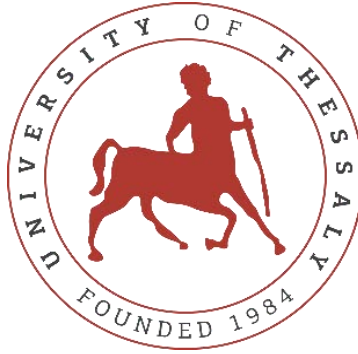




UNIVERSITY OF THESSALY
SCHOOL OF ENGINEERING
DEPARTMENT OF MECHANICAL ENGINEERING

Diploma Thesis
CURRENT PROSPECTS OF FUEL CELLS (PEMFC AND SOFC)
IN VEHICLE APPLICATIONS

By
Stavridis Dimitrios & Thomas Mpoutlas

Supervisor
Prof. Tsiakaras Panagiotis

Submitted in partial fulfillment of the requirements for the degree of Diploma in Mechanical
Engineering at the University of Thessaly
Volos, 2024



ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΙΑΣ
ΠΟΛΥΤΕΧΝΙΚΗ ΣΧΟΛΗ
ΤΜΗΜΑ ΜΗΧΑΝΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ

Διπλωματική Εργασία

**ΤΡΕΧΟΥΣΕΣ ΠΡΟΟΠΤΙΚΕΣ ΚΥΨΕΛΩΝ ΚΑΥΣΙΜΟΥ (PEMFC ΚΑΙ
SOFC) ΣΕ ΕΦΑΡΜΟΓΕΣ ΟΧΗΜΑΤΩΝ**

Υπό
Σταυρίδης Δημήτρης & Θωμάς Μπούτλας

Επιβλέπων:
Καθηγητής Τσιακάρας Παναγιώτης

Υπεβλήθη για την εκπλήρωση μέρους των απαιτήσεων για την απόκτηση του Διπλώματος
Μηχανολόγου Μηχανικού
Βόλος, 2024

Οι υπογράφοντες ΣΤΑΥΡΙΔΗΣ ΔΗΜΗΤΡΙΟΣ & ΜΠΟΥΤΛΑΣ ΘΩΜΑΣ γνωρίζοντας τις συνέπειες της λογοκλοπής, δηλώνουν υπεύθυνα ότι η παρούσα εργασία με τίτλο « ΤΡΕΧΟΥΣΕΣ ΠΡΟΟΠΤΙΚΕΣ ΚΥΨΕΛΩΝ ΚΑΥΣΙΜΟΥ (PEMFC ΚΑΙ SOFC) ΣΕ ΕΦΑΡΜΟΓΕΣ ΟΧΗΜΑΤΩΝ » αποτελεί προϊόν αυστηρά προσωπικής εργασίας και όλες οι πηγές που έχουμε χρησιμοποιήσει έχουν δηλωθεί κατάλληλα στις βιβλιογραφικές αναφορές. Τα σημεία όπου έχουμε χρησιμοποιήσει ιδέες, κείμενο ή και πηγές άλλων συγγραφέων, αναφέρονται ευδιάκριτα στο κείμενο με την κατάλληλη παραπομπή και η σχετική αναφορά περιλαμβάνεται στο τμήμα των βιβλιογραφικών αναφορών με πλήρη περιγραφή.

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THE DECLARANTS

STAVRIDIS DIMITRIOS & THOMAS MPOUTLAS

Approved by the Committee on Final Examination:

Advisor Dr. Tsiakaras Panagiotis (Supervisor)

Professor of Department of Mechanical Engineering

School of Engineering

University of Thessaly

Member Dr. Charalampous Georgios

Associate Professor of Department of Mechanical Engineering

School of Engineering

University of Thessaly

Member Dr. Brouzgou Angeliki

Assistant Professor of Department of Energy Systems

School of Technology Sciences

University of Thessaly

Acknowledgements

We would like to express our heartfelt gratitude to our thesis supervisor, Professor Tsiakaras Panagiotis, for his precious guidance and support throughout the entire process of our thesis. His insights and encouragement have been instrumental in shaping our work. We are also deeply appreciative of the members of our examination committee, Brouzgou Angeliki and Sotiria Kontou, for taking the time to carefully review our thesis and for offering thoughtful feedback and constructive suggestions that helped us refine our research.

Our deepest gratitude goes to our parents for their unwavering love, encouragement, and support over the years. Their belief in us has been a constant source of strength. We are equally grateful to our family members for their patience and for always standing by us. Lastly, we want to extend our warmest thanks to our friends, who have been by our side every step of the way, offering their support, motivation, and companionship throughout this journey.

ΕΥΧΑΡΙΣΤΙΕΣ

Επιθυμούμε να εκφράσουμε την εγκάρδια ευγνωμοσύνη μας προς τον επιβλέποντα της διπλωματικής μας εργασίας, Καθηγητή Τσιακάρα Παναγιώτη, για την πολύτιμη καθοδήγηση και υποστήριξή του καθ' όλη τη διάρκεια της υλοποίησης της εργασίας μας. Οι γνώσεις και η ενθάρρυνσή του υπήρξαν καθοριστικές στη διαμόρφωση του έργου μας.

Εκφράζουμε επίσης τη βαθιά μας εκτίμηση προς τα μέλη της εξεταστικής μας επιτροπής, Αναπληρώτριες Καθηγήτριες Μπρούζγου Αγγελική και Κοντού Σωτηρία, για τον χρόνο που αφιέρωσαν στη λεπτομερή αξιολόγηση της διπλωματικής μας εργασίας, καθώς και για τις εύστοχες παρατηρήσεις και τις εποικοδομητικές τους προτάσεις, που συνέβαλαν στη βελτίωση της έρευνάς μας.

Η βαθύτατη ευγνωμοσύνη μας ανήκει στους γονείς μας, για την αδιάκοπη αγάπη, ενθάρρυνση και υποστήριξή τους όλα αυτά τα χρόνια. Η πίστη τους σε εμάς υπήρξε αστείρευτη πηγή δύναμης. Είμαστε εξίσου ευγνώμονες προς τα υπόλοιπα μέλη της οικογένειάς μας για την υπομονή και τη διαρκή τους στήριξη.

Τέλος, θέλουμε να εκφράσουμε τις πιο θερμές μας ευχαριστίες προς τους φίλους μας, που στάθηκαν δίπλα μας σε κάθε βήμα αυτής της διαδρομής, προσφέροντάς μας υποστήριξη, κίνητρο και συντροφικότητα καθ' όλη τη διάρκεια αυτού του ταξιδιού

Abstract

The harmful impacts of pollutants emitted by conventional fuel-powered vehicles, as well as the draining of fossil fuels, have prompted vehicle manufacturers to turn to alternative energy sources. One of them is fuel cells (FC) which are one of the most efficient ways of converting chemical energy (of a fuel and an oxidizing agent) into electricity. They are also widely recognized as extremely environmentally friendly and offer significantly greater energy densities and efficiency compared to conventional technologies. Following approximately ten years of substantial investment in polymer electrolyte fuel cell (PEMFC) and solid oxide fuel cell (SOFC) technology, both are being actively considered for vehicle applications. Specifically, PEMFCs offer advantages such as quick startup at cold temperatures and negligible emissions, making them well-suited for various transportation sectors. PEMFCs primarily use hydrogen due to its high energy density and clean combustion, making it ideal for fueling fuel cell electric vehicles (FCEVs). However, they can also potentially utilize other hydrogen-rich fuels like methanol, ethanol, or formic acid. On the other hand, SOFCs present potential in specific types of vehicles, leveraging their flexibility to use various fuels, high electrochemical reaction speed, impurity tolerance and high efficiency. This variety of fuels includes hydrogen, natural gas, biogas, and certain biofuels like ethanol or biodiesel. However, challenges including cost, infrastructure development, and durability persist, hindering widespread use for both types of fuel cells.

Περίληψη

Οι επιβλαβείς επιπτώσεις των ρύπων που εκπέμπονται από τα συμβατικά οχήματα, αλλά και η αφαίμαξη των ορυκτών καυσίμων έχουν παρακινήσει τους κατασκευαστές οχημάτων να στραφούν σε εναλλακτικές πηγές ενέργειας. Μια από αυτές είναι οι κυψέλες καυσίμων (ΚΚ) οι οποίες αποτελούν έναν από τους πιο αποτελεσματικούς τρόπους μετατροπής της χημικής ενέργειας (ενός καυσίμου και ενός οξειδωτικού παράγοντα) σε ηλεκτρική. Ακόμη αναγνωρίζονται ευρέως ως εξαιρετικά φιλικές προς το περιβάλλον αφού τα μονά υποπροϊόντα τους είναι νερό και θερμότητα και προσφέρουν σημαντικά μεγαλύτερες ενεργειακές πυκνότητες και υψηλότερη απόδοση σε σύγκριση με τις συμβατικές τεχνολογίες. Μετά από περίπου δέκα χρόνια σημαντικών επενδύσεων στην τεχνολογία των κυψελών καυσίμου πολυμερούς ηλεκτρολύτη (PEMFC) και των κυψελών καυσίμου στερεού οξειδίου (SOFC), και οι δύο εξετάζονται ενεργά για εφαρμογές σε οχήματα. Συγκεκριμένα, οι PEMFC προσφέρουν πλεονεκτήματα όπως η γρήγορη εκκίνηση σε χαμηλές θερμοκρασίες και οι αμελητέες εκπομπές, καθιστώντας τις κατάλληλες για διάφορους τομείς μεταφορών. Τα PEMFC χρησιμοποιούν κυρίως υδρογόνο λόγω της υψηλής ενεργειακής του πυκνότητας και της καθαρής καύσης του, γεγονός που το καθιστά ιδανικό για την τροφοδοσία οχημάτων κυψελών καυσίμων FCEV. Ωστόσο, μπορούν επίσης να χρησιμοποιήσουν άλλα καύσιμα πλούσια σε υδρογόνο όπως μεθανόλη, αιθανόλη ή μυρμηκικό οξύ. Από την άλλη πλευρά, οι SOFC παρουσιάζουν δυνατότητες σε συγκεκριμένους τύπους οχημάτων, αξιοποιώντας την ευελιξία τους στη χρήση διαφόρων καυσίμων, την υψηλή ταχύτητα ηλεκτροχημικής αντίδρασης την ανοχή σε ακαθαρσίες και την υψηλή τους απόδοση. Αυτή η ποικιλία καυσίμων περιλαμβάνει υδρογόνο, φυσικό αέριο, βιοαέριο και ορισμένα βιοκαύσιμα όπως η αιθανόλη ή το βιοντίζελ. Ωστόσο, εξακολουθούν να υπάρχουν προκλήσεις, όπως το κόστος, η ανάπτυξη υποδομών και η ανθεκτικότητα που εμποδίζουν την ευρεία χρήση και των δύο τύπων κυψελών καυσίμου.

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Chapter 1

1.1 Introduction

One of the fundamental elements that determine the economy, infrastructure, transport and therefore the quality of life of a country is energy. Today, though, the global energy sector is in crisis, as fossil fuel reserves are depleted and the harmful effects of traditional energy sources on the environment become increasingly apparent. Most countries are still primarily dependent on fossil fuels (**Figure 1**), which are neither renewable nor environmentally friendly. The fossil fuels or otherwise conventional ones used today are oil, coal, natural gas, propane and nuclear substances such as uranium. Therefore, the drain on traditional energy resources makes it imperative for alternative and sustainable energy solutions that minimize the burden on the environment. Some international environmental agreements, such as the Paris Agreement and the Kyoto Protocol, aim to limit climate change due to the increase in anthropogenic greenhouse gas emissions. However, this effort is hampered by the ever-increasing demand for energy, which is due to population growth and technological development. The automotive sector is one of the biggest consumers of fossil fuels, contributing significantly to greenhouse gas emissions. The use of fossil fuels today remains high and is estimated to cover about 75% of energy production by 2050. Nevertheless, environmentalists estimate that the ecological measures expected to be taken by governments and the green initiatives that various organizations will follow will prevent the catastrophic scenario of global warming.

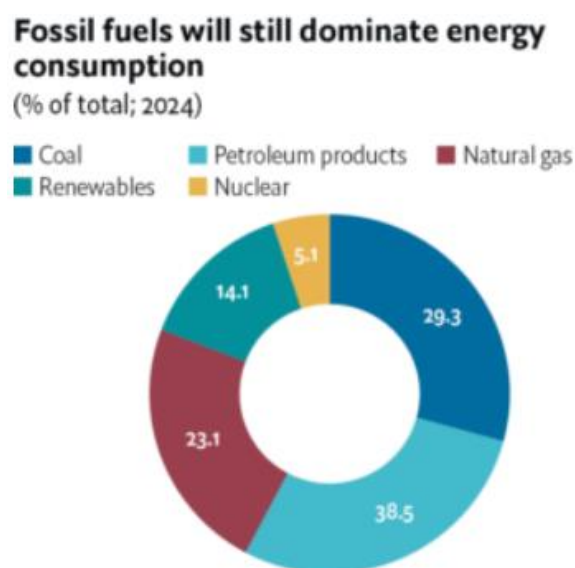


Figure 1: Percentage of global energy production by type of fuel of the year 2024 [57].

Despite the significant progress made in recent years in the development of hybrid and electric vehicles (EVs), challenges remain. Battery electric vehicles (BEVs), while operating with a powertrain efficiency of around 80% and capable of regenerative braking, have limited range and require long charging times compared to conventional vehicles. The above disadvantages combined with the need to reduce the dependence of the transport sector on oil have led the scientific community to search for alternative fuels (e.g. hydrogen, biofuels) as well as to develop new green technologies such as fuel cells (FCs), which will be powered by these fuels. FC is a technology that combines the advantages of both batteries and internal combustion engines, which is why it has piqued the interest of experts. Unlike pollutant-emitting internal combustion engines, fuel cells convert the chemical energy of fuels directly into electricity through an electrochemical redox reaction, with water being the only by-product. Hydrogen is a promising solution as an alternative fuel, since it is an energy carrier with minimal harmful emissions during combustion as well as with a high energy density per unit mass up to 39.39 KWh/kg, which exceeds most batteries. Another advantage is that it has a heating value 2 to 3 times higher per unit mass than oil. By combining hydrogen fuel cell technology with electric vehicles, the transport sector can achieve greater efficiency and sustainability, making hydrogen the candidate fuel of the future. However, to achieve this, certain obstacles must be addressed, such as the difficulty of storage and the lack of an organized distribution network [1-3].

In addition to hydrogen, biofuels (e.g. ethanol, methanol) are worth mentioning as feasible fuels for FCs. Biofuels are offered as a viable alternative to the use of fossil fuels due to their biodegradability and environmentally friendly nature as they greatly reduce the occurrence of greenhouse gases. These fuels are produced from biomass, a renewable energy source derived from waste or residues of organic matter (from agriculture, forestry and other related industries) [4]. More specifically, ethanol as a fuel is non-toxic (unlike methanol), cheap, renewable and readily available. It is usually produced from a range of vegetable raw materials containing starch or sugars (e.g. sugar cane, barley, wheat, corn) through the fermentation process. On the other hand, methanol is processed by synthetic processes and is extremely poisonous. All these factors make ethanol a very good choice from both an economic and environmental perspective. However, the power densities and lifetimes achieved by ethanol fuel cells are significantly lower than those required for their commercialization. This is due to the sluggish movement of electrons since 12 electrons are needed per ethanol molecule for direct electrochemical oxidation ($\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$) and the cleavage of the C-C bond, while for hydrogen only 2 electrons are required. Therefore, it is necessary to

develop a suitable anode catalyst that can facilitate the oxidation of ethanol, as well as a cathode catalyst that has a high tolerance to ethanol and its by-products [5].

The first fuel cell was invented in 1839 by Sir William Grove. For its manufacture used a combination of iron, copper and porcelain sheets and a solution of copper sulfate and dilute acid. A Sketch of Sir William Grove's fuel cell is illustrated in **Figure 2**. However, the first commercial use of fuel cells took place about a century later, in 1932 when English engineer Francis Thomas Bacon developed a 5 KW FC. This alkaline FC, also known as the Bacon Fuel Cell, has been used in NASA space programs (e.g. the Gemini mission) since the mid-1960s to provide power to satellites and space capsules. Fuel cells are superior in several respects to internal combustion engines. Some advantages are smaller size, high efficiency since efficiencies of up to 85% are achieved (with heat recovery) as well as zero emissions. These features make them ideal for application in the transport sector. However, there are serious challenges and obstacles that need to be overcome in order to achieve universal consumer acceptance and advance their commercialisation [3].

This thesis will investigate the current state of fuel cell applications, evaluate their advantages and disadvantages, as well as the technological developments required for their wider adoption. Finally, it examines how fuel cell technology and the use of hydrogen, as a fuel for transport, can transform the energy landscape and help achieve green growth and fight climate change, providing a way to a cleaner energy future.

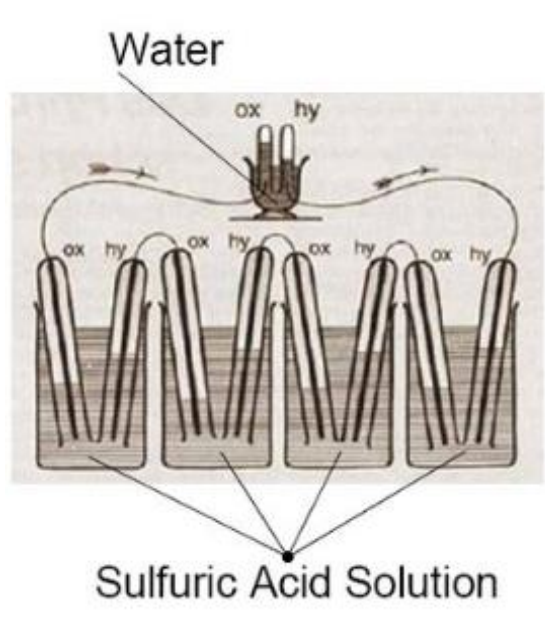


Figure 2. Sketch of Sir William Grove's fuel cell [58].

