components for fuel, air, and water management is therefore eliminated, streamlining the system and reducing its complexity. Another key advantage of this system is its impact on manufacturing costs. Traditional fuel cell stacks require intricate assembly processes and the use of additional frames and gaskets for sealing. In the Flexi-Planar design the assembly and sealing are made simple, as no frames or gaskets are necessary. This reduces both material costs as well as assembly time and labor expenses. The cost-saving potential of this patent is substantial, with projections indicating that it could bring the cost down to as low as 26 \$/kW [5].

4.2.2 Power and durability

In order to be commercially successful, any product must fulfill the end user acceptance criteria. In our case, those criteria are functionality, impact on the environment, overall cost, and

performance. Since fuel cell cars run with zero emissions they have no environmental impact. For their function, they use a motor, and the overall idea is not that different from cars powered by ICEs. Therefore, the problem is in their performance, and particularly reliability. Fuel cell vehicles are far superior in efficiency compared to ICE vehicles, but not quite as reliable [51]. As it is an important tool in people's lives, they want to be able to rely on their car running without any significant issues for many years and under all conditions. Currently, when studied under real operating conditions that involve frequent starts and stops and cyclic loads, PEMFCs seem to be able to function for up to two thousand hours or approximately 100 thousand km. This falls short of the target for passenger cars which is set between three and five thousand hours of operation and far below the target of 20000 hours that is set for buses [57].

The development and commercialization of FCEVs face distinct challenges based on the type of vehicle that is under development, whether it is a bus, a heavy-duty truck, or a passenger car. Each type has unique power requirements and spatial constraints, necessitating tailored solutions in the stack design and technology. Buses and heavy-duty trucks are promising candidates for early commercialization due to their relatively ample space available both for larger FC stacks and hydrogen storage systems. Furthermore, the need for higher power output required for these vehicles means that the high cost for FC systems can be more easily justified. On the other hand, as these types of vehicles undergo heavy usage, the fuel cell systems used on them must be durable to ensure the efficient function of the vehicle. The power output is also a significant issue, as FCEBs require an output of approximately 200kW to be on par with the 200 to 300HP internal combustion engines used on traditional ones. Similarly, a typical diesel engine currently used in heavy-duty trucks produces about 500HP that will need to be matched by a stack producing 375kW. As for passenger cars, the main problem lies in their confined space. Passenger cars typically require around 10 to 100kW of power, and that can be achieved, but due to their small size, fuel cells with a high power density have to be used, so as not to compromise either the passenger or the cargo space with more bulky ones. For example, the Toyota Mirai achieves a power density of 4.4kW/L, while the New Energy and Industrial Technology Development Organization (NEDO) of Japan has set a target of 9.0 kW/L by 2040, meaning that the power density will have to be at least doubled in the future.

One way to improve performance in terms of increased output is to manage the pressure ratios and air supply within the system. Older research identified a critical issue with the pressure ratio

in fuel cells. It was observed the pressure ratio had an upper limit of 2.5 bars, while it was shown that an increase in fluid pressure would negatively affect the overall efficiency of the system, decreasing performance in power output. This posed a challenge, as optimizing the pressure is crucial for maximizing the power-generating capabilities of the cell. An innovative solution came from Honda Motor Corporation Limited. The company introduced a turbo-compressor to increase pressure in the air going in the FC, therefore maintaining a lower pressure ratio. This turbo-compressor allowed Honda to produce more power with its fuel cell vehicle compared to any other similar model from other manufacturers. Building on Honda's advancements, Capata and Hernandez (2014) found a way to further improve on that idea, by utilizing the excess air coming out of the stack. The air coming out has a higher temperature and pressure, compared to the ambient conditions. A system incorporating a turbo compressor and a turbo-expander was added, so when the high-pressure and temperature air comes out of the stack it flows directly into the expander, and its kinetic energy is used to turn the driveshaft and generate mechanical power. This power is then utilized to drive the compressor. This approach utilizes the otherwise wasted energy from the exhaust air and as a result, the system's consumption is decreased, and overall power is increased [8].