Chapter 2

2.1 Electrochemistry

Electrochemistry is a scientific field, which combines the branches of chemistry and electricity. In recent years, electrochemistry has undergone significant development and is at the centre of attention in both academia and industry. This development is mainly due to environmental awareness but also to the need that has arisen for advanced energy storage solutions due to the demand of large electrical loads. In particular, electrochemistry focuses on methods by which electricity is either used to trigger chemical reactions (e.g. electrolysis) or produced by them (e.g. fuel cells, batteries) [6].

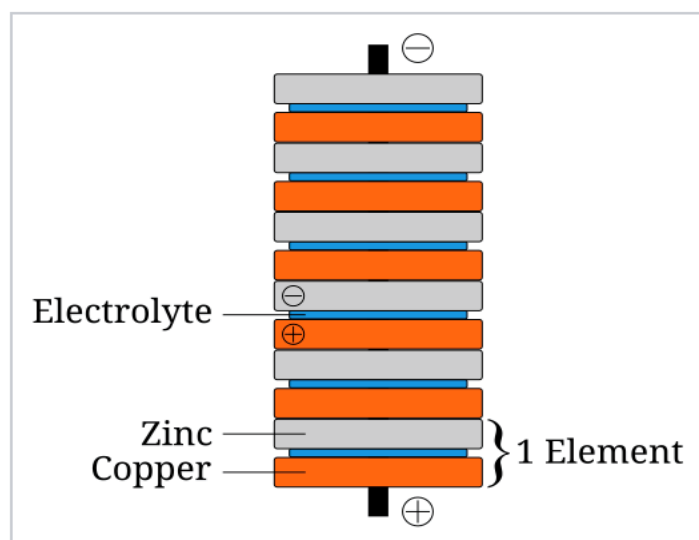
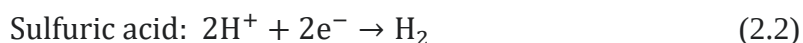


Figure 3. A voltaic pile [8].

From the 18th century onwards, several scientists tried to study the relationship between electricity and chemistry. The first experiment was carried out in 1781 by Italian physicist Luigi Galvani. When the nerve of a frog accidentally came into contact with a knife, muscle contraction occurred despite the fact that the frog was not connected to any electrical machine. Then, in an effort to investigate the cause further, he used two rods, one made of lead and the other of iron and connected them to the frog's legs. From this experiment, Galvani concluded that contractions are caused by the flow of electricity created due to the contact of the two metals and that when a contraction occurs, a neuroelectric fluid is channeled from nerves to muscle. The phenomenon was called the "electrical force of animal organisms" [7]. The baton was taken by the Italian physicist Alessandro Volta, who in 1800 managed to build the first

electric (voltaic) column (**Figure 3**), known today as the battery. This battery is counted as the first electrochemical cell and consists of two electrodes, one made of zinc and the other of copper. Its electrolyte is either sulfuric acid mixed with water or brine, i.e. water containing a large percentage of salt (usually NaCl). Since the electrolyte is mixed with water, it dissociates into hydrogen ions (H^+) and sulfate ions (SO_4^{2-}). Zinc, because of it is higher in the electrochemical series of metals than both hydrogen and copper, is oxidized to zinc cations (Zn^{2+}) and creates electrons that are directed to the other electrode, that of copper. The positively charged hydrogen ions bind electrons from the copper electrode, resulting in bubbles of hydrogen gas (H_2). Therefore, the zinc rod acts as a negative electrode, while the copper rod acts as a positive. By connecting the two electrodes, an electrical circuit is formed and an electric current flow. The chemical reactions in this voltaic cell are as follows:



Copper, which does not take part in a chemical reaction, acts as a catalyst that contributes to the formation of hydrogen gas and at the same time as an electrode that allows electric current to flow through it. Despite its drawbacks, Volta's discovery inspired many scientists who, building on his ideas, proceeded to further research that led to significant progress in the development of batteries. Few weeks after Volta's invention William Nicholson and Anthony Carlisle after conducted a lot of experiments revealed that when electrical current permeates water, it creates gaseous bubbles of H_2 and O_2 . The electrode potential exceeded 1.5V (the thermodynamic potential), and Pt was used as the electrocatalyst to minimize kinetic losses. This marked the first case where chemical materials altered their identity as distinct substances, laying the foundation for catalysis [8-10].

The field of electrochemistry examines the phenomena (e.g. chemical reactions) that occur at the contact surface between an electron conductor (electrode) and an ion conductor (electrolyte solution). Electrochemistry also deals with issues related to the structure of solid electrolytes and the behavior of ions in solutions. The five main fields in which the science of electrochemistry is applied are: Production of chemicals through catalytic reactions, Generation and storage of electricity, Corrosion protection, Environmental applications and analyses and sensors [11].

2.2 Electrochemical Cell

2.2.1 Description of Electrochemical Cells

Electrochemical cells are one of the fundamental discoveries of electrochemistry and represent how the principles of this science are applied. In their general form they consist of two electron conductors which are connected to each other by another electron conductor, while they are separated by an ionic conductor. These devices are divided into two categories. The first is galvanic cells, and the second is electrolytic cells. Both cells are represented in **Figure 5**. In the former, electricity is generated by chemical reactions, while in the latter, electricity is applied to trigger chemical reactions. In galvanic cells, redox reactions take place on the surface of the two electrodes. One takes place on the anode and the other on the cathode. The electrode on which oxidation takes place is called the anode while the electrode on which the reduction takes place is called the cathode. The anode is the negative pole for a galvanic cell, since during oxidation electrons are left behind in the electrode, and the positive pole for an electrolytic cell, because in electrolysis the electric current applied externally stimulates the flow of electrons in the opposite direction to that of the galvanic cell. For the cathode, exactly the opposite applies, it is the positive electrode in a galvanic cell and the negative in an electrolytic cell. A liquid/solid solution called an electrolyte is inserted between the anode and cathode, allowing ions (either positively or negatively charged), but not electrons, to move between the two electrodes, allowing electrochemical reactions to be completed [12], [13]. In order to better understand the above, it would be helpful to introduce and describe some basic terms:

- **Conductor:** It is the material that allows the free movement of either ions or electric charges through it resulting in the flow of electric current. There are three categories of conductors: ionic (which carries charge through ions), electronic (which carries charge through electrons) and mixed conductors (which combine the flow of ions and electrons) [14].
- **Electrode:** It is a conductive electrical surface that comes into contact with the non-metallic parts of an electrochemical element such as an electrolyte. Electrodes are very important for performing electrochemical reactions, which are responsible for creating or storing energy. Each electrochemical cell consists of two electrodes, the anode and the cathode, which have different functions. As mentioned above, oxidation takes place at the anode while at the cathode the reduction.

- **Redox**: Redox refers to chemical reactions where two processes occur simultaneously: electron loss (oxidation) and electron acquisition (reduction) as shown in **Figure 4**.
- **Half-cell reaction**: It is either the oxidative or reducing reaction that is part of a complete oxidation-reduction reaction (redox). This reaction is determined by the change in the oxidation states of the substances involved in the reaction, looking at how the atoms or ions change during the reaction [11].

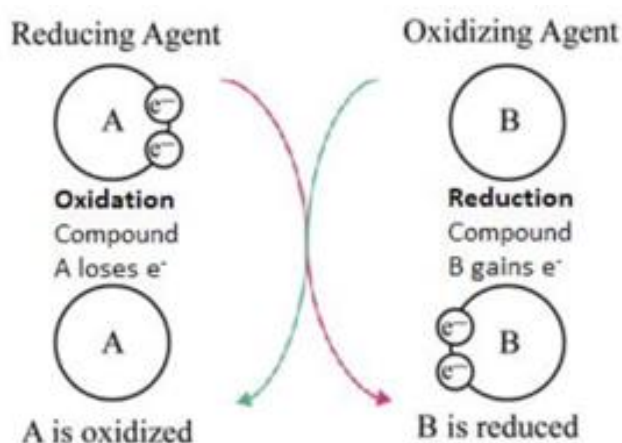


Figure 4. Illustration of a redox .

In an electrochemical cell, two complementary processes, known as redox reactions, occur simultaneously. Equation (2.3) below represents the redox reaction at equilibrium.:



where O is the oxidized species, R is the reduced species and n is the number of electrons exchanged between O and R.

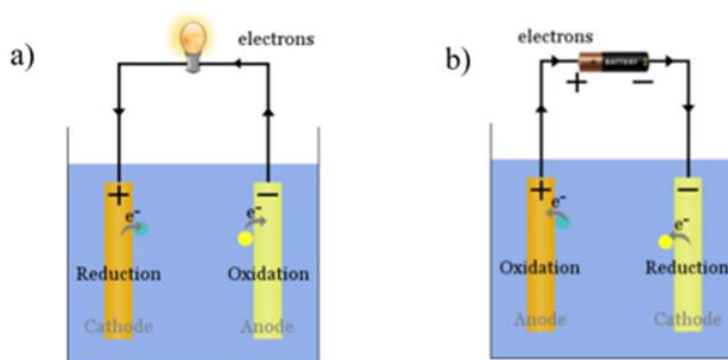


Figure 5. a) galvanic and b) electrolytic cell.

Equation (2.4) shows the relationship between Gibbs energy and concentrations of oxidized and reduced species.

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{[R]}{[O]} \right) \quad (2.4)$$

In the above equation the symbol T expresses the temperature in Kelvin [K], R is the universal constant of gases ($8.3145 \text{ J/mol}^{-1} \text{ K}^{-1}$) and [O] are the concentrations of oxidized and [R] of reduced species. The main point of this equation is that it creates a new relationship between the Gibbs energy change and the reaction potential E, as illustrated in equation (2.5).

$$\Delta G = -nFE \quad (2.5)$$

Here ΔG represents the change of Gibbs free energy in a reaction under real system conditions, E is the maximum potential between the electrodes when no current passes through the electrochemical cell, and F is Faraday's constant ($96.485 \text{ C mol}^{-1}$). However, when the reaction takes place under standard conditions (1 atm pressure for gases, 1 M concentration for solutions, 298 K temperature), equation (2.5) is written as:

$$\Delta G^\circ = -nFE^\circ \quad (2.6)$$

Here, E° refers to the standard potential of the electrode, and ΔG° is the change in Gibbs free energy in standard conditions. A basic principle of electrochemistry is the Nernst mathematical equation which links the potential to the concentration of oxidized and reduced species.

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (2.7)$$

The potential of an electrochemical cell is calculated from the equation:

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \quad (2.8)$$

Also worth mentioning is the term electromotive force (emf, ϵ) which represents the maximum potential when the circuit is open and measured in Volts. Due to oxidation and reduction reactions, the transition to emf involves changes in the signs of the terms and results in the equation below:

$$\epsilon_{\text{cell}} = \epsilon_{\text{anode}} + \epsilon_{\text{cathode}} \quad (2.9)$$

Whether a reaction is spontaneous or not is determined by the sign of the electromotive force (emf). This is because of the relationship between emf and Gibbs free energy (ΔG). Specifically, when emf is positive, the Gibbs free energy change (ΔG) is negative (there is a net release of free energy) which indicates a spontaneous reaction. Whereas if emf is negative, then ΔG is positive, which indicates that energy is absorbed, and the reaction is not spontaneous.

2.2.2 Kinetics of a chemical reaction

The kinetics of chemical reactions is a field that deals with the study of the conversion rates of reactants of a chemical reaction into products. It is very important for determining the amount of electricity that can be generated with a standard amount of overpotential. In redox reactions, besides chemical reactions, there is also the process of mass transfer, which plays a decisive role in the completion of the reaction. Electrochemical reactions are heterogeneous processes, which means that they take place in different phases or materials. Therefore, it is necessary to consider convection phenomena as well, starting with the overpotential, which affects the reaction efficiency, and the electricity produced [11].

2.2.3 Overpotential

The potential of an electrochemical cell is theoretically calculated under the assumption that the system is in a state of equilibrium. Reactions on the electrode surfaces are conducted at finite rates and sometimes even high reaction rates are required. A typical example is the batteries of modern electric vehicles in which fast charging and discharging is one of the most important requirements. For this to occur, the reactions in the electrochemical cell must take place at very high currents, which leads to the system deviating from the equilibrium state and the displacement of the actual cell potential (E) from the equilibrium value (E^0). This phenomenon is called polarization and thus the overpotential is created, which is expressed as:

$$\eta = E - E^0 \quad (2.10)$$

where η is the overpotential, E is the actual potential (the voltage applied to the cell to advance the reaction) and E^0 is the theoretical or equilibrium potential of the reaction (the potential that would be required in the absence of resistances and kinetic constraints). Essentially the overpotential is the additional energy (voltage) that must be applied in order to overcome energy barriers and losses in the process of transferring electrons and ions between the electrodes and the electrolyte. By applying this additional stress, it becomes possible to overcome motor obstacles, allowing reactions to be performed at a satisfactory speed. The relationship between current and potential in an electrochemical cell is described through the polarization curve illustrated in **Figure 6**. The magnitude of the overpotential depends on several factors, such as the geometry and size of the electrodes, the concentration and composition of the electrolyte, the temperature, as well as the density of the current applied. Each of these factors can affect the overall performance of the cell and require further improvements in system design and operation.

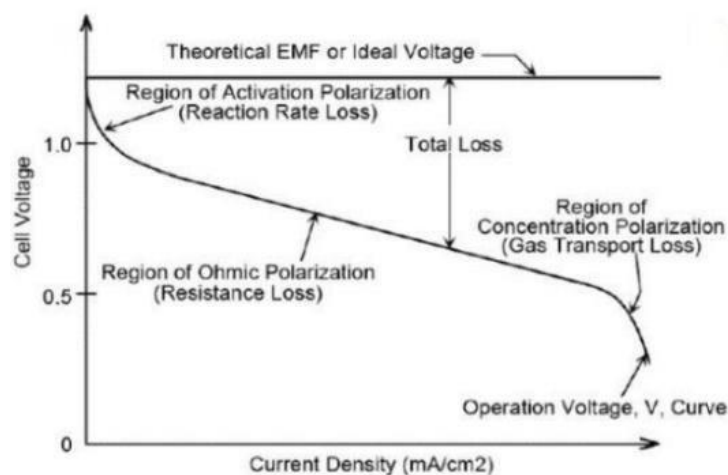


Figure 6. Typical curve of electrochemical cell overpotential.

The function of overpotential differs between the two types of electrochemical cells. Specifically in electrolytic cells, the presence of overpotential means that the energy required for the reaction must be greater than thermodynamically expected. In contrast, in galvanic cells, losses due to overpotential during reaction result in less energy being produced than would theoretically be possible. In both cases the extra/missing energy is lost in the form of heat.

- In **Electrolytic cells**: $E > E^0$ to overcome obstacles.
- In **Galvanic cells**: $E < E^0$ due to losses.

The main goal of the overpotential is to get as close as possible to the ideal voltage line, as shown in **Figure 6**. The blank region between the actual curve and the ideal voltage line (or emf line) represents entropy and corresponds to the losses of the system. Entropy increases every time an isolated system undergoes some change. This change is identified with thermal energy that can no longer be converted into useful work. In particular, when energy losses are limited, the curve shifts upwards, which leads to a decrease in entropy. Overpotential is divided into three main categories and equals the sum of these [11], [15]. In other words, it applies:

$$\eta = \eta_a + \eta_{con} + \eta_{ohm} \quad (2.11)$$

1. Activation Overpotential (η_{act} , η_a)

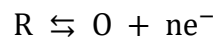
The activation overpotential η_a , also called the surface overpotential, is the resistance that occurs at the surface of an electrode when many chemical reactions take place and electrons are transferred. This resistance is created due to the need to overcome an energy barrier to initiate the electrochemical reaction. Electrons often accumulate on the electrode blocking the entry of new incoming electrons so that they cannot be transferred from anode to cathode.

Therefore, the efficiency of the cell is reduced. Certain chemical reactions that act on the electrode such as catalytic decomposition and crystallization can increase the overpotential, making the electrochemical process more difficult. In general, the activation overpotential is the most important form of voltage loss, as it reflects the additional energy required to overcome barriers and achieve the desired current density in the system.

The η_a consists of $\eta_{a, \text{anode}}$ the anode activation overpotential, and $\eta_{a, \text{cathode}}$ the cathode activation overpotential, such that:

$$\eta_a = \eta_{a, \text{cathode}} + \eta_{a, \text{anode}} \quad (2.12)$$

Assuming the first-order electrode reaction (2.3) mentioned above:



When mass transfer is not a rate-limiting step in the electrochemical reaction, i.e. the system is not limited by diffusion, migration or convection, then the Butler-Volmer equation describes the relationship between the current, i , and the activation overpotential, η_a , as shown below by Equation (2.13) :

$$i = i_0 \left[e^{\frac{-\alpha n F \eta_a}{RT}} - e^{\frac{(1-\alpha) n F \eta_a}{RT}} \right] \quad (2.13)$$

i_0 is the current exchange between oxidation and reduction processes at an electrode, α is the transfer coefficient, F is Faraday's constant, T temperature (Kelvin), R the global gas constant and n the number of electrons transferred. The first term of the equation represents the rate of the anodic direction while the second term is the rate of the cathodic direction. In general, the higher the exchange current, the faster the reaction to the electrode. The transfer coefficient, for its part, determines the geometry of the energy barrier, indicates whether the reaction at the electrode tends to proceed in the upward or downward direction under the influence of the applied potential. In sufficiently small activation overpotentials, according to the Taylor series spread of the exponential function, the Butler–Volmer equation is approximated as follows:

$$i = i_0 \frac{n F \eta_a}{RT} \quad (2.14)$$

This relationship indicates that there is a linear relationship between the i current and the overpotential activation η_a at potential values close to the equilibrium potential. The slope shown in the line diagram is called load transfer resistance, denoted as R_{ct} and describes how easily the reaction takes place in the cell from a kinetic point of view. Specifically, R_{ct} is given by the formula:

$$R_{ct} = \frac{RT}{n F i_0} \quad (2.15)$$

At high activation overpotentials one of the two terms in equation (2.16) can be omitted, since they are negligible. Therefore, the equation becomes:

$$i = i_0 e^{\frac{-\alpha n F \eta_a}{RT}} \quad (2.16)$$

Taking the logarithm of equation (2.16) and solving for η_a we arrive at the following expression, which represents the activation overpotential.

$$\eta_{act} = \eta_a = \frac{RT}{\alpha n F} \ln\left(\frac{i_0}{i}\right) = \frac{RT}{\alpha n F} \ln(i_0) - \frac{RT}{\alpha n F} \ln(i) = a + b \ln(i) \quad (2.17)$$

The above relationship is called the Tafel equation and was established in 1905 by Swiss chemist Julius Tafel. In equation (2.17) the $a = \frac{RT}{\alpha n F} \ln(i_0)$ and the $b = -\frac{RT}{\alpha n F}$. Specifically, a denotes the overpotential at unit current density while b is the Tafel slope, which denotes the rate of change of the overpotential as a function of the logarithm of the current density. **Figure 7** illustrates a typical Tafel diagram [15].

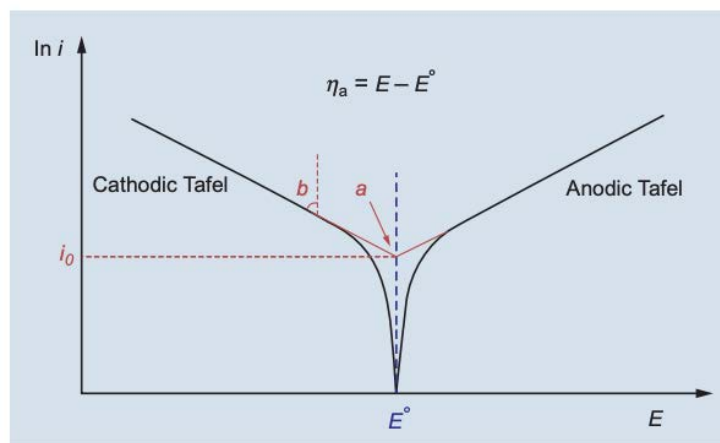


Figure 7. A typical Tafel plot for the electrode reaction: $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$ [15].

2. Ohmic Overpotential (η_{ohm})

The ohmic overpotential refers to the sum of the resistances of the components that make up an electrochemical cell, such as the resistance of the electrolyte, the electrodes and any other conductive parts of the system. This type of overpotential is mainly due to the ionic resistance rather than the electronic resistance since it is most often higher, except in cases where semiconducting materials are present or there is a passive membrane coating on the electrode. The ohmic losses are usually due to the resistance of the electrolyte and much less to those of the interconnecting conductors (at least for metallic elements) and electrodes. When the electrolyte is in the form of a membrane (e.g. in fuel cells with a polymer electrolyte membrane), the movement of ions across the membrane is affected by the distance between

the electrodes and the conductivity of the solution. In particular, as the distance between the two electrodes decreases, the resistance decreases. Unlike other forms of resistance (such as the activation overpotential), the ohmic resistance is independent of the rate of chemical reactions. The ohmic overpotential leads to a reduction in the total voltage available for useful electrochemical reactions, thus reducing the efficiency of the cell. Furthermore, the energy lost due to it, is converted into heat, which can cause a temperature rise in the system and degrade the components of the electrochemical cell. The ohmic overpotential is usually linear and can be described by Ohm's law:

$$\eta_{\text{ohm}} = iR_{\text{ohm}} \quad (2.18)$$

Where R_{ohm} is the resistance (electronic and/or ionic) and i is the current applied to the cell. But when local changes in conductivity are observed, this don't happen often, an Arrhenius equation is used to model losses over a wide temperature range:

$$R_{\text{ohm}}(T) = \frac{T}{B_{\text{ohm}}} e^{\frac{E_{\text{act}}}{RT}} \quad (2.19)$$

Where B_{ohm} is a constant related to the specific conductivity of the material and E_{act} is the activation energy for charge transfer [11], [15], [16].

3. Concentration Overpotential (η_{con})

This type of overpotential refers to the loss of voltage due to the difference in concentration between ions or molecules (reactants or products) in the bulk electrolyte and on the electrode surface as the reaction progresses. Essentially, the concentration overpotential represents resistance due to mass transfer within the electrochemical cell and occurs when the reaction of the cell is fast enough while mass transfer is relatively slow. In particular, the mass transfer process fails to provide the necessary rate of reactant delivery or product removal, especially at high current densities, resulting in depletion of reactants and accumulation of products on the electrode surface. There are three mass transfer mechanisms (**Figure 8**). The first is diffusion, a process in which a species moves from areas of high concentration to areas of lower concentration due to the difference in concentration between the two regions (concentration gradient). The second mechanism is migration, i.e. the motion of a charged species driven by an electric field created by differences in electric potential gradient. The third one is convection which is the movement of a species imposed by the bulk fluid electrolyte. This movement occurs due to the imbalance of forces in electrolyte such as hydrodynamic forces (density gradient) or external forces (stirring). It is important to mention that applying forced flow can

significantly improve the mass transfer of electroactive materials to an electrochemical cell. A prime example is the use of flow-through electrolytes from redox flow batteries. (flowing electrolytes by redox flow batteries).

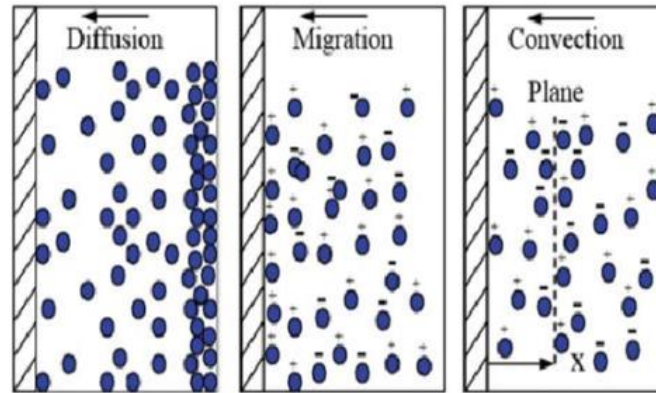


Figure 8. The 3 main types of mass transfer [11].

The mass transfer of a species from the bulk electrolyte to the electrode is described by the Nernst-Planck equation:

$$J_i = D_i \nabla c_i - u_i c_i \nabla \Phi + c_i v \quad (2.20)$$

Where J_i is the net flux density of the species i , D_i is the diffusion coefficient of i , ($\text{cm}^2 \text{s}^{-1}$), c_i is the concentration of i , $u_i = \frac{D_i n_i F}{RT}$ is the ionic mobility which relates to how fast the species moves in response to the electric field, ∇c_i is the concentration gradient, $\nabla \Phi$ the electric potential gradient and v is the speed of the bulk electrolyte. The first term on the right side of the Nernst-Planck equation represents the contribution of diffusion to the flow of the species, illustrated by Fick's first law, while the second and third terms describe the contribution of the other two mass transfer mechanisms, namely migration and convection, respectively.

Let's consider a reaction that takes place on the electrode and is controlled by mass transfer (rather than charge transfer). If the kinetics of electron transfer in this reaction are fast, the surface concentration of the reactant decreases with increasing current, because the reactant is consumed at a faster rate. At a certain current value, the moment the reactant reaches the electrode it is consumed immediately and its surface concentration is zero. This critical value of current is called the limit current. Under the application of the limit current, the reaction on the electrode surface is performed at the maximum rate for a given set of mass transfer conditions. For a diffusion-controlled electrode reaction, the limit current density is given by the following formula:

$$i_l = \frac{nFDc^*}{\delta} \quad (2.21)$$

where D is the diffusion coefficient of the reactant, c^* is the bulk concentration of the reactant and δ is the thickness of the diffusion layer. At a certain current value, i , the surface concentration of the reactant, c , is expressed as:

$$c = \frac{i_l - i}{i_l} \quad (2.22)$$

When there are low current densities the concentration overpotential is smaller than ohmic overpotential or activation overpotential and is omitted in these cases. However, at high current densities it occupies a dominant position and affects the performance of the system. The concentration overpotential is equal to the sum of the concentration overpotentials at the anode and cathode, $\eta_{\text{con,a}}$ and $\eta_{\text{con,c}}$, respectively: $\eta_{\text{con}} = \eta_{\text{con,a}} + \eta_{\text{con,c}}$.

$$\eta_{\text{con,a}} = \frac{RT}{nF} \ln \left[\frac{i_{l,\text{anode}}}{i_{l,\text{anode}} - i} \right] \quad (2.23)$$

$$\eta_{\text{con,c}} = \frac{RT}{nF} \ln \left[\frac{i_{l,\text{cathode}}}{i_{l,\text{cathode}} - i} \right] \quad (2.24)$$

where $i_{l,\text{anode}}$ and $i_{l,\text{cathode}}$ are the limit current densities at the anode and cathode respectively [15], [17].

2.2.4 Electrical Double Layer

When an electrode is immersed in an electrolyte solution, a specific region forms at their interface, known as the electrical double layer. This layer is characterized by unique electrical properties that play a critical role in the accuracy of electrochemical measurements. Additionally, it is crucial for studying electrode kinetics, as it influences the electron transfer rate. Every reaction occurring on the electrode surface is an interfacial (heterogeneous) reaction, meaning it takes place between two phases. The completion of such reactions requires the transfer of electrical charge as well as a series of rearrangements of the electrolyte reactants prior to discharge on the electrode surface. Any charged solid surface, such as a metal electrode immersed in a liquid electrolyte, requires the presence of nearby compensating charges for charge balance. However, when the two phases come into close contact, tension arises at their interface due to the potential difference between them. This results in a spontaneous organization of charges at the electrode-electrolyte interface. The high dielectric constant of water facilitates charge dispersion in the liquid environment, causing many molecules to acquire negative charges when distributed within it. The ions in the solution, attracted to the charge on the surface of metal electrodes, accumulate around the particles in the liquid. This leads to the formation of a well-organized, stable surface layer of cations that neutralizes the initial charge of the electrode, namely its anionic surface. When the surface of a metal accumulates

a significant amount of charge, an additional layer is created due to the lower adhesion of the molecules to this area (lower attractive force). This second layer is called the diffusion layer and exhibits a disorder in its internal structure. These two layers, namely the stable layer and the diffusion layer, together make up the double electrical layer as represented in **Figure 9 b**).

The electrical double layer has been shown to behave as a typical electrical capacitor. The models used to explain the behavior of this interface are based on principles that are like those that describe the operation of a capacitor, namely the storage and exchange of charge on the two surfaces of the "capacitor" (one on the electrode and the other in the electrolyte solution). **Figure 9 a**) illustrates a specific situation where the electrochemical cell is represented by an electrical circuit, and the capacitor C_d corresponds to the differential capacitance resulting from the double layer at the electrode-solution interface. To achieve the desired potential at the working electrodes, the double layer capacitor must first be charged, causing a capacitive current to flow in the circuit. This current is not directly related to the oxidation or reduction of the substrates, although it contains information about the structure and properties of the electric double layer. Despite the existence of several theoretical models for the double layer, there is no generally accepted model that covers all cases. This is because the structure of the double layer and its capacitance depend on several factors, such as the electrode material (e.g. metals, carbon types, semiconductors, materials porosity, the presence of layers of either oxides or polymer films or other solid materials on the surface), the type of solvent, the supporting electrolyte, the specific adsorption of ions or molecules and the temperature. As mentioned above, the composition of the double layer has a significant effect on the rate of electron transfer. For example, in the case of heterogeneous electrocatalysis, ions and molecules adsorbed on the electrode surface accelerate the rate at which the process takes place at the electrode. On the contrary, there are compounds that, after adsorption, slow down the electron transfer, acting as inhibitors of the electrochemical process. For any given potential imposed by an external source (potentiostat/voltammograph) on a metal electrode, a charge is created on both the electrode and the solution. The charge on the electrode, Q_{el} , and the charge on the solution, Q_s , are determined by the voltage applied to the system and the composition of the solution. These characteristics determine whether the charge on the electrode is positive or negative with respect to the solution. In general, the charge on the electrode is always equal and opposite to that in the solution $Q_{el} = -Q_s$. The charge of the electrode is directly related to the capacitance of the interface. There are two basic approaches that can be used to describe the capacitance of an electrode.

- **The differential capacitance, C_d** : It describes how vulnerable the charge of the electrode surface is to small changes in voltage. In the case of the potential of zero charge, the total net charge on the electrode surface is zero, reflecting a balanced state without a surplus of positive or negative charges. The differential capacity is also minimized to the zero-load potential. This is easily evident from the equation (2.25) that describes it:

$$C_d = \frac{\partial Q_{el}}{\partial E} \quad (2.25)$$

- **The integral capacitance, C_i** : Expresses the total ability of an electrode to store a charge relative to the applied voltage. It is described by the equation (2.26) :

$$C_i = \frac{Q_{el}}{E - E_{Q=0}} \quad (2.26)$$

The extra charge accumulated on a metal electrode depends on its potential. In the case of mercury electrodes, this behavior is described more simply, as excess charge has a significant effect on the surface tension of mercury and thus the latter can be easily measured through experiments. One of the basic measurement methods involves calculating the time required for drops of mercury to fall from an electrode that is immersed in electrolyte solution. The relationship between the surface tension of mercury and the potential is usually represented by a parabolic curve, to which the maximum point corresponds to the zero-charge potential, $E_Q = 0$ [11], [18].

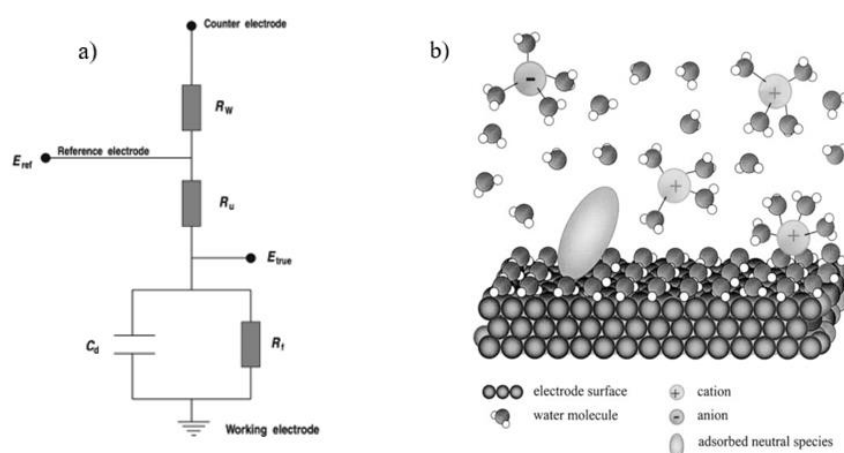


Figure 9. a) A simple electronic scheme equivalent to the electrochemical cell. R_u , resistance uncompensated in the regular three-electrode system. C_d , differential capacity of the double layer. R_f , resistance to faradaic current at the electrode surface, R , solution resistance compensated in the three-electrode b) General representation of the double layer the double layer formed at the metal–electrolyte interface.

2.3 Catalysis

2.3.1 Fundamentals of catalysis

Although some chemical processes are thermodynamically feasible, they cannot be carried out at a satisfactory rate on their own, i.e. without some external intervention. The main factors determining a reaction are temperature, pressure, concentration of reactants and duration of contact. In most industrial applications, reactions are carried out at high temperatures and pressures, to speed up processes and achieve desired production levels. However, the implementation of the above conditions is accompanied by serious problems such as wear and corrosion of equipment, while at the same time large amounts of energy are required and often lead to the creation of unwanted by-products or reactions. To address these challenges, catalysis technology has been developed. This technology refers to the action of substances (catalysts), which accelerate the rate of a chemical reaction while remaining unchanged and not consumed during it. The reaction rate is determined by the energy path followed to convert the reactants into products. Catalysts in particular contribute to improving process efficiency in terms of production as well as energy consumption, by providing an alternative energy pathway. They essentially reduce the activation energy required to perform the reaction, thus making it easier to switch from reactants to products and vice versa. The catalyzed pathway requires a lower activation energy than the non-catalyzed pathway, resulting in more molecules having sufficient energy to react effectively, as shown in **Figure 10**. From the diagram in **Figure 10** we observe that the presence of a catalyst does not affect the energy of the reactants (initial state) or products (final state). Therefore, the ΔE remains constant. More specifically, free energy and enthalpy are not affected by the presence of the catalyst [19], [20].