To increase the power output, another way is to accelerate the electrochemical process where it suffers the most, and that is the slow Oxygen Reduction Reaction (ORR) that has been a bottleneck in achieving higher power outputs. Fortunately, in the last few years, researchers from the Georgia Institute of Technology found a way to accelerate it. A new catalyst that is reportedly eight times faster than the usual ones was developed. This new catalyst consists of a coating about 24 nanometers thick, made by two nanotechnology solutions. First, nanoparticles attract Oxygen molecules that lose some of their electrons, thus creating two O^+ ions. The free electrons are sucked by electron vacancies, i.e., special "holes" in the nanoparticle structure designed to attract and efficiently transfer electrons, and are sent to the next phase of the catalytic process. The second phase involves a similar coating that has Oxygen vacancies, allowing for the O^+ ions to travel faster through the catalyst structure and reach their final destination where they combine with Hydrogen and produce water, therefore completing the electrochemical reaction [13].

As mentioned before, efforts have been made to tackle performance issues through several approaches. Such solutions that have shown significant promise include alloying transition metals with Pt, controlling dimensions, and performing surface etching. It has been reported that employing a Pt-rich shell core-shell nanostructure offers many benefits. These benefits are enhanced utilization of Pt

since Pt is only used on the surface, while cheaper metals are added to the core, thus decreasing usage of Pt without compromising performance, and protection of the core elements through core–shell interactions, as they protect the core elements from oxidation and other forms of degradation. An additional highly effective solution involves the utilization of ultrathin nanostructures, such as nanowires, nanotubes, and nanosheets. These structures offer a unique advantage by maximizing the utilization of Pt while maintaining a special low-density morphology, which is essential for achieving high catalytic activity with minimal material usage. Combining the core–shell nanostructure with ultrathin nanostructures has proven to be a viable approach for enhancing both activity and durability, with the core–shell elements designed to finely tune the shell interactions, while the ultrathin morphology ensures maximum surface area for catalytic reactions. A notable example of this combined approach is Au@Pt₃Ni nanowires. By alloying Au through a Pt–Ni shell, atomic migration is prevented. Gold acts as a one-dimensional support that stabilizes the structure and offers better durability. By further experimenting with various values for the radius of the shell, it was found that a shell of moderate thickness showed the best ORR activity as well as the most endurance when compared with differing values of shell thickness [21].

Generally speaking, structural disorder within catalytic materials leads to a higher mass activity. A study by Chattot et al. actually proved that disordered structures are more stable for usage in a PEMFC environment and are the best candidates to be used commercially [6]. Furthermore, they have a multitude of active sites, which could be used to optimize more than one electrochemical reaction with the same material. One development in this field is the formation of a self-etched Pt–Co nanodendrite within a nanoframe structure, protected by a Pt skin, that introduces an innovative method for enhancing catalytic performance. This novel catalyst material, termed Pt–Co ND–NF, shows great promise and opens up new possibilities for improving catalytic efficiency. Pt–Co ND–NF catalyst represents a significant advancement in catalytic technology due to its highly exposed catalytically active sites and unique structural design. This catalyst demonstrates remarkable performance in the oxygen reduction reaction (ORR), boasting a mass activity nearly ten times higher than that of conventional commercial Pt/C catalysts. Moreover, the external frame structure with a Pt-skin coating contributes to the catalyst's durability, further enhancing its overall efficiency and longevity [23]. Researchers have, also, successfully prepared Pt–Pd–Ni octahedra nanoparticles, featuring an ultra-small size of 4.71 nm, through a Pd seed-inducing-growth route. The Pt–Pd–Ni octahedra nanoparticles exhibited a significantly improved mass activity in the oxygen reduction reaction (ORR). Notably, this mass

activity was found to be 5.81 times higher compared to commercial Pt/C catalysts [25]. Such advancements highlight the potential of finely tuned nanostructures in achieving superior catalytic performance. In addition to advancements in catalytic technology, innovations in membrane technology also add to the improvement of fuel cells. For example, a patent that demonstrated notably high power density was made by ITM Power. The idea was to replace the standard perfluorosulfonic acid membrane with one made of ionic polymers, and as increased power density translates to lesser cost, it achieved an output of 35\$/kW [5].

ICEs have set a high benchmark for durability, with many engines operating reliably for more than 300,000 kilometers, equivalent to approximately 10,000 hours of runtime. This reliability stems from over a century of refinement and optimization, making ICEs a tough competitor for new technologies like fuel cells. Before dealing with reliability problems though, we have to identify them. These problems occur because of the buildup of degradation both to materials and catalysts due to fuel and/or oxidant starvation, bad water management that leads to flooding or drying, corrosion, and chemical reactions.