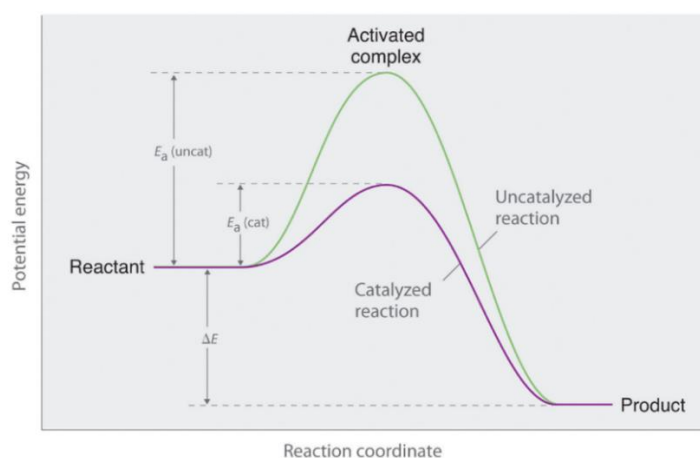


Figure 10. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of catalyst [134].

Catalysis is divided into two main categories: homogeneous and heterogeneous catalysis. In the first category, the catalyst is in the same phase as the reactants, usually in solution. The catalysts used in this category, known as homogeneous catalysts, are defined chemical compounds, such as molecules, ions or enzymes, that are evenly distributed in the solution. During homogeneous catalysis, the catalyst interacts with one of the reactants, forming a temporary intermediate, which then breaks down or reacts with another reactant. After one or more reactions, the catalyst is recreated and the final product is produced. In contrast to heterogeneous or otherwise surface catalysis, the catalyst is in a different phase from the reaction reactants and the process of catalysis takes place mainly between a solid surface and a gas. In this category, catalytic activity is located only at specific points on the catalytic surface, also known as active sites, and the reactive molecules are adsorbed from the solid surface before the reaction with the catalyst takes place to produce the product [21]. Active site is a very important concept for understanding the mechanism of heterogeneous catalysis. It essentially consists of an atom or a group of atoms on the surface of the catalyst that act as the point of action for the catalytic reaction. The number of accessible active sites (depending on the catalyst material) per unit area or volume of the catalyst is what determines the performance of the catalytic process. In particular, an increase in the number of active sites entails an increase in the accessible area, which in turn increases the overall activity and rate of reaction, leading to improved catalyst performance. For this reason, catalysts are often designed with a porous honeycomb-like structure to enhance their performance in surface reactions [22].

Below will be a more extensive description of the process followed in heterogeneous catalysis. First, adsorption of reactants on the surface of the catalyst is carried out. In this first stage the initial bonds are broken and new bonds are formed in cooperation with the active sites of the catalyst. This is followed by the activation of the adsorbed reactants and immediately after that the chemical reaction of the adsorbed molecules takes place. In the last stage, the products created diffuse from the surface in the gas or liquid phase (desorption), completing the catalytic process [11], [19].

2.3.2 Figures of Merit

The three basic parameters (Figures of Merit) that determine the performance of a catalyst are Activity, Stability, Selectivity. These parameters must always be considered when choosing the right catalyst.

Activity: It is related to the ability of a catalyst to accelerate a chemical reaction. It usually represents the rate of reaction per unit mass of catalyst or per unit of active area. It is determined by the rate at which products are formed or the rate at which reactants are eliminated and is described by the relationship below.

$$r = \frac{1}{v_i N} \frac{dn_i}{dt} \quad (2.27)$$

Where v_i is the stoichiometric coefficient of the reactant, n_i is the number of moles reactant, t is the time and N is the volume, weight or surface area of the catalyst. The main factors affecting the activity of the catalyst are the catalytic structure, chemical composition and interaction with the reactants.

Selectivity: It is the ability of the catalyst to direct a reaction in such a way as to promote a particular product over other thermodynamically feasible but undesirable products. This ability results in increased energy efficiency of the process. In other words, the catalyst can amplify a specific reaction while preventing the occurrence of other unwanted side reactions. Instead of having only one energy barrier resulting from the activation energy for the formation of a product, multiple energy barriers are observed, with small energy differences. Organic reactions catalyzed by platinum and rhodium at temperatures below 600 K were selected to perform an experiment, usually leading to the formation of two different product molecules.

Figure 11 shows the potential-energy diagram for the competitive formation of two products. The relative energy difference required to overcome activation barriers is the key factor determining reaction selectivity. Even very small energy changes, e.g. of the order of 2 kcal/mol, can cause drastic changes in product distribution, as shown in **Figure 11**. These changes are due to factors such as co-adsorbents, minor structural modifications or the addition of substances that act as electron donors or acceptors and affect the binding energies of reaction intermediates or adsorbed reactants or products. The heights of activation barriers are greatly influenced by the molecular structure and electronic and chemical properties of catalytic surfaces. Research shows that the size and shape of nanoparticles play a key role in selectivity, as surface configuration is directly affected by these characteristics. Beyond the catalysts themselves, factors such as the type of reaction as well as the conditions (temperature, pressure, reaction time and nature of the catalyst carrier) under which the reaction is carried out alter the intermediate products of the reaction and surface mobility (since different paths are followed during multimodal catalytic reactions) thus affecting selectivity. At the molecular level, the main parameters that determine the difference in the heights of the trigger barriers and allow

the selectivity of a reaction to be adjusted are the mobility of adsorbed substances, surface structure, surface composition, oxidation state of catalyst, intermediate reaction products and charge transfer during catalysis [23]. A way to assess the ability of a catalyst to accelerate a reaction in a particular direction, for instance we want product B to be produced from A ($A \rightarrow B$), is the input of the Y_B parameter. This parameter represents selectivity with respect to product B and is given by:

$$Y_B = \frac{C_B}{C_{A0}} \quad (2.28)$$

In the above equation C_B denotes the concentration of product B while C_{A0} denotes the initial concentration of A. Efficiency B is another parameter used to evaluate catalysts. This yield is expressed by means of the following formula:

$$S_B = \frac{C_B}{C_{A0} - C_A} \quad (2.29)$$

Where C_A indicates the concentration of A after reaction [11].

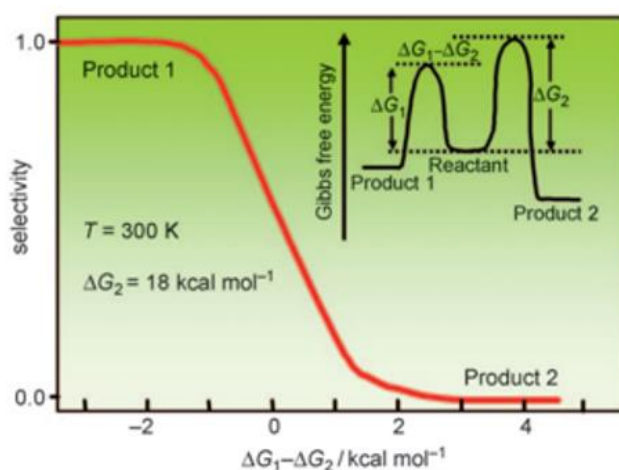


Figure 11. The relative heights of the activation barriers for different reactions determine the selectivity of catalytic processes.

Stability: Stability describes the catalyst's ability to remain durable and maintain its performance over time. The drop in performance is due to phenomena such as loss of deactivation, which is one of the main problems encountered in heterogeneous catalysis. The deactivation of the catalyst is due to both chemical and physical factors and can only be avoided or slowed down and thus prevented some of its serious implications. Two very important characteristics of catalysts are Turnover Number (TON) and Turnover Frequency (TOF). Without them it would not be possible to make a quantitative comparison of the performance of different catalysts and therefore an accurate assessment of their activity would not be

possible. TON is a dimensionless number in both homogeneous and heterogeneous catalysis and is defined as the number of product molecules formed per one catalytic position before complete deactivation of the catalyst, i.e. to the point where a catalyst can no longer catalyze. TON is described by the equation:

$$\text{TON} = \frac{N}{n_a} \quad (2.30)$$

Here N is the number of reactants converted, or products produced and n_a is the number of active sites of the catalyst. The TOF is given by:

$$\text{TOF} = \frac{N}{t \cdot n_a} \quad (2.31)$$

Where t is the time of reaction [24]. The main mechanisms that cause the deactivation process in heterogeneous catalysis are poisoning, coking, sintering and phase transformation.

1. **Poisoning:** Poisoning refers to the loss of catalyst activity due to the strong chemisorption of reactants, products or impurities in the active sites available for catalysis. An example of this phenomenon is the adsorption of a basic compound into an acid catalyst (e.g. isomerization catalyst). Poisons usually act in two ways: either by directly blocking an active site (geometric effect) or by altering the ability of other species to be adsorbed through an electronic interaction. Whether a substance acts as a poison depends on the strength at which it is adsorbed, compared to other substances competing for active catalyst sites. For example, oxygen can act as a reactant to the partial oxidation of ethylene to ethylene oxide using a silver catalyst, while in the process of hydrogenation of ethylene with a nickel catalyst it can act as a poison. In addition, the phenomenon of poisoning affects the chemical composition of the active sites or causes the formation of new compounds, which can permanently alter the performance of the catalyst. Poisons are divided into selective or nonselective. In the first case the active sites on the catalyst surface have different characteristics (e.g. different strength in acidity). As a result, the sites that are most potent are poisoned first, thus causing complex relationships between the activity of the catalyst and the amount of poison adsorbed. Sometimes, however, this type of poisoning is desirable to regulate the selectivity of catalysis. In contrast, in the case of non-selective poisons, all sites on the surface of the catalyst are equally accessible by the poison, so adsorption occurs uniformly, and surface activity decreases linearly relative to the amount of venom adsorbed. A conceptual model of poisoning is illustrated in **Figure 12** [25], [26].

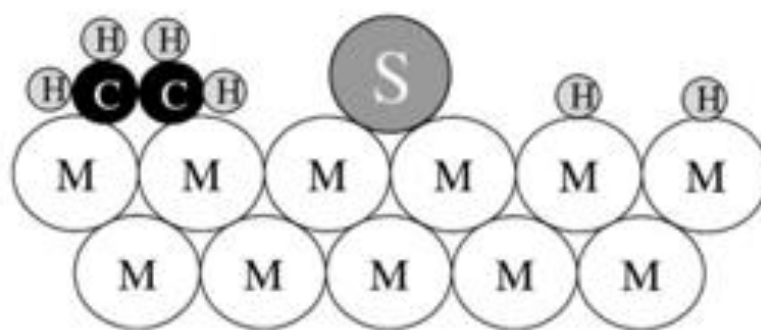


Figure 12. Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation.

2. **Coking:** It is commonly found in the oil industry, where catalytic reactions with hydrocarbons (or even carbon oxides) take place. During these reactions, carbon residues are formed due to the side reactions that take place on the surface of the catalyst. The carbonaceous residues then end up either covering the surface of the active centers or clogging the pores of the surface, thereby deactivating the catalyst. "Coke" deposits have the ability to reach up to 15% or even 20% (w/w) of the catalyst.
3. **Sintering:** It is a physical and thermally activated process in which the structural modifications that occur during the increase in temperature in catalytic reactions lead to a decrease in the active surface area of the catalyst. Sintering can occur either in supported metal catalysts (metal catalysts with support) or in unsupported ones (without support). In the former, the loss of active surface area is due to the fusion of smaller metal crystallites into larger ones, which reduces their surface area to volume ratio. Experimental data show that the sintering rates of supported metal catalysts depend to a large extent on temperature, but the effect of the atmosphere is not that significant. The sintering process in these catalysts is described by two general models. These are the atom transfer model and the crystallite transfer model. In the first model, the procedure followed is as follows. Initially, the metal atoms are removed from one crystallite, through the surface of the substrate or the gas phase and then trapped by another crystallite. This causes aggregation. In general, the size of the smaller crystallites decreases while the larger ones increase, because the larger crystallites are more stable (metal-metal bonds are usually stronger than metal-support bonds). The second model refers to the aggregation that occurs due to the movement of the crystallites along the surface of the support followed by collision between them and ultimately the merging of two crystallites, thus creating larger formations.

4. **Solid-state transformation:** It is a deactivation mechanism that is considered an extreme version of sintering. It occurs at high temperatures and causes the transition of one crystal phase to a different one. Such phenomena can be observed in both supported metal catalysts and catalysts based on metal oxides [25].

2.4 Electrocatalysis

2.4.1 Basics Principles in Electrocatalysis and Electrolysis

The main object of electrocatalysis study is the chemical reactions that take place at the interface between the electrode and the electrolyte, where breaks and bond formations occur. It is essentially a catalytic process in which redox reactions take place through the direct transfer of electrons and ions. The electrode material, which acts as an electrocatalyst, determines the rate of electron transfer in an electrocatalytic reaction, and is also used to reduce the overpotential of these reactions. It therefore requires the presence of electric current. Electrocatalysts, like all catalysts, are characterized by activity, selectivity and stability. In general, the electrocatalysis process facilitates the conversion between electrical and chemical energy both for the storage of electricity in the form of chemical energy (as in batteries, fuel cells and electrocatalytic devices) and for the production of chemicals through electricity supply, thus promoting the development of environmentally friendly technologies and supporting sustainable energy infrastructure. **Figure 14** Illustrates the three essential phases that take place during an electrocatalytic reaction. This technology aims to perform new reactions under the same potential without adversely affecting the rate of electron transfer. Electrolytic processes take place both at the anode and cathode of electrolysis devices and fuel cells. As for fuel cells, they rely on an exergonic reaction to convert chemical energy directly into electricity. In anode electrocatalytic processes, it is possible to use various fuels, such as methane, ammonia, alcohols, hydrogen and sugars. On the cathodic side, other oxidants, such as hydrogen peroxide (H_2O_2), can be harnessed, although using oxygen from the air is considered the most practical option for large-scale fuel cell applications. In proton exchange membrane (PEM) fuel cells (**Figure 13a**), hydrogen is oxidized at the anode, producing electrons and protons, while at the cathode oxygen is reduced to form water (H_2O) [27].

On the other hand, electrolysis technologies harness electricity to trigger endergonic reactions and break down substances (**Figure 13b**), such as splitting water into hydrogen and oxygen. During water electrolysis, hydrogen ions move to the cathode, gain electrons through reduction, and form hydrogen gas, while oxygen forms at the anode. Although this process is

promising for green hydrogen production, it remains expensive. Catalysts are essential to speed up these reactions. Platinum is widely used for hydrogen evolution reaction (HER), while iridium and ruthenium oxides are preferred for oxygen evolution reaction (OER). However, these catalysts are costly and limited to single reactions, prompting research into bifunctional catalysts that are efficient and affordable for both methods. Metallic glass (MG) electrodes are a promising option due to their resistance to acidic and alkaline conditions, but improving their performance is critical. Methods like de-alloying and material composition optimization are being used to enhance their surface area and efficiency. Transition metal-based catalysts, such as phosphides (e.g., Fe_xP , Co_xP , Ni_xP), nitrides, and oxides, are emerging as cost-effective alternatives to noble metals. Phosphides are particularly promising for HER due to their stability, conductivity, and fast charge transfer. Similarly, transition metal oxyhydroxides (e.g., MOOH) have shown strong performance for OER. Developing affordable, stable, and efficient catalysts for both reactions remains key to advancing water electrolysis and green hydrogen production [28-48].

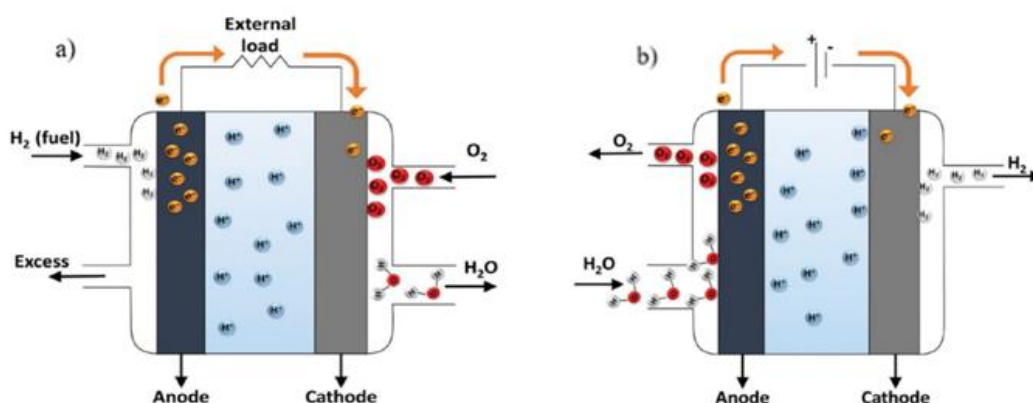


Figure 13. a) Diagram of a proton exchange membrane fuel cell system that converts exergonic H_2 and O_2 to water. b) Diagram of a proton exchange membrane fuel cell system, where a Hydrogen derived from endergonic water electrolysis [27].

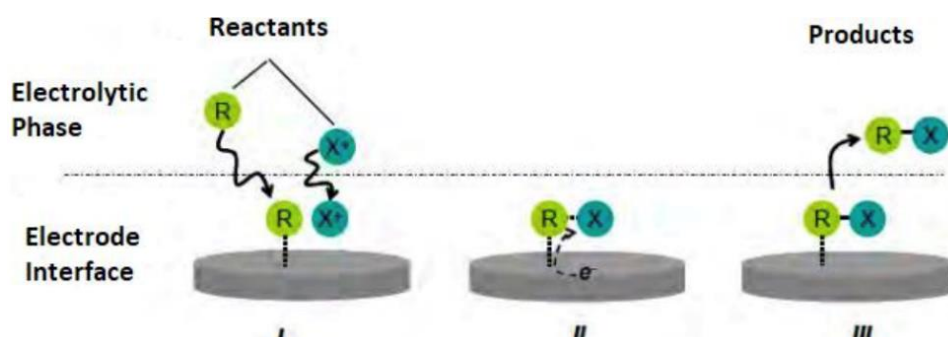


Figure 14. The three essential phases that take place during an electrocatalytic reaction: (I) transfer and adsorption of the reactants to the electrolyte-electrode interface (II) electron transfer between reactant and electrode, and (III) desorption of the formed products from the electrode surface [11].

2.5 Electrochemical Devices

Devices that have the ability to harness electrochemical energy and convert it into a useful form of energy are called electrochemical devices. These devices include one or more electrochemical cells to perform specific functions. Some examples of electrochemical devices are batteries, supercapacitors, electrochemical sensors and fuel cells, etc. In general, they have piqued the interest of the scientific community because they offer the possibility of direct energy production from one type to another, resulting in high efficiency with almost zero polluting emissions. Consider for example, fuel cells, which can produce electricity with an efficiency close to 60%, which can even reach 80% if waste heat is captured in a cogeneration system. Each of these devices has a separate function (e.g. Batteries can provide power for long periods of time until they gradually lose power and become discharged). Despite their advantages, there are still some challenges to overcome in order to fully commercialize them [9], [17] [49].

2.5.1 Batteries

Batteries are characterized as electrochemical or galvanic cells, since their main function is to store electrical energy in the form of a chemical, as well as converting chemical energy into electrical energy through certain electrochemical reactions called galvanic reactions. These reactions are thermodynamically favorable (that is, the free Gibbs energy, ΔG , has a negative value), which means that they take place spontaneously. More generally it can be either an individual electrochemical cell or a group of cells that can generate electricity. An ideal battery should continuously supply the same voltage, never lose its efficiency and work perfectly in extreme temperature and humidity conditions. However, it is impossible to have the ideal battery, and its right choice depends on the application and factors such as how much the battery weighs, cost, reliability and capacity. Batteries are divided into two main categories: primary, which is not rechargeable, and secondary, which is rechargeable. The most popular type of rechargeable battery used, and especially for portable devices, is the Li-ion battery. In this type of battery, movement of lithium ions from the negative electrode to the positive electrode occurs during discharge and vice versa during charging. They are preferred over other batteries due to their high efficiency, which comes from the use of graphite at the anode and LiCoO_2 at the cathode. The basic parts of the battery are the anode and cathode electrodes and the electrolyte which facilitates the movement of ions between the two electrodes. **Figure 15** shows the components of Li-ion Battery. During discharge, the

operation of lithium-ion batteries relies on the oxidation of Li_xC at the anode, which releases lithium ions (Li^+) and electrons. These move to the cathode, where the reduction of lithium occurs resulting in the formation of LiMO_2 [50-52]. The reactions are described below [53]:

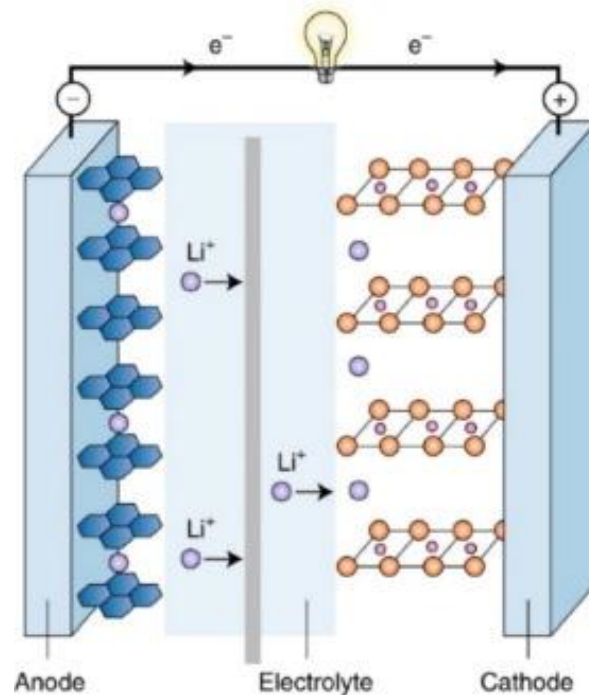


Figure 15. Components of Li-ion Battery [11].

1. Discharge:

- Anode (Negative electrode): $\text{Li}_x\text{C} \rightarrow \text{C} + x\text{Li}^+ + e^-$ (2.32)
- Cathode (positive electrode): $\text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiMO}_2$ (2.33)

Where M is a transition metal.

2. Charge :

- Anode (Negative electrode): $\text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}$ (2.34)
- Cathode (Positive electrode): $\text{LiMO}_2 \rightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^-$ (2.35)

2.5.2 Supercapacitors (ultracapacitors)

Supercapacitors are also included in the category of electrochemical devices and are distinguished by their high-power density and specific capacity. An important advantage is that they have the ability to offer energy with high density in short periods of time compared to conventional capacitors. Like all electrochemical cells, supercapacitors consist of two electrodes located close to each other and an electrolyte that allows ions to move. These devices are used in cases where repeated storage and fast delivery of large amounts of energy are

required, since the charging and discharging time takes only a few seconds. The basic principle of their operation is based on the storage of electricity through the electric double layer created between the electrodes and the electrolyte. When applying an electric potential to the supercapacitor, anions penetrate into the pores of the positively charged electrode, while cations are directed towards the negative electrode. This is done through charging. Therefore, the charge accumulates on the surface between the electrode and the electrolyte, creating two double layers that are located at a very short distance from each other and act as a natural capacitor. Specifically, one is formed on the surface of the electrode and the other inside the electrolyte. The capacitance of a supercapacitor is described by equation (2.36):

$$C = \varepsilon \frac{A}{d} \quad (2.36)$$

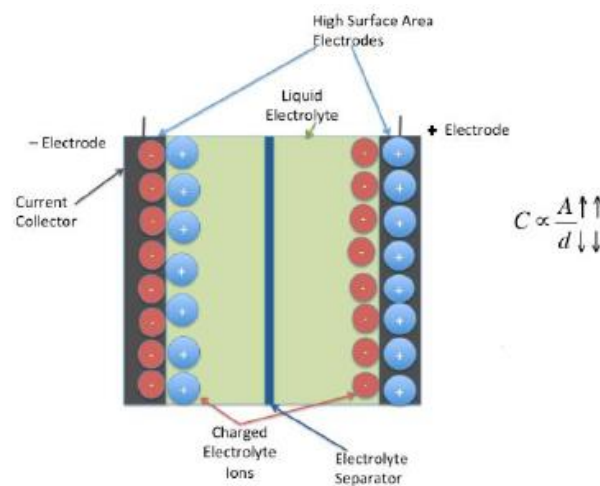


Figure 16. Diagram of a Supercapacitor [11]

Where A is the overlap surface of the electrode plates, d is the distance between the plates and ε is the permeability of the electrolyte. Based on their mechanism of operation, they are divided into two main categories: Pseudocapacitors and Double Layer capacitors. Among the candidate materials for the manufacture of electrodes in supercapacitors, carbon-based materials have stood out due to their excellent efficiency. Mainly, graphene, thanks to its excellent energy transfer properties, is among the most efficient electrode materials. Several forms of graphene, such as fibers, quantum dots and thin films, have been successfully tested as electrodes in supercapacitors. Hybrid electrodes that combine graphene with other materials, such as transition metal oxides, carbon nanotubes or soot, can also be used with equal efficiency. Through the manufacturing process of hybrid electrodes, the accumulation of graphene during thermal or chemical treatments is significantly reduced, and the available

surface area is increased. So electrodes with higher specific capacity are created, making them suitable for applications with high energy storage requirements. **Figure 16** illustrates a typical diagram of a supercapacitor [54-56].

2.5.3 Electrochemical Sensors:

These devices are used to measure the concentration of specific analytes through chemical reactions, providing real-time insights into the composition of a system. In other words, these sensors detect and quantify chemical species using oxidation and reduction reactions. Their simplicity and versatility assisted them to become increasingly famous as possible tools for a wide range of applications. They can be used in environmental applications to measure gas pollutants, air quality and water quality. Industrial applications include detecting exhaust gases and harmful substances such as carbon monoxide (CO) and volatile organic compounds (VOCs). In the automotive market they play a key role in technologies like lambda sensors and hydrogen sensors. Furthermore, they are widely utilized in food and pharmaceutical industry detecting microbial pathogens, toxins, and viruses, as well as drugs and cancer biomarkers.

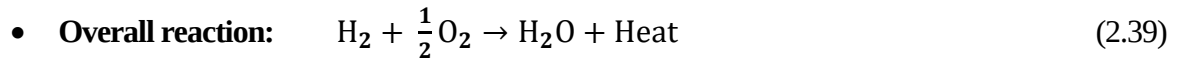
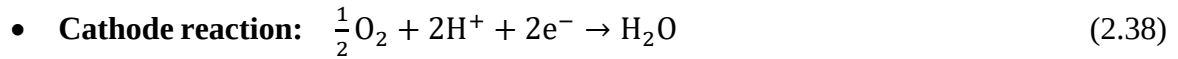
Electrochemical sensors are classified into three main categories: Potentiometric sensors which measure changes in voltage or potential under constant current, Amperometric/Voltammetric sensors which track changes in current at either constant or varying potential and Conductometric sensors that measure changes in conductivity. Many studies have explored advanced chemical sensors using yttria-stabilized zirconia (YSZ) solid electrolytes. For example, G. Fadeyev and colleagues experimented with various sensing electrodes, including silver and complex oxides in a perovskite structure, to measure CO and hydrogen content in the air. Another study reviewed recent advancements in glucose oxidation mechanisms using cobalt, nickel, and copper oxides on graphene. Similarly, other researchers have focused on the principles and designs of solid oxide gas sensors, analyzing data from earlier studies to improve performance and broaden applications [59-80].

2.5.4 Fuel cells

2.5.4.1 Principal Features of fuel Cells

A fuel cell is an electrochemical cell that converts the chemical energy of a fuel and an oxidizing agent into electrical energy through some redox reactions. In fuel cells, energy is generated by an electrochemical reaction in a similar way to that of a battery. However, the battery stores energy inside and, when it runs out, it needs to either be replaced or recharged from an external power supply. This recharging process reverses the electrochemical reaction that occurs during discharge. On the other hand, a fuel cell runs continuously, as long as it is supplied with external energy sources, e.g. fuel and oxygen (usually from the air). Therefore, the main difference between fuel cells and most batteries is that to maintain their chemical energy, a continuous source of fuel and oxygen supply is required. Individual fuel cells produce relatively small electric potentials of about 0.7 V. To achieve a higher voltage meeting the needs of a particular application, the FCs are stacked or arranged sequentially. These systems achieve an energy efficiency of around 60% which can be increased even further by up to 85% when waste heat is captured by a cogeneration system. The basic parts of the individual fuel cells are the cathode and anode electrodes as well as the electrolyte that lies between them and separates them. Bipolar plates are also placed on both sides of the cell, facilitating the flow of gases and the transfer of electric current to the external circuit. They are made of graphite, providing high electrical conductivity and resistance to corrosive phenomena. The Gas diffusion layers are also a very important part of fuel cells and that's why they ensure the smooth removal of byproducts from electrochemical reactions and evenly distributing fuel and oxidant to the electrodes. Typically made from materials like carbon paper or Teflon-coated sheets, these layers are designed to be hydrophobic. In hydrogen FCs, hydrogen gas flows to the anode through channels. There, hydrogen atoms react with those of oxygen during oxidation in the presence of a catalyst, which enables hydrogen molecules to separate into electrons and ions. Electrons flow through an external circuit and create an electric current while protons pass through the electrolyte and reach the cathode. The electrons and protons that eventually reached the cathode react with each other and with oxygen to form water and other products. **Figure 17** shows a fuel cell operation diagram. The chemical energy contained in hydrogen is converted directly into electricity using pure water and useful heat as its only by-products [1], [2], [17],[81-93].

The electrochemical reactions for a hydrogen fuel cell (HFC) utilizing an acidic electrolyte are presented below:



(Exothermic reaction, $\Delta\text{H} = -286 \text{ kJ/mol}$)

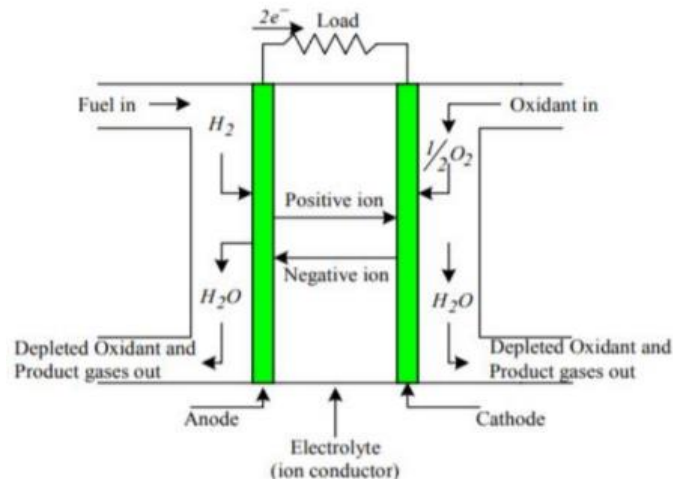


Figure 17. Fuel cell operation diagram [2].

2.5.4.4 Types of fuel cells

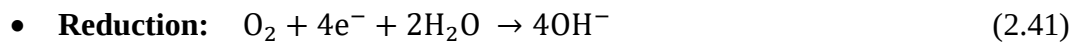
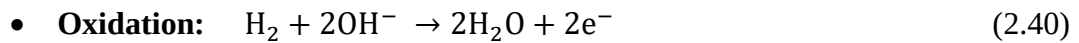
There are several types of fuel cells which are classified based on some criteria. The type of electrolyte fuel cells use is the main classification characteristic as it influences the fuel cell's operating temperature. Fuel cells above 600 °C are classified as “high-temperature” fuel cells. Under these high temperatures hydrocarbon fuels are spontaneously transformed into hydrogen and efficiently drive electrochemical reactions without the use of catalysts. Efficiency in fuel cells decreases as reaction temperature rises, meaning that exceeding certain temperature limits significantly impacts energy output. High-temperature fuel cells, such as molten carbonate and solid oxide fuel cells operate in this range. Fuel cells running below 250°C are classified as "low-temperature" fuel cells. These require expensive rare-earth metal catalysts and external hydrogen sources, as they cannot perform internal reforming. However, their lower operating temperatures offer advantages such as faster start-up times and reduced material wear, making them particularly suitable for automotive applications. Examples of low-temperature fuel cells include alkaline (AFC), phosphoric acid (PAFC) and proton exchange membrane fuel cells (PEMFC) [3]. The characteristics of every fuel cell type are depicted in Table 1.

Table 1. Characteristics of Fuel cell types [2].

Fuel Cell Type	Operating Temperature	Electrolyte	Anode Material	Cathode Material	Anode reaction	Cathode reaction	Efficiency
SOFC	600-1000 °C	Ceramic as stabilized zirconia & doped perovskite	Ni-ZrO ₂	Sr doped LaMnO ₄	$H^+ + O_2^- \rightarrow H_2O + 2e^-$	$O_2 + 4e^- \rightarrow 2O_2^-$	45-60%
MCFC	650 °C	Molten salt as Nitrate Sulphate, carbonates	90% Ni 10% Cr	Li-doped NiO	$H^+ + CO_3^{2-} \rightarrow H_2O + CO + 2e^-$	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$	50-60%
PEMFC	60-100 °C	nafion	Pt, Pt/C	Pt,Pt/C	$H_2 \rightarrow 2H^+ + 2e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	40-60%
PAFC	150–220 °C	Phosphoric acid	Pt/C	Pt/C	$H_2 \rightarrow 2H^+ + 2e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	40-50%
DMFC	25-90 °C	nafion	Pt, Pt/C	Pt,Pt/C	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$\frac{2}{3} O_2 + 6H^+ + 6e^- \rightarrow H_2O$	40-55%
AFC	<100 °C	Potassium Hydroxide KOH	Pt-Pd	Pt-Au	$2H_2 + 2OH^- \rightarrow 4H_2O + 4e^-$	$O_2 + H_2O + 2e^- \rightarrow OH^-$	50-55%

1. Alkaline Fuel Cell (AFC):

They were the first type of fuel cell to find application in electric generators, but due to their range of operating temperatures, they were developed mainly by the space industry and used in missions such as the Apollo flights and the Space Shuttle program. More specifically, alkaline cells operate in a wide range of pressures and temperatures ranging from 0.22 to 4.5 MPa and from 80 to 230 °C respectively. However, they are capable of launching even at sub-zero temperatures for space applications. The basic structure of an AFC includes porous anodes and cathodes, which are usually made of nickel or silver as a catalytic material. The role of the electrolyte is played by the KOH solution that separates the two electrodes of the anode and cathode. Even microporous separators such as potassium titanate, cerium (ceria) and zirconium phosphate gel are used to strengthen the structure, replacing asbestos, which has now been excluded due to its toxicity. The system operates with hydrogen fed to the anode and oxygen to the cathode. The electrolyte facilitates the movement of ions between the two electrodes, creating electricity through the electrochemical reaction. A typical AFC diagram is represented in **Figure 18 a)**. The voltage produced by each cell varies between 0.5 and 0.9 V, while the total electrical efficiency can approach 65%. Since the electrolyte is alkaline, the ion conduction mechanism is different from PEMFCs. Specifically, the ion carried by the KOH electrolyte is a hydroxide (OH) ion, which affects various functions of the fuel cell. The half-cell reactions are :



At the cathode, where oxygen depletion occurs, water is required, which makes its management critical. Often, to address this issue, waterproof electrodes are used while keeping a sufficient amount of water in the electrolyte. In the cathodic reaction, water is consumed by the electrolyte, while in the anodic reaction, the produced water is released. The extra water created (2 mol per reaction) is removed from the stack by evaporation [1],[2], [94].