Before continuing it would be better to further analyze some of the root causes that lead to shorter cell life as well as the degradation mechanisms. Those causes are fuel or oxidant starvation, poor thermal or water management, load cycling, and exposure to impurities and freezing conditions [57]. In **Figure 4.17** processes that will be discussed, like the water formation, back diffusion, etc. occurring inside a cell can be seen so the reader can have a visual representation and a better understanding of where they happen inside the cell.

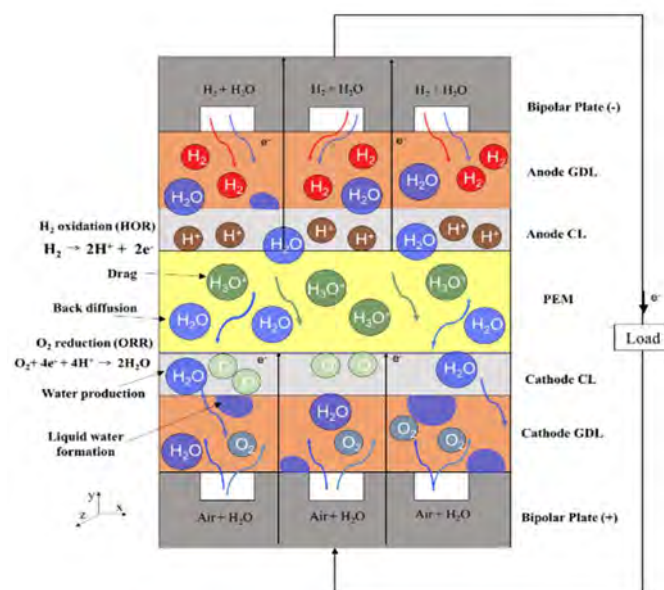


Figure 4.17: Processes occurring inside the cell [57].

A variety of reasons, such as high current, ice, or fuel impurities can cause the reactants to be unevenly distributed leading to fuel or oxidant starvation. Fuel or oxidant starvation represents a critical challenge in the operation of FC systems, with potentially severe consequences for their performance and longevity. In that state, there is a significant drop in the performance as well as the voltage of the cell. Starvation also leads to extreme degradation. In extreme cases, with a lack of fuel, cell voltage can become negative as the anode can reach positive potential and the carbon will be corroded and produce CO_2 in order to provide the anodic current, thus leading to permanent damage to the anode and compromising the integrity of the cell. Furthermore, the lack of any of the reactants can trigger the unwanted generation of oxygen in the anode or hydrogen in the cathode. This happens, as the high potential caused by the starvation splits the present water into hydrogen and oxygen. Additionally, the presence of fuel or oxidant on the wrong electrode leads the cell potential to reverse and damages the cell in the way described above, causing even more damage and degradation to accumulate [57].

Transitioning between low and high-power states can affect performance in the short term but also have an impact on the cell's lifespan in the long run. This transition introduces dynamic changes in operating conditions, which can impose considerable stress on cell components and lead to degradation when done frequently. Usually, at low currents and temperatures, there is a high relative humidity that causes the membrane to expand while the opposite is true in higher currents and temperatures where the membrane shrinks and dries due to lower relative humidity. These variations in membrane size lead to material stress that slowly destroys the membrane, therefore highlighting the need for good thermal management, especially when the operation is in conditions below 0°C or above 80°C , so as to mitigate these effects and ensure long-term reliability. Furthermore, operating in high temperatures can cause some of the electrochemical surface area to be lost, affecting both durability and performance. Additionally, cycling between sub- and above-freezing conditions for extended periods of time causes the MEA and other components to delaminate [57].

Water management is crucial since the very idea of the PEM cell is connected with the presence of water. To properly manage water two opposing needs must be balanced, prevention of flooding in the catalyst, gas flow channels, and bipolar plates, and adequate hydration of the membrane. When water is present within the cell, hydronium complexes (H_3O^+) are formed on the boundaries of the membrane and the catalyst layers. These complexes transport the protons from the anode catalyst layer to that of the cathode, thus increasing or maintaining a high performance [57].