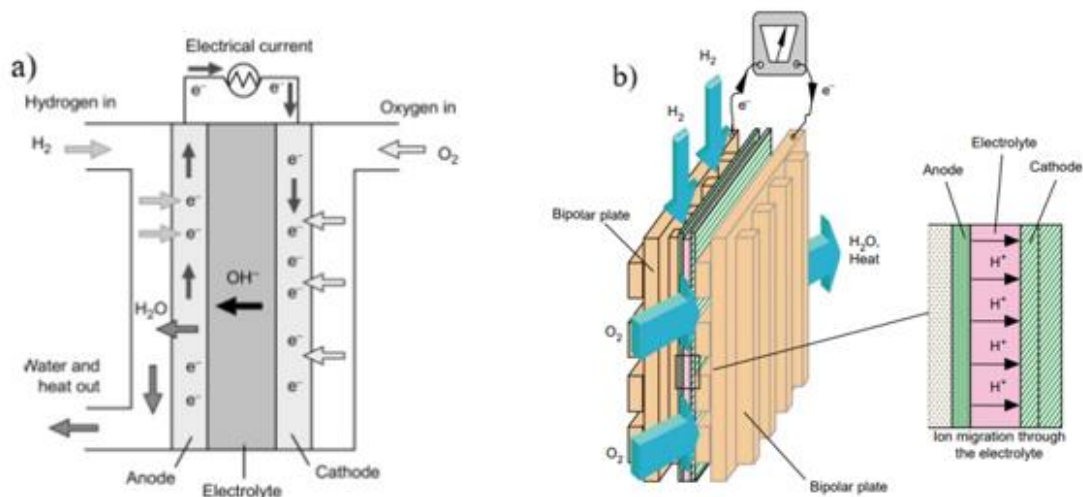


Figure 18. Alkaline fuel cell [94], b) Polymer electrolyte fuel cell [104].

2. Polymer Electrolyte Membrane Fuel Cell (PEMFC) :

In these fuel cells, a proton exchange membrane is used as an electrolyte. These were the first to be applied in space missions, with the Gemini program incorporating a 1 kW fuel cell array to provide auxiliary power. Their operating temperature is from 60-100 °C, that is, they belong to low-temperature fuel cells. Hydrogen is fed into the anode where oxidation takes place and protons and electrons are released. On the other hand, oxygen is supplied to the cathode and reduced. The protons produced at the anode penetrate the proton exchange membrane and are directed towards the cathode. The electrons in turn move through the external electrical circuit because they are not allowed to pass through the membrane, creating an electric current. **Figure 18 b)** illustrates a PEMFC. The voltage present in the cell varies between 0.6 and 0.7 V for a current density of 0.5 A/cm². PEM fuel cells allow quick activation of the fuel cell due to their short warm-up time. This reduces wear on system components by increasing cell life. However, in order to start at low temperatures, it needs a catalyst made of noble metals and most often platinum [1],[95-100] .

3. Solid Oxide Fuel Cell (SOFC):

The first solid oxide fuel cell was built in 1937 by Baur and Preis, using coke as fuel and magnetite as an oxidizer. SOFCs are high-temperature fuel cells, operating at temperatures from 800°C to 1000°C. The electrolyte consists of a thin layer of solid ceramic material, usually yttrium stabilized zirconia (YSZ), which ensures excellent ionic conductivity, chemical stability and mechanical strength. The cathode electrode requires a porous structure to allow oxygen to disperse on the cathode-electrolyte surface, the most common being materials that include strontium-doped LaMnO_3 . The anode is also porous and consists of a composite ceramic metal material e.g. Nickel-YSZ. The operation of SOFC is based on the use of fuels such as methane or syngas, which are directly oxidized or converted to hydrogen (H_2) and carbon dioxide (CO_2). The hydrogen produced can be harnessed directly in the SOFC. At the cathode, oxygen molecules separate into oxygen ions (O^{2-}) and electrons. **Figure 19 a)** shows the anode and cathode reactions in a SOFC. The oxygen ions are transported through the electrolyte and react with hydrogen at the anode, producing heated water and releasing electrons, which create an electric current. An important advantage of SOFCs is their ability to carry out fuel reforms internally due to high operating temperatures thus making it possible to use various fuels containing hydrogen. **Figure 2.19 b)** shows the SOFC components [1], [2],[101-103].

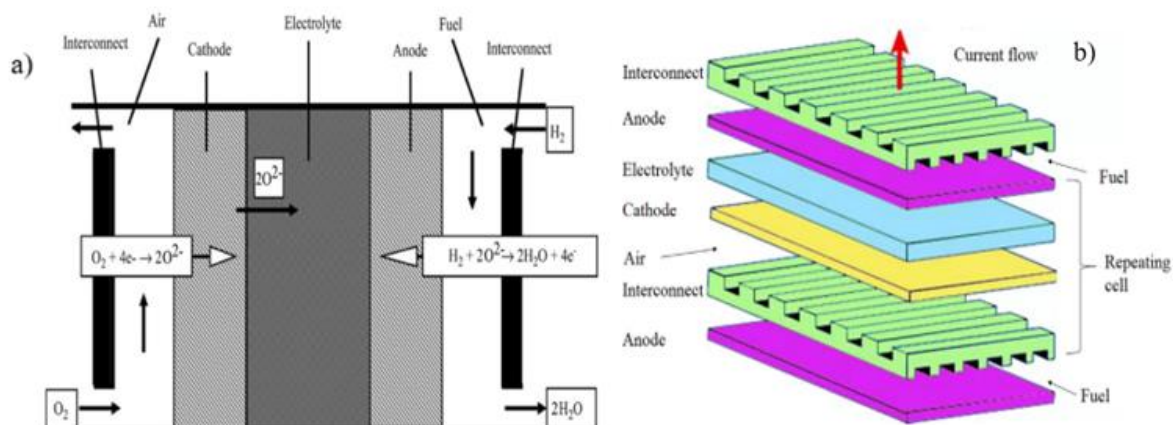


Figure 19. a) Anode and Cathode reactions of a solid oxide fuel cell [105], b) Construction layout of the solid oxide fuel cell stack [106].

4. Molten Carbonate Fuel Cell (MCFC) :

MCFCs were developed in the mid-20th century and use liquid alkaline carbonates as an electrolyte so that they can operate at high temperatures up to 650 °C. In their fields of application, the power produced ranges from 125 kW to 1 MW. Two possible alternatives to electrolyte are the combination of lithium carbonate with potassium carbonate or lithium and

sodium carbonate which are diffused in a porous ceramic matrix made of chemically inert aluminate lithium (LiAlO_2). An anode is a porous electrode made of a nickel alloy, such as Ni-5Cr or Ni-xAl, that plays the role of a catalyst. The alloy contains small amounts of aluminum or chromium in order to reduce thermal creep in the electrode structure. A porous nickel catalyst is also used in the cathode. During the cell start-up process, nickel reacts with the electrolyte (eutectic mixture of Li_2CO_3 and K_2CO_3), converted into nickel oxide by impurity of high conductivity lithium ($\text{Li}_x\text{Ni}_{1-x}\text{O}_2$). In addition, through the high operating temperatures of MCFCs, it is possible to internally reshape fuels and utilize waste heat in the combined cycle. At the same time, they increase the speed of reactions associated with oxygen reduction, thus limiting the use of large quantities of catalysts made of precious metals. **Figure 20 a)** illustrates an MCFC diagram [1], [2].

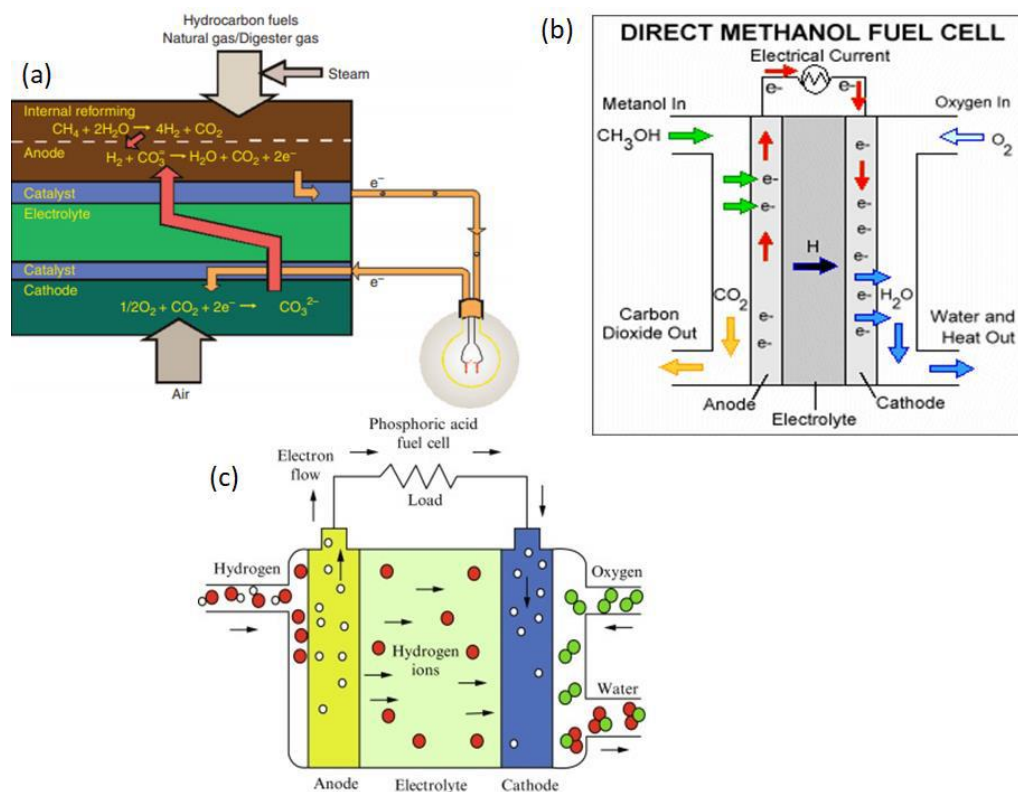


Figure 20. Configuration and working principle of a) MCFC [107], b) Direct methanol fuel cell [108], c) PAFC [109].

5. Direct Methanol Fuel Cell (DMFC):

DMFC fuel cell systems also consist of a membrane (PEM) and operate in a temperature range of 70 to 100 °C. In the DMFC, diluted methanol in a water mixture (usually 1-2 molar), is delivered directly to the cell without the need to transform alcohol into hydrogen and makes it a fairly good choice as fuel choice because it can be made from natural gas or renewable

biomass. In DMFCs both the anode and the cathode contain platinum catalysts or are Platinum adopted-catalysts and trifluoromethanesulfonic acids have the role of electrolyte. They do not emit polluting products e.g. nitrogen oxides or sulphur, only carbon dioxide, for this reason and are considered environmentally friendly. Compared to PEMFCs, however, they do not perform as well. **Figure 20 b)** shows a DMFC diagram [1], [2].

6. Phosphoric Acid Fuel Cell (PAFC):

Phosphoric acid fuel cells were the first to be commercially marketed around the mid-60s. They are used in stationary power plants covering needs ranging from distributed generation to on-site power plants with a capacity ranging from 5 to 20 MW and provide electricity, heat and hot water to small communities, towns, commercial sites or hospitals. They use phosphoric acid (H_3PO_4) as an electrolyte, which has a low ionic conductivity and needs operating temperatures between 150°C and 220°C in order to function properly. PAFCs therefore do not belong to fast start and low operating temperature fuel cells. The necessary fuel for their operation is hydrogen, however the very high operating temperatures of PAFCs provide the possibility to use hydrogen fuel with impurities, processed through the fuel reforming process. The basic structure of these fuel cells is made from a ceramic matrix impregnated with a solution of phosphoric acid. This is interfered with by some porous electrodes used to bind ions and diffuse gases. The hydrogen fed into the anode decays, releasing electrons and protons. Through the matrix layer the protons diffuse into phosphoric acid until they reach the cathode where they react with oxygen to create heated water. These cells are considered to be the most reliable on the market, with stable and efficient operation in a wide range of applications. **Figure 20 c)** illustrate a PAFC diagram [1], [2].

2.5.4.5 Application of Fuel Cells

Fuel cells are incredibly versatile because of their modular design. They can be used in a wide range of applications, from powering large stationary power generation systems to providing energy in small compact, portable devices.

- **Stationary Power Plants:** Over the past decade, a steady number of stationary power plant projects have been successfully developed. One notable example is the Ballard Generation Systems plant, which delivers 250 kW of power, making it the largest power generation unit to date. This PEM fuel cell system runs on natural gas and can effectively support critical facilities like hospitals or even small neighborhoods as a backup power

source. Stationary power plants typically use natural gas or other conventional fuels and are known for their very high operational efficiency. Unlike smaller portable systems, warm-up times are not a critical concern for these applications. Additionally, these plants generate significant amounts of waste heat and hot water, which are often repurposed by the surrounding community, further boosting the system's overall efficiency.

- **Submarines:** Fuel cell systems are almost silent, and the heat produced as a byproduct can be utilized through onboard reformers, enhancing efficiency. The low infrared signatures of fuel cells are another significant advantage for military applications like submarines. Over the past few years, a substantial number of prototype systems have been successfully tested, showcasing their potential in this field.
- **Ammonia and Iron Production:** Ammonia production systems are widely used today, while direct reduced iron (DRI) production has seen significant growth only in the past decade. Thanks to recent advancements in fuel cell technology, global DRI production reached 100 million tons in 2018. Beyond serving as a renewable fuel of the future, hydrogen is currently in high demand for refinery operations, especially for hydrocracking processes that refine middle distillates.
- **Portable power system:** These Portable power systems can substitute batteries effectively in a lot of compact/mobile systems such as powering camping equipment, drones, medical devices. Today, commercial units are capable of an electrical output approximately 1.2 kW or 4100 Btuh.
- **Automotive industry:** Fuel cells are transforming the automotive industry by offering a cleaner and more efficient alternative to traditional engines. These systems run on hydrogen and biofuels i.e. ethanol, methanol and produce electricity to power vehicles while emitting only water vapor, making them an environmentally friendly choice. One of their biggest advantages is the ability to refuel in just a few minutes, like gasoline-powered cars, while offering long driving ranges and excellent energy efficiency. Fuel cells are already being used in various types of vehicles, from passenger cars to buses and even heavy-duty trucks. For personal cars, they provide a sustainable solution for daily commuting and long-distance travel. In public transportation, hydrogen-powered buses are gaining popularity in cities aiming to reduce urban emissions. Meanwhile, heavy-duty trucks with fuel cells are being developed to handle long-haul routes, offering a viable option for decarbonizing freight transportation [3].

Chapter 3

3.1 Hydrogen as a fuel source

3.1.1 Properties of Hydrogen

Hydrogen has the simplest form of all molecules and has the lowest energy content by volume and the highest energy content of any fuel by weight, making it a very good choice in applications such as FCs. It exists free in nature in two forms, either as a liquid from water or as a gas from the atmosphere. A very important advantage of hydrogen is that it produces zero harmful emissions to the environment but also that it has three times the heating value of oil. Specifically, the lower heating value of hydrogen is 120 MJ/kg, and its Higher Heating Value is 142 MJ/kg. But its production costs are very high because it is a man-made fuel whose refining is three times higher than that of oil. The exothermic combustion of hydrogen with oxygen produces only water as a byproduct, releasing a significant amount of energy (1.4×10^8 J/kg). Compared to gasoline, which has an ignition temperature of approximately 501 K, hydrogen has a significantly higher ignition temperature of around 858 K. However, hydrogen ignites more easily and has a broader flammability range than any other fuel. Its flammability limits range from 4% to 75% by volume in air and from 4% to 95% in pure oxygen. Hydrogen detonation range in air varies between 11% and 59% by volume. The optimal combustion occurs at a 29% hydrogen-to-air volume ratio, where the energy required to ignite the mixture is lower in relation to other conventional fuels [2], [110].

3.1.2 Methods of Hydrogen Production

Although hydrogen is abundant in the atmosphere, it is not in the purest form, hence it must be produced through a chemical, thermal, or electrical process, or a combination of these methods. A few examples of these methods are natural gas steam reforming, wind electrolysis and coal gasification. In natural gas the primary compound is methane, but it includes many other components such as ethane, propane and butane, as well as carbon dioxide and nitrogen.

Natural gas is collected and stored once it has been recovered from various sources and reserves. It is then chemically treated before being piped to fuel processing units that are located at the already existing refueling stations. In these units the production of hydrogen is happening through a combination of steam reforming and fuel oxidation processes. **Figure**

21 illustrates these processes. Based on connectivity and transport network, natural gas can be transported through the current pipelines to refueling stations where hydrogen and heat are produced on-site. This way uses the existing network without demanding modifications to materials or supply points, keeping costs relatively low and manageable. Otherwise, hydrogen is produced at the fuel processing plants and from there it is transported through the same network again to the hydrogen demand centers. But some changes in the existing network have to be made which refers to reinforced steel materials, increasing the cost of this process. The overall steam reforming reaction is presented below :



Ammonia, a chemical compound with a high hydrogen content, has been proposed as a fuel for internal combustion engines, utilizing its decomposition into hydrogen and nitrogen. Hydrogen can be sourced from both renewable and non-renewable energy resources. While renewable-based hydrogen production is environmentally friendly, hydrogen derived from non-renewable sources contributes to greenhouse gas (GHG) emissions. Producing hydrogen through the electrochemical processing of waste biomass is an efficient approach that minimizes GHG emissions and does not demand excessive energy or high production costs. Potential biomass feedstocks include bread waste, cypress sawdust, and rice husks. One more way hydrogen can be generated is the electrolysis of liquefied methane [110-113]. One more method hydrogen can be produced is the widely known but not so economical electrolysis of water which was described before. **Figure 22** shows the feedstock share of global H₂ production and the Hydrogen consumption in the world.