Contrary, too much water decreases both the lifetime and performance of the cell. The accumulation of excess water is called flooding, and it can block the gas flow channels, reaction sites, or the pores of the GDL. Flooding can rapidly lead to starvation and its consequences mentioned above. Furthermore, water presence can reduce the pore size of the GDL, impeding the flow of reactants and leading them to be dissolved in the liquid water rather than reaching the catalyst sites, or it can force the gas to flow through alternate channels resulting in a decrease in pressure [57].

Flooding is generally caused by high current density but can also be attributed to other conditions like low gas temperatures or inadequate gas flow rates. Excess water is usually accumulated at the cathode, caused by two main mechanisms: water generation by the electrochemical reaction or by over-humidified or saturated reactants [57]. Even though it is rare, flooding can also happen at the anode and greatly affect performance and degrade the cell. What is even worse is that, unlike the cathode, the fuel flow rates at the anode are low and therefore it is harder to remove the excess water from this side. Anode flooding can be caused by a combination of factors, including the reactants being saturated or by water back-diffusion from the cathode in combination with fuel gas not being adequately humidified [57].

Many authors have proposed solutions to better monitor and prevent flooding on the anode. Het et al. developed a methodology that correlates partial pressure with the flooding level providing a reliable index of performance, so they designed a tool to monitor it [57]. Similarly, Diperno and Fronk also patented a method and a device that measures pressure drop in the flow fields enabling real-time detection of flooding occurring within the cell [57]. On the other hand, a loss of water can cause the membrane to dehydrate and dry, something that most often happens on the anode side and causes an increase in the protonic resistance of the membrane and therefore a decrease in voltage and cell power in general. Operation for a long time in an anhydrous environment causes increased degradation. Dehydration commonly occurs due to the evaporation of water when operating in high temperatures or not hydrated fuel at the anode side. Water back-diffusion to the anode is higher at the channel outlet and that is also enhanced by the shrinking of membrane pores under dehydrating conditions. Therefore, dehydration at the anode is more severe at the inlet of the cell [57].

A drying membrane can be faulty and will have performance issues. Conversely, flooding aids the phenomena of corrosion on critical components, such as the membrane, the gas diffusion media, the catalyst, and electrodes, further impairing cell performance and life expectancy. We

can therefore easily deduce that a change in materials or flow conditions will greatly affect durability and reliability [5]. Flow conditions should be controlled by a dynamic control system that adapts to and tackles environmental conditions that can impede the function of the cell. For example, extreme thermal cycles (temperature variations outside the safe temperature range designated by the manufacturer) that can be caused by extreme demands in power or cold starts can affect the waterproofing of the membranes and as a consequence their strength and conductivity. It is therefore highly important to adjust the flow conditions to avoid such thermal cycles and preserve cell integrity and performance [57].

In the dynamic environment where cars are utilized rapid changes in power demand occur very often. It has been observed that even though platinum is stable at both low and high potentials, it may dissolve fast when transitioning from one to the other [57]. A good example of such power demand fluctuations is the process of starting and stopping the cell, which can inflict significant damage if not managed effectively. One specific concern is the filling of the anode gas channel with air after shutting down. Then, when the operation starts again, there arises a transient condition during which the beginning of the channel receives sufficient fuel, but the end still remains starved. This is called the “air-fuel front”.

Start-up procedures under freezing conditions present a unique challenge that significantly impacts the durability of PEM FCs. Any water left in the cell, when it shuts down, can freeze, and that causes mechanical and thermal stress to the membrane. As the water freezes, it expands, exerting pressure on the surrounding components potentially causing damage. Repeating cycles of icing and thawing can cause delamination of the catalyst layer and decrease the interface contact. Obviously, these stresses are relative to the amount of water left in the cell at the moment of shutdown as more water leads to a thicker ice layer and therefore more damage done. Studies done in certain repetitive temperature change cycles (change from -30°C to 20°C) have revealed that the membrane is more severely cracked when it was fully hydrated when the cell stopped working than it is when the membrane had a lower humidity [57].

Managing impurities in both the air and fuel streams is critical for ensuring optimal performance and durability in proton exchange membrane fuel cells, as they are sensitive to them, and a small concentration of impurities can have a big impact on the cell’s operation. Dealing with those impurities is currently of high importance, as Hydrogen is currently mostly produced by reforming hydrocarbons (methanol, propane, and mostly natural gas). Despite efforts to purify

the hydrogen produced with this method, trace amounts of impurities can still remain and end up in the cell's intake [57]. Furthermore, the ambient air which serves as an energy source also contains a number of pollutants and contaminants as it is widely known. These impurities can adversely affect cell performance by interfering with key electrochemical processes within the cell. Different impurities act upon the cell in various ways depending on their type and concentration. Some are absorbed from the catalyst layers at the electrodes affecting the process responsible for transferring the charge resulting in overpotential losses [57]. Other impurities increase the ohmic losses by forming cations that reduce the membrane's ability to conduct protons. One such substance is ammonia [57]. Finally, impurities may have either an irreversible or a reversible effect on the cell. For example, the performance degradation caused by CO contamination can be easily reversed by stopping and restarting the cell. Below, in **Table 4.2** the most common impurities are mentioned together with their source and their effect.

Impurity	Source	Effect
Fuel impurities		
Hydrogen Sulphide (H ₂ S)	The process of reforming fossil-originated fuels	Causes irreversible damage to the cell by blocking the Pt's active sites
Ammonia (NH ₃)	The process of reforming various hydrocarbons	At levels as low as 13 ppm, Ammonia decreases performance at a fast rate. Exposure of less than 60 min can be reversed, but exposure for a long time causes permanent damage
Carbon monoxide (CO)	The process of reforming various hydrocarbons	Known as CO poisoning, the adsorption of hydrogen on active Pt sites is blocked causing electrode overpotential and loss in performance. Restarting the fuel cell or introducing Oxygen in the fuel flow can reverse the condition but both methods have negative consequences
Anions/Cations	Water electrolysis	Protonic conductivity of the membrane is reduced
Hydrocarbon contaminants	The process of reforming various hydrocarbons	Effects are not clear yet, as some stationary systems operate in their presence.
Air impurities		
Nitrogen dioxide (NO ₂)	ICE emissions	Decreased performance, although reversible
Sulfur dioxide (SO ₂)	Combustion of fossil fuels. High concentrations in the urban environment	Reversible with certain techniques such as cyclic voltammetry. Causes strong chemisorption on the surface of the Pt catalyst. Similar effects to the presence of H ₂ S in the anode
Sodium Chloride (NaCl)	Mist from the sea or salt used to de-ice roads	Exchange of H ⁺ by Na ⁺ affects the membrane's ability to conduct protons

Table 4.2: Most common impurities, their sources, and effects [57].

The degradation of the membrane can manifest through various mechanisms, including mechanical, chemical/electrochemical, or thermal processes [57]. A faulty MEA fabrication process may lead to tears, pinholes, or cracks, and dimension changes due to environmental conditions while operating can also affect mechanical durability. All these types of degradation can be considered as mechanical degradation. If the membrane is breached and reactants reach their respective reverse

electrodes, the exothermic reaction of the reductant and oxidant occurs on the catalyst and creates points of elevated temperature. The crossover is then increased and as the hot points grow in number the degradation is accelerated. It is suggested that a mechanical failure may start as a random imperfection that leads to a total failure [51].

Thermal stability and chemical degradation are significant concerns in the performance and longevity of Nafion membranes used in PEMFCs and therefore those have been the target of many studies. At elevated temperatures above 150°C the side sulfonate acid groups cause a decomposition of the membrane [51]. As for the chemical degradation, it can arise from various processes. As mentioned before, the exothermal reaction/ combustion between Oxygen and Hydrogen can create holes in the membrane and destroy the MEA. Even worse, the reaction on the electrodes can lead to the production of peroxide and hyperoxide radicals which can cause further damage to the membrane and the catalyst. It is also found that the production of those radicals and chemical degradation of the membrane see a rapid increase when the cell is operating under OCV and in conditions with insufficient humidity [57]. The catalyst carbon support can be also corroded. In PEMFCs two mechanisms are thought to cause this corrosion: 1) transition between shutdown and startup cycles and 2) fuel starvation during steady-state conditions [57]. During the first one, the air-fuel front can be caused by uneven distribution of fuel on the anode and crossover of the oxygen through the membrane. The second mechanism can be the result of non-uniform flow sharing between the cells during high-performance operation in subfreezing temperatures which can cause the formation of ice that blocks the gas flow. In both cases, partial coverage of the anode by hydrogen can occur leading the anode potential to go negative until carbon oxidation takes place. However, if there is enough water in the cell, the carbon is protected from corrosion because water is oxidated in its stead [57].