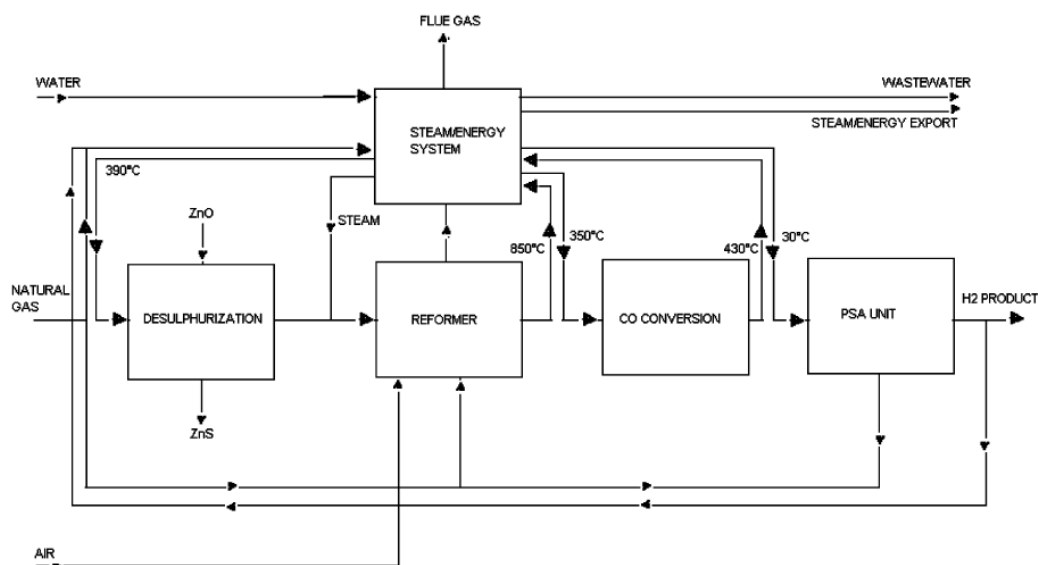


Figure 21. Hydrogen production from natural gas steam reforming [112].

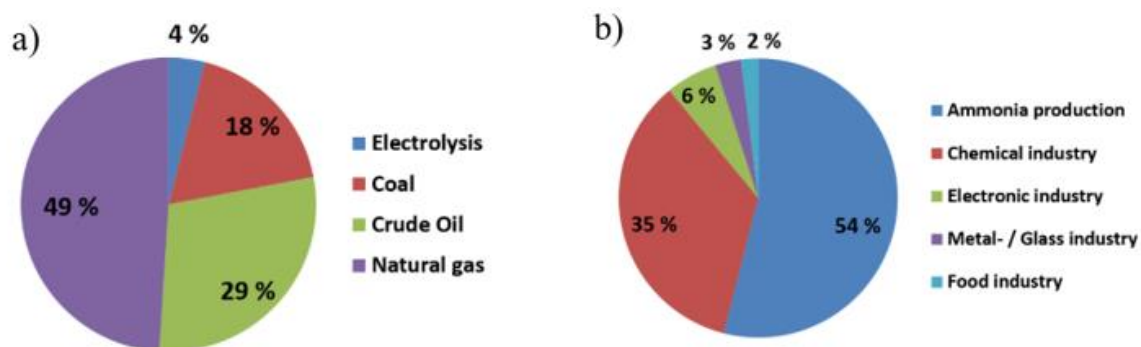


Figure 22. a) Feedstock share of global H₂ production, b) Hydro consumption in the world [135].

3.1.3 Hydrogen in FCVs

Generally, Hydrogen fuel is regarded as one of the most promising energy carriers for widespread future use. The adoption of fuel cell (FC) systems has paved the way for the successful use of hydrogen fuel in the transportation sector. Hydrogen-powered engines, particularly those based on polymer exchange membrane fuel cells, are currently in operation worldwide. The key advantages of FC systems include high efficiency in well-to-wheel assessments, an energy-efficient drivetrain, and silent operation. Hydrogen, as a fuel, provides significantly higher energy per unit weight compared to other fuels such as kerosene, diesel, petrol, and methanol. As a result, new markets have emerged for automobiles, buses, other transportation vehicles, industrial trucks and scientists are heavily focused on finding efficient and sustainable ways to produce hydrogen and use it in transportation. Companies like Honda, Toyota, and Hyundai are leading the way by introducing fuel cell vehicles (FCVs) powered by hydrogen. These vehicles are now available in regions like North America, Asia, and Europe. By mid-2018, over 6,500 FCVs had been sold worldwide, with California standing out as the largest market. About 3,000 were in California, thanks to its extensive network of hydrogen refueling stations and the strong presence of automakers promoting these vehicles. FCVs are often compared to battery electric vehicles (BEVs) since both are emission-free, can use renewable energy sources, and are powered by electric motors. However, they differ in important ways. FCVs typically offer a driving range of over 300 miles and can be refueled in under 10 minutes, much like traditional gas-powered cars. Hydrogen has enormous potential as a future fuel source. By 2030, advancements in technology and wider availability are expected to make fuel cells cost-competitive with internal combustion engines (ICEs). However, one major hurdle is finding efficient ways to store hydrogen. **Figure 23** shows the Fuel Cell System for Electric Vehicle (FCEV) [2], [114].

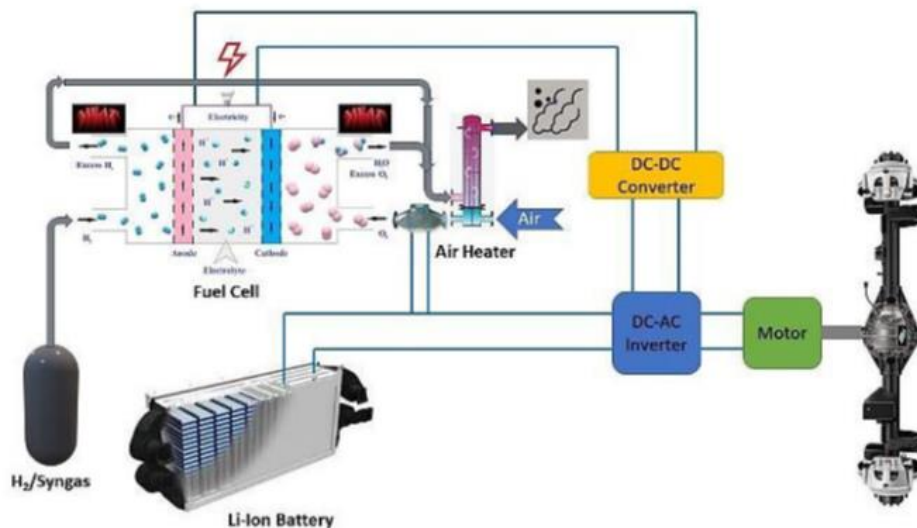


Figure 23. Fuel Cell System for Electric Vehicle (FCEV) [1].

3.1.4 Hydrogen storage

Hydrogen storage is one of the most critical challenges in the development of fuel cell vehicles (FCVs). Hydrogen storage systems are being developed to introduce new methods that meet customer needs. The most common storage method today involves compressed hydrogen tanks made from advanced composite materials. These tanks can be filled quickly, like conventional fuel, but their high cost and public concerns about safety, due to the high pressure they operate under (70 MPa), are significant challenges. One alternative being explored is tanks with an internal framework, designed to handle the forces of compressed gas more effectively. Liquid hydrogen (LH₂) storage has also made significant strides, offering the best storage capacity by weight. However, it faces issues like energy loss and evaporation (boil-off) that need to be addressed before it becomes a mainstream option. Cryo-compressed tanks, which store hydrogen at extremely low temperatures under high pressure, are another promising innovation. While further research is needed to test their durability and public acceptance, they could offer a viable solution. Hydrides, such as NaAlH₄, are also being studied as a potential storage medium, though their capacity remains limited. Meanwhile, there is an interest growing in tanks designed to absorb hydrogen onto surfaces, which could simplify storage systems if the technology is refined. One more challenge comes from hydrogen's low energy density thus it is difficult to store enough of it onboard a vehicle to achieve a sufficient driving range without making the storage tank excessively large or massive. While challenges remain, advancements in hydrogen storage and fuel cell technology are steadily bringing us closer to a future where hydrogen plays a key role in transportation. The 3 main techniques of hydrogen storage will be analyzed below:

1. Pressurized Tank Storage: Pressurized hydrogen storage tanks are designed with carbon fiber-wrapped cylinders, providing sufficient strength and impact resistance to ensure safety in case of a collision. These tanks typically store hydrogen at a pressure of 34 MPa, with a mass of 32.5 kg and a volume of 186 liters, which is sufficient for a driving range of approximately 500 km. The tank's volume is roughly 90% of a 55-gallon drum, making it relatively large for individual vehicles. While the target of 6 wt% hydrogen storage can be achieved, the tank's size presents a significant challenge. Higher pressures of up to 70 MPa have been successfully tested. In 2002, Quantum Technology's 10,000 psi (68 MPa) integrated storage tank received certification in Germany. A policy report from the Technology Office stated that Toyota and Honda vehicles utilized hydrogen stored in high-pressure tanks. However, due to hydrogen's low density, even at high pressures, the amount of hydrogen that can be stored in a tank remains limited. **Figure 24** presents a fuel cell vehicle with on board storage [2].

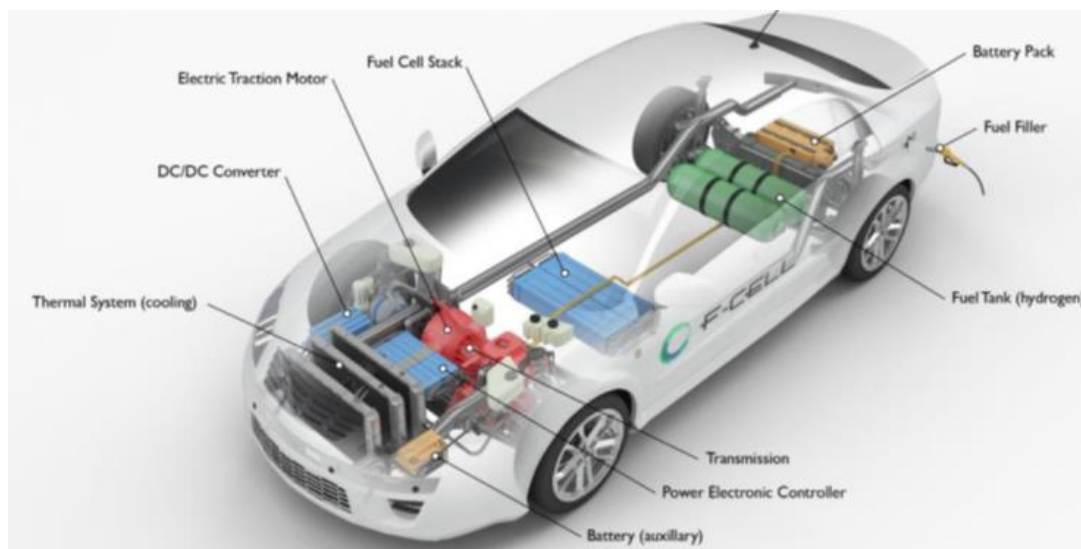


Figure 24. Fuel cell vehicle with on board storage.

2. Cryogenic Liquid Hydrogen Storage: In cryogenic liquid storage, hydrogen is stored in liquid form and reaches a cryogenic temperature of $-253\text{ }^{\circ}\text{C}$ via adiabatic expansion. Cryogenic liquid storage tanks are typically made from high-quality, insulated materials like steel and aluminum. These materials that are used for insulation leads to high cost of storage. These tanks are designed to safely store liquids at extremely low temperatures, keeping them in the right conditions for various industrial or scientific uses. Liquid hydrogen becomes explosive when mixed with certain other gases, so before refueling the tank with hydrogen, nitrogen gas should be used to drain off the residual gases present in the tank. Storing liquid

hydrogen at cryogenic temperatures (around 20 K) is not practical for regular vehicle use. Liquid hydrogen storage systems face significant challenges, including boil-off losses of up to 1% of the storage volume per day and the need for extensive refrigeration to maintain the required low temperatures. **Figure 25** presents a cryogenic tank for storing liquid hydrogen at -253°C [2],[114].

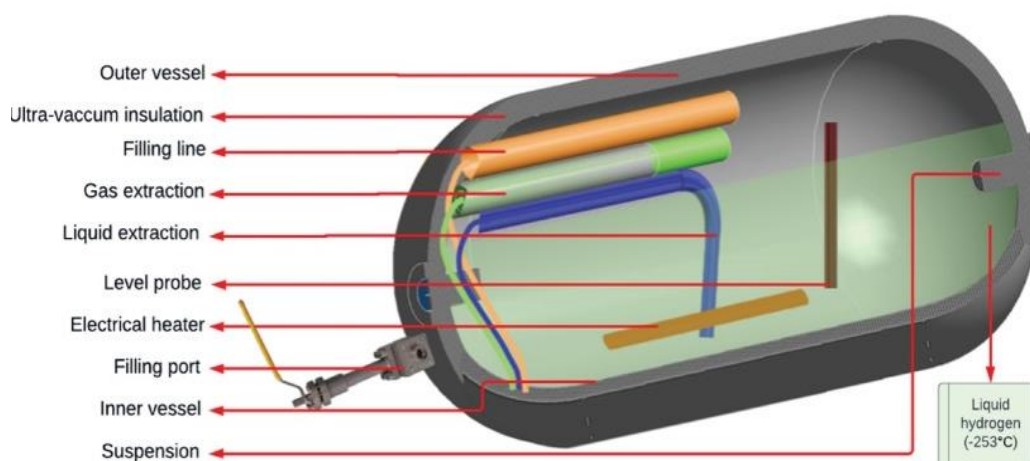


Figure 25. A cryogenic tank for storing liquid hydrogen at -253°C .

2. **Hydrogen Uptake in Metal-Based Compounds:** Another way of storing hydrogen is metal hydration. This technique can be used to store hydrogen below 3 or 4 MPa at temperatures above room temperature. However, metals add more weight to vehicles and are also expensive. One metal that can store large quantities is lithium nitride which stores hydrogen rapidly in the temperature range $170\text{--}210^{\circ}\text{C}$ and obtained an uptake of 9.3 wt% when the sample was held at 255°C for 30 min. Under high vacuum (10^{-9} MPa, 10^{-5} mbar) about two-thirds of the stored hydrogen was released at temperatures below 200°C . However, the remainder required temperatures above 320°C to be released. The hydrogen was delivered as lithium amide (LiNH_2) and lithium hydride (LiH). The researchers suggest that metal-NH systems should be studied to find more practical pressures and temperatures for suitable hydrogen storage [2].

3.1.5 Hydrogen safety

Hydrogen safety remains a significant concern, especially for public use, due to its not good reputation shaped by past accidents. The primary risk with hydrogen fuel is its potential for leakage, which increases the possibility of fire during its production, storage, transport, and use (whether in homes or as vehicle fuel). As hydrogen is increasingly recognized as the fuel of the future, its widespread adoption will inevitably lead to more incidents during various stages of its lifecycle, from production to storage, transport, and use. With more people interacting with hydrogen technology, it's crucial to note that engineering standards for hydrogen are still not as widely established or as advanced as those for today's petrochemical facilities. Additionally, as hydrogen energy is used more in densely populated areas, there is a risk to public safety. Serious incidents, especially those involving fatalities, could significantly hinder the growth of hydrogen fuel adoption for many years. Safety professionals including engineers, designers, technicians at refueling stations and maintenance workshops, and first responders must receive thorough training to handle high-pressure hydrogen systems (up to 100 MPa) and liquid hydrogen (at temperatures as low as -253°C), whether in confined spaces or open environments. Hydrogen fuel comes with a mix of chemical, physical, and physiological risks that need to be carefully managed. Ensuring its safe use requires expert knowledge and close attention to detail at every stage, from production to transportation and use.

Chemical Hazard: Hydrogen mixed with air is highly explosive and can ignite or detonate rapidly. The flammability limits depend on factors like temperature, pressure, the presence of diluents, ignition energy, and the size and design of the equipment involved. Even a small shock wave can trigger the detonation of hydrogen gas, liquid hydrogen (LH_2), or solid hydrogen when combined with oxygen. With an extremely low ignition energy threshold of just 0.02 mJ, it's crucial to ensure that heating systems, electrical equipment, and open flames are kept at a safe distance from areas containing hydrogen. Hydrogen's small molecular size allows it to escape easily from storage systems. Hydrogen is odorless and invisible to human senses, and when accumulated, it can reach explosive concentrations. Adding to the challenge, hydrogen flames are pale blue and nearly invisible in daylight, making them difficult to detect. With high pressure storage (e.g., >200 psi) another layer of risk is added. Leaks from pressurized tanks can produce high-velocity jets extending several meters. If ignited, these jets can generate flame streams capable of causing substantial damage to the surrounding people and objects.