Corrosion of the bipolar plates also has a great impact on the lifespan and performance of the cell. Under permanent contact with water, the material of the plate undergoes corrosion leading it to dissolve in the water. The dissolved material may then either travel to the membrane or be flushed with the water flow. If the product of the corrosion on the other hand stays in the cell it can accumulate and consequently poison the membrane. Moreover, if a resistive surface layer is formed on the plates as a result of corrosion, the ohmic resistance increases and efficiency drops. Finally, the high pressure applied during manufacturing to seal the stack and ensure that the electric conductivity is good can also subject the bipolar plates to huge mechanical stress. This stress may result in the deformation or fracture of the plates [57].

Developing bipolar plates with high corrosion resistance is one idea, but they also need to be cheap to make. Over the years graphite was used because of its low surface contact resistance, high surface conductivity, and corrosion resistance. In an environment with lots of vibrations, like a car, though, brittle materials like graphite will soon fall apart, so the idea is to replace graphite in bipolar plates with other metals, alloys, or composites made of carbon. It is shown that metals like Aluminum, Titanium, Palladium, and Nickel, just to name a few, are easily affected by corrosion, increasing their electrical resistance, and thus decreasing performance. Palladium stands out, though, as it exhibits high performance as a catalyst on its own and is stable under harsh conditions [20]. It is therefore evident that we must use corrosion-resistant coating on those materials. Coating is divided into two categories. Carbon-based coatings that include conductive polymers, polypyrrole, graphite, and composite coating, and metal-based ones that include noble metals, metal nitrides and carbides, and conductive metal oxides, like fluorine doped Tin oxide ($\text{SnO}_2: \text{F}$), or Ruthenium oxide (RuO_2), just to provide a few examples. Metal alloys tend to be better than carbon composites because less amount is needed due to their higher mechanical strength, and furthermore, they can be made thinner and thus increase the power output and density [5].

Another place where degradation greatly accumulates is the catalyst layer. As we have said earlier, the most common catalyst is Pt. Platinum nanoparticles supported on carbon black (Pt/C) that typically serve as catalysts, are simultaneously in contact with the gasses as well as with protons and electrons. However, in automotive applications where strong electric currents are required, Pt/C catalysts face challenges related to durability. Under high current density conditions, platinum particles tend to break free from the carbon support, thus deteriorating performance. To address this issue, researchers have explored alternative catalyst formulations that offer better durability without compromising performance. One promising approach is mixing graphene with Pt/C, resulting in the creation of channels through which electrons travel much faster, with low resistance, under high current density. Graphene enhances the electrical conductivity of the catalyst layer while also stabilizing Pt nanoparticles, reducing the likelihood of detachment from the carbon support. Therefore, graphene provides a great and more durable substitute for carbon black [5].

Carbon poisoning is another problem when not using pure Hydrogen as a fuel. Pt/C, unfortunately, fails to maintain stability under high CO concentrations for extended periods, typically lasting no more than 6 hours before experiencing performance degradation. However, promising alternatives have been discovered that offer improved durability and stability in CO-rich environments.

Among these alternatives, PtIr/C and PtPd/C catalysts, have emerged as highly resilient options, as they demonstrate excellent durability even after undergoing 5000 accelerated durability test (ADT) cycles. Additionally, Pt3Pd/C and PtPd/C exhibit the highest mass activities, surpassing commercial Pt/C by 4 and 5 times, respectively [22]. According to theoretical findings, isolated platinum-atom centers bound to individual pyridinic nitrogen (PN) sites acting as highly active species during the oxygen reduction reaction (ORR) pathway demonstrate remarkable tolerance against the presence of methanol and carbon monoxide [26].

The recently developed FeOx@graphitic carbon core-shell nanoparticles embedded in an N-doped carbon matrix, featuring an ordered and mesoporous structure (FeOx@GC-NOMC), represents a significant advancement in electrocatalysis, offering several remarkable characteristics: i) Enhanced Electrocatalytic Activity: FeOx@GC-NOMC demonstrates superior electrocatalytic activity, particularly in acidic media, outperforming other catalysts. ii) Four-electron ORR Process: The catalyst follows a highly efficient four-electron oxygen reduction reaction (ORR) process, which is crucial for maximizing energy conversion in fuel cells and other electrochemical devices. iii) Superior Stability and Methanol Tolerance: In addition to its superior electrocatalytic activity, FeOx@GC-NOMC exhibits remarkable stability and resistance to the negative effects of methanol, making it more durable and inert in comparison to commercial Pt/C catalysts with 20 wt % platinum content. These exceptional properties make FeOx@GC-NOMC a highly promising and valuable catalyst for various electrochemical applications [24].

Proper hydration is essential for the optimal performance of Polymer Exchange Membranes. However, excessive hydration will cause issues like voltage loss at high current density or voltage instability at low current density, the probability of not starting up in freezing conditions, and corrosion of the supporting carbon due to hydrogen starvation. To tackle this issue innovative designs of membrane and material combinations must be developed to balance hydration levels by themselves or improve on the standard Nafion membranes that are already in use, although they suffer from problems caused by dryness. A membrane developed by [19] (the sPP-b-PAES(6.5K)-3.0) looks promising as it shows high proton conductivity, and high performance and is more dependable and durable than Nafion [5].

Generally, PFSA membranes are the most common membranes used in low-temperature PEMFCs, because of their chemical, thermal, and mechanical stability, and high conductivity. That being said, they still have some shortcomings that lead research to explore other avenues for improvement. One promising approach involves developing fluorinated polymer composite membranes by

incorporating a variety of organic, inorganic, and hybrid filler materials. One notable advantage of PFSA composite membranes is their ability to maintain a high conductivity even when under low humidity conditions, thus solving a great problem for the commercial viability of PEMFCs [10].

Finally, while speaking of durability, it is worth mentioning that ACAL Energy Ltd managed to run a PEMFC for more than 10,000h without signs of degradation, marking a significant milestone and making it competitive against ICEs while at the same time surpassing 2010 US DoE's targets. Being creative, ACAL Energy did not use Pt as a catalyst, rather it used FlowCath®, mentioned earlier in this study, which acts both as a coolant and a catalyst. The result was the removal of most known mechanisms that cause degradation, giving us an exceptionally durable fuel cell [5].

The above-mentioned failures that can occur in a fuel cell can be seen in **Figure 4.18** along with the cause for each one and the solutions that are currently used. It should be noted that Electrodes have the most known types of failures and require the most expensive solutions, such as more use of Pt.

Component	PEM	Electrodes	GDLs	Bipolar plates	Sealing gasket
Failure mode	• Mechanical degradation; • Thermal degradation; • Chemical degradation	• Catalyst loss; • Conductivity decrease; • Decreased transportation; • Reformate tolerance loss; • Deteriorated water management	• Mechanical degradation; • Conductivity decrease; • Deteriorated water management	• Mechanical degradation; • Conductivity decrease	• Mechanical degradation
Causes	• Uneven mechanical stress; • Inadequate humidification; • Corrosion of catalysts and seal materials; • Thermal stress and cycles; • Contamination; • Radical attack	• Catalyst sintering; • Corrosion of catalysts or supports; • Mechanical stress; • Contamination; • Change in hydrophobicity	• Degradation of backing materials; • Chemical corrosion; • Mechanical stress; • Change in the hydrophobicity; • Chemical corrosion	• Corrosion; • Oxidation; • Mechanical stress; • Thermal stress and cycles	• Corrosion; • Mechanical stress
Mitigation solution	• Use of radical scavengers such as CeO₂ nanopowder to cathode catalyst ink; • Thicker membrane to delay failure due to membrane thinning; • Use of composite membrane; • Larger radiator; • Wetter running with less RH variability	• More Pt loading; • Particle agglomeration management by novel catalyst geometries and formulations; • Use of inherently durable catalysts such as Pt alloy and Pt membrane with high surface area carbon supports; • Use of inherently durable catalysts such as Pt alloy and Pt membrane with high surface area carbon supports; • Cell-by cell voltage monitoring system; • Limit voltage slew rate; • Drier running with lower RH; • Shut-down to prevent voltage from going up	• Dummy cells on stack ends to prevent condensation; • Gas-purge of anode at shut-down	• New bipolar plate base materials such as Ti, graphite, surface modified or doped metals, and conductive polymer composites	• Limit leaching by Co in cathode catalyst ink

Figure 4.18: Major failure nodes of different components in PEMFC [53].

To summarize, according to **Figure 4.18**, Gas Diffusion Layers can suffer from mechanical degradation, a decrease in conductivity, and deteriorated water management. Those can be caused by degradation of backing materials, chemical corrosion or mechanical stress, and a change in hydrophobicity. Those problems can be mitigated by adding dummy cells on the ends of the stack to prevent condensation from forming, or gas-purging the anode side at shut-down. As for bipolar plates, new base materials such as Ti, graphite, doped or surface-modified metal, and conductive polymer

composites can limit the mechanical degradation and conductivity decrease that is caused by corrosion, oxidation, and mechanical and thermal stress. Going forward, the Polymer Electrolyte Membrane has to deal with inadequate humidification, corrosion of catalysts and seal materials, thermal stress and cycles, and contamination among others that cause problems with mechanical, chemical, and thermal degradation. There are some proposed solutions for these challenges, which include the use of composite membranes, wetter running with less variability in relative humidity, and the usage of a thicker membrane in order to delay failure that comes eventually due to membrane thinning. Finally, electrodes can fail due to a number of factors. Those include a decrease in conductivity, poor water management, and loss of catalyst. These can be the result of contamination, corrosion at the supports of the catalyst, or mechanical stress. The solutions to these issues are rather expensive as they include the utilization of even more Platinum or Platinum alloys and Platinum membranes with high surface area carbon supports. Other ideas proposed include shutting down to prevent voltage from going up, drier running with lower relative humidity, cell-by-cell voltage monitoring systems, and the usage of new catalyst geometries and formulations.

CHAPTER 5

CONCLUSIONS

Fuel cells have been around for more than a century and have been commercially available for a few decades in various stationery and mobile applications. Their usefulness has been proven not only for mundane tasks but also for projects of cutting-edge technology, such as space travel. As they enter the automotive industry though they are challenged to be on par or even better than ICEs in terms of power output and durability without exceeding the ICE's cost of production and maintenance. Many new ideas are proposed daily targeting to make fuel cell systems more power-dense and lots of new patents are filed, promising a greater power output and hitting the various targets set by organizations like the US DOE. In terms of durability, the causes and mechanisms that lead fuel cell systems to degrade or fail are known and are being researched even further with new solutions being tested. As microcontrollers and measuring technologies improve it is expected that failures will be more easily monitored and averted and therefore durability will increase, while also new and better materials will make for more sturdy components and systems. As for the cost, the main problem lies in the exotic materials needed to construct a fuel cell, and mostly in the usage of Platinum. New materials with different microstructure and properties offer the chance to use less to no Platinum for the catalyst leading to a decrease in price and more commercial availability, as production can then be increased. The biggest car manufacturers around the planet have taken an interest in cars powered by fuel cells and research has been ongoing for a few decades, with some OEMs being successful in developing, manufacturing, and selling a quite large number of commercial passenger cars. At the same time, heavy machinery is slowly but steadily being replaced by new machines powered by Hydrogen. Long haul trucks, buses, and inner city buses have also been taken over from FC-powered ones, with inner city buses being the top candidate to be fully replaced due to their fixed routes. City buses are also great candidates for experimentation as they are running all day, cover many miles and can provide data on how the fuel cell technology is affected by driving for extended periods in real conditions. Experiments and comparisons have shown that FC buses offer greater mileage and less sound and air pollution than ICE buses and do not lack driving performance.

Geopolitical changes in the last few years have made oil and gas prices go up dramatically and made many countries unsure of their future oil supply, showing that finding a different way to produce power is mandatory. Recent floodings in various normally anhydrous regions of the world like Dubai have shown that climate change is becoming worse and therefore it is critical to transit to clean power sources. The lack of pollution coming from FCVs has intrigued governments and organizations around the world with many of them making plans and strategies to increase the number of FCVs on the street in the upcoming years. In hindsight, after the blow dealt to the economy of most countries by COVID-19, the targets set for 2025 seem difficult to achieve. However, many countries have given and continue to give incentives in the form of tax cuts or funding of research to boost the development of FC technology and give people a reason to buy FCVs. On a positive note, however, even more OEMs like BMW, Porsche, Kia Motors, and Tata Motors just to name a few are either already producing or set to produce their own version of fuel cell-powered cars and the next couple of years. As a result, the targets for 2030 may still be reached.

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