Physical Hazard (embrittlement and component failures): Hydrogen can cause embrittlement, weakening the mechanical properties of metals used in storage systems. This degradation increases the risk of tank failures and hydrogen leaks. Several factors influence embrittlement, including the metal's purity and surface condition, the duration of hydrogen exposure, as well as ambient pressure and temperature. Hydrogen embrittlement is more severe at temperatures between 200 K and 300 K. Strategies to mitigate this include applying oxide coatings, reducing stress concentrations, adding specific additives to hydrogen and selecting suitable alloys. At low temperatures, such as those encountered with liquid hydrogen (LH₂) around 20 K, metals may undergo a ductile-to-brittle transition due to changes in their crystalline structure. This transition affects both elastic and plastic properties, leading to potential structural failures. Additionally, the thermal contraction coefficients of materials must be considered to prevent hydrogen leakage caused by dimensional changes in cryogenic conditions. For instance, metals contract less than 1% at LH₂ temperatures, while plastics can contract by 1%–2.5%. Careful material selection and design are essential to ensure system safety and reliability.

Physiological Hazard (frostbite and suffocation): Although hydrogen is nontoxic, it can displace oxygen in the air. If the oxygen concentration drops below 19.5% by volume, asphyxiation can occur, leading to oxygen deprivation in the body. In the event of a hydrogen explosion, the resulting blast waves can create overpressure, potentially causing lung damage. Thermal burns are another risk associated with hydrogen, caused by the radiant heat emitted during a hydrogen fire. The intensity of this heat depends on factors such as humidity, wind conditions, the size of the burning surface, the heat of combustion, and the duration of exposure. For example, skin exposure to radiation of 0.95 W/cm² can result in burns within 30 seconds. Cryogenic burns and hypothermia are additional hazards when dealing with large spills of liquid hydrogen (LH₂). The extremely low temperature of LH₂ can cause severe frostbite upon contact. Hydrogen has the highest flammability range among common fuels, but proper ventilation reduces the risk of reaching these limits. The flammability limits also vary with temperature; for example, at standard conditions, the lower flammability limit is 4% by volume, decreasing to 3% at 100°C. The minimum ignition energy of hydrogen is remarkably low, it is 0.0012 MJ in oxygen and 0.017 MJ in air, significantly less than most of combustible fuels, which range from 0.1 to 0.3 MJ. Unlike gasoline or diesel, which are dense and tend to pool near the ground, hydrogen's low density causes it to dissipate quickly into the air. This property makes hydrogen-fueled vehicles safer in car accidents compared to those powered by

petrol, as hydrogen is less likely to ignite or cause lingering fire hazards. In controlled tests, snapshots of fire generated by hydrogen and gasoline illustrate the stark differences in combustion. After 3 seconds and 60 seconds from ignition, hydrogen flames demonstrate rapid dissipation and vertical propagation, while gasoline fires tend to spread laterally and persist near the ground (**Figure 26**) [110].



Figure 26. Generated fire by hydrogen and gasoline fuel at 3 s (left) and 60 s (right).

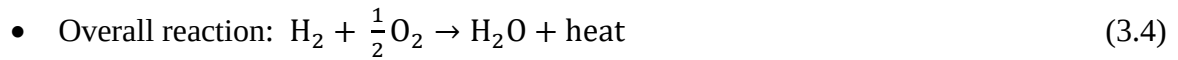
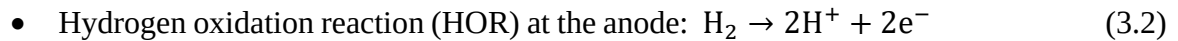
3.2 Study and Analysis of SOFC and PEMFC Technologies

Among the types of fuel cells that were presented in chapter 2, PEMFCs and SOFCs are the most efficient power sources for vehicles. That's the reason why we have to focus and analyze these two fuel cell types.

3.2.1 Proton Exchange Membrane Fuel Cell (PEMFC)

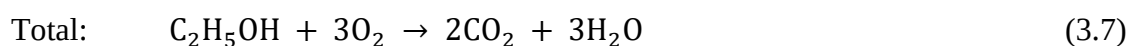
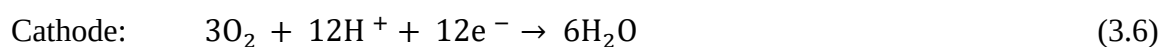
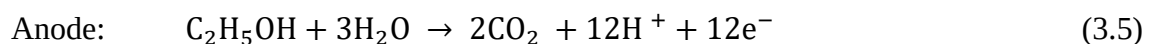
The Proton Exchange Membrane Fuel Cell (PEMFC) commonly referred to as the Polymer Electrolyte Membrane Fuel Cell, is one of the most famous types of fuel cells and it is considered as the most proper technology for vehicles, as evidenced by its use in the platforms of the most important FCEVs manufacturers, namely Hyundai, Toyota, and Honda. PEMFC offers several advantages, such as cost-effectiveness, high durability, high efficiency compared to other FCs, quick start-up process, good cold start capability under low-temperature conditions, lightweight compact system and low corrosion. For all these it is recognized as a potential candidate to replace the internal combustion engine in the transportation sector by the United States Department of Energy. A common PEMFC is composed of the membrane electrolyte assembly MEA, bipolar plates and gaskets. In a direct hydrogen PEM fuel cell, hydrogen is supplied to the anode, while oxygen is delivered to the cathode, often by ambient air through channels. To prevent degradation caused by contaminants, pure hydrogen is

typically required unless advanced technologies are implemented to handle impurities. The reactions that take place in the Hydrogen PEMFC are:



In this type of FCs, hydrogen is considered as the preferred fuel. However Hydrogen isn't naturally available as a fuel, and it needs external reforming for its use in PEMFCs. This makes the system bulkier, more complex, and costly. Moreover the tiny amounts of CO (>10 ppm) can degrade performance, making fuel purity a major issue. All these problems have driven scientists to concentrate on biofuels like methanol and ethanol, which are easier to store, transport, and handle while reducing system weight and volume. Methanol was the first fuel tested due to its high electrochemical activity. But its toxicity, slow anode kinetics, and crossover issues have limited its commercialization, despite significant research on DMFCs. These challenges with methanol, combined with non-toxicity, renewability, higher power density, and zero greenhouse gas pollutants of ethanol led the scientific community to give greater attention to this new promising fuel . Over the last decade, research on Direct Ethanol Fuel Cells (DEFCs), especially DE-PEMFCs, has expanded significantly. A key point was the discovery that PtSn catalysts outperform PtRu as described in chapter 4, sparking increased focus on ethanol-based fuel cells, with some researchers also studying DE-SOFCs [136], [137].

The reactions on the two electrodes for direct ethanol PEMFC (DE-PEMFC) are described below:



The structure of DE-PEMFCs is similar to those of H₂-PEMFC using a membrane electrolyte assembly MEA, based on Nafion. The correct choice of catalysts is crucial for the performance of bioethanol fuel cells. In DE-PEMFCs, cathode catalysts are similar to those used in H₂-PEMFCs, but they must also resist ethanol crossover, which can interfere with the Oxygen Reduction Reaction (ORR). The ethanol Crossover in MEA of Nafion-115 as studied by Song et al. , depends on the working cell temperature and ethanol concentration. Compared to methanol ,ethanol has a lower crossover rate, due to its larger molecular size [138], [139].

3.2.1.1 The membrane electrolyte assembly (MEA):

It is made up of a polymer electrolyte membrane placed between two porous carbon electrodes (anode and cathode) and is the most crucial component of a PEMFC. These electrodes form the interface between the reactant gases and the electrolyte and are required to allow the permeability of gaseous fluids and the conduction of free electrons from anode to cathode. They are comprised of different layers: the Catalyst Layer (CL) in direct contact with the electrolyte membrane, followed by a Microporous Layer (MPL) and a Gas Diffusion Layer (GDL). MPL and GDL are called Diffusion media. Typical dimensions and materials are presented in **Table 2**. **Figure 27** presents the components of a fuel cell stack .

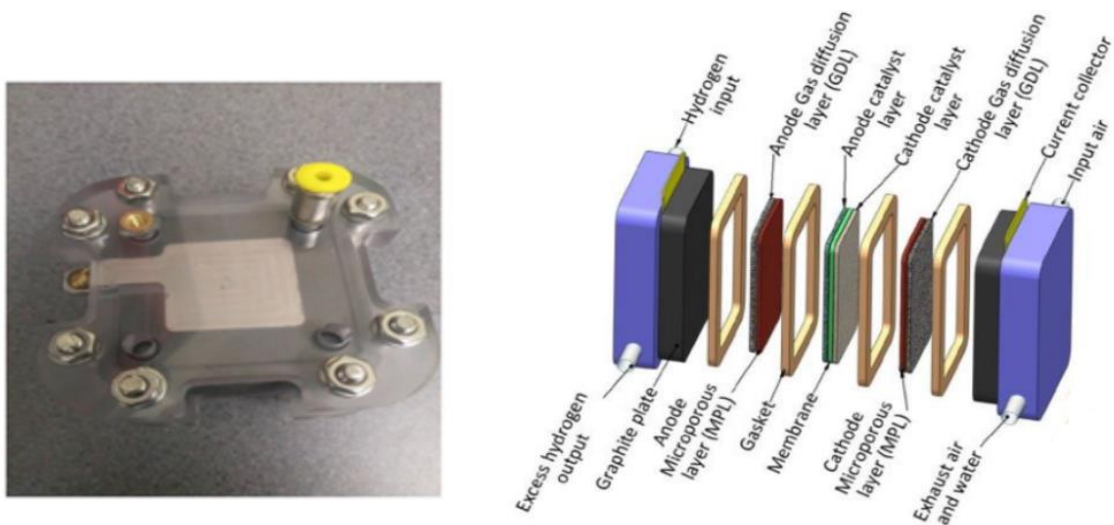


Figure 27. Schematics of a fuel cell stack [115], [3].

Table 2. Typical materials of PEM fuel cell components.

Name	Thickness	Density (g/cm ³)	Typical Material
Polymer electrolyte membrane (PEM)	0.01–0.1 mm	~2	Nafion
Catalyst layer (CL)	100 nm–0.05 mm	~0.4	Carbon-supported catalyst and ionomer porous composite
Gas diffusion layer (GDL)	0.1–0.4 mm	0.3–0.5	Carbon fiber-based porous paper
Microporous layer (MPL)	~0.05 mm	0.3–0.5	Carbon black and PTFE binder
Bipolar plate (BP)	0.3–2 mm	1.7–8	Carbon-based composites or materials

Representation of MEA Components:

1. Electrolyte: The materials used for PEM should be impermeable to gases, to separate the anode and cathode reactant gases, electrically insulating and have high ionic conductivity to facilitate the protons transportation from anode to cathode. Furthermore, membranes should have sufficient mechanical resistance and be chemically and thermally stable in their operating

ranges. For the above reasons the most suitable material that has been used widely in automotive applications is perfluoro-sulfonic acid (PFSA). This material has a hydrophobic perfluorinated chain that ensures mechanical strength and chemical durability, while the hydrophilic sulfonic acid end-groups allow it to absorb water, supporting proton conduction. During the operation of PEMFCs the ions H^+ diffuse through the membrane in the form of hydronium ions (H_3O^+). If the membrane becomes too dry, its ionic conductivity drops, leading to increased ohmic voltage losses. Conversely, excessive hydration can cause membrane flooding, which disrupts the transport of reactant gases. Under typical operating conditions, the membrane can absorb water, causing its volume to expand by up to 20% and its weight to increase by as much as 50% compared to its dry state. Achieving the ideal hydration level depends on several factors like electro-osmotic drag, hydraulic permeation across the electrolyte, water production and back diffusion. DuPont's Nafion is the most widely used long-side-chain PFSA for PEMs. It exhibits a proton conductivity of 0.13 S/cm at 75°C and 100% relative humidity, with a durability of over 60,000 hours and excellent chemical stability. It's important to say that the length of the chain affects the electrolyte performance and stability. On the other side an example of a short side-chain material for membranes is Solvay's Hyflon. **Figure 28** illustrates the polymer structures of Hyflon ion/dow and Nafion.

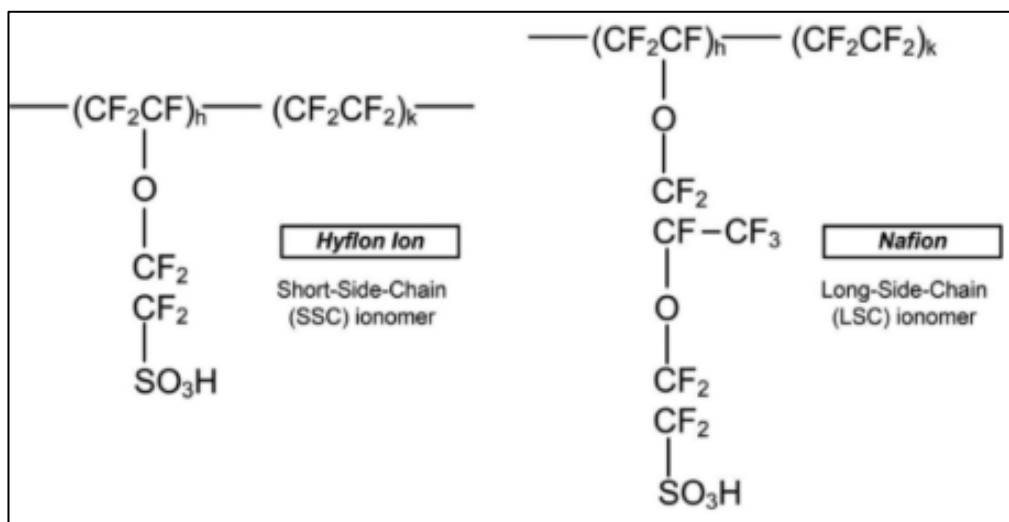


Figure 28. Polymer structures of Hyflon ion/dow, and Nafion.

Despite the present of PFSA several disadvantages exist such as decomposition of polymer chains due to susceptibility to metallic cations, high production costs, temperature limits (around 80°C) for hydration and mechanical reasons, PEM swell/ shrinking during cyclic operation, which leads in membrane failure, environmentally unfriendly materials and possible degradation of the polymer backbone ($-CF_2-$) for the reaction with hydrogen. To overcome

these disadvantages and extend the operational ranges to low humidity conditions (i.e. 0% RH) and various temperatures (i.e. ≥ 120 °C) different studies have been conducted. Some techniques we can follow are :

- **Blending Sulfonated Polymers with Ionic Liquids:** Combining sulfonated polymers with non-volatile, thermally stable ionic liquids can enhance ionic conductivity, although it may diminish mechanical strength.
- **Incorporating Nanoparticles:** Adding nanoparticles like graphene oxide, carbon nanotubes, silica, PTFE, ZrO₂, TiO₂, or TiSiO₄ can help maintain hydration and improve performance.
- **Using Alternative Materials:** Employing sulfonated hydrocarbon polymers such as polysulfones, polyetheretherketones, or polybenzimidazoles reduces the dependence on excessive humidification.
- **Thinner Membranes:** Reducing membrane thickness lowers transport resistance for protons and water, improving humidification. However, this makes membranes more susceptible to mechanical damage and degradation, requiring reinforcement.
- **Water Retention and Humidification Strategies:** Strategies like using microporous layers (MPLs) to retain water or employing counterflow configurations for reactant gases can enhance membrane humidification.

2. Diffusion Media : Diffusion media layers offer electron conduction between the bipolar plate (BP) and the catalyst layer (CL), ensures uniform and direct distribution of reactant gases, aids in by-product removal, provides mechanical support for the membrane electrode assembly (MEA), and protects the CL from corrosion and erosion. However, water droplet accumulation on the GDL surface can obstruct the flow of reactants, making efficient water management essential. The state-of-the-art material for GDLs is carbon paper, composed of almost 7 μm diameter fibers bonded with a binder. To enhance water removal, hydrophobic compounds like Polytetrafluoroethylene (Teflon) are often added to the GDL. However, overloading with these compounds can reduce pore volume, restricting gas flow. Recent advancements are exploring alternative materials, such as metallic and porous silicon GDLs, which show promise for improved performance and durability. A Microporous Layer (MPL) is often placed between the gas diffusion layer (GDL) and the catalyst layer (CL) to enhance performance and durability. Its key roles include protecting the catalyst, creating a smoother and more consistent

interface between layers, and improving multi-phase contact. MPLs are typically made from carbon black powder bound with Polytetrafluoroethylene (PTFE), which imparts hydrophobicity and forms a porous structure. The pores in MPLs are larger than the voids in CLs but smaller than those in GDLs, optimizing their role in water and gas diffusion.

3. Catalyst Layers (CLs): They are the surfaces of electrodes where the electrochemical reactions happen, and their role is to accelerate and facilitate these reactions. Also, CLs provide pathways for reactant gas supply, water removal, proton transport towards the membrane, and electron conduction towards the current collector. A typical catalyst layer (CL) consists of platinum nanoparticles, supported on carbon particles and impregnated with thin ionomer films. This structure creates a network of tortuous pores, forming the triple-phase boundaries where redox reactions occur. To ensure effective ionic conduction between the CL and the membrane, the Pt/C powder is mixed with an ionomer with an optimal loading of around 30 wt%., typically derived from the membrane material itself.

Excessive ionomers can block gas diffusion and reduce catalyst accessibility. These mixes are prepared as inks or pastes and applied to membranes or gas diffusion media using techniques like spraying, screen printing, or rolling. Even though platinum is highly effective as a catalyst and is considered the state-of-the-art material as a PEM catalyst, its high price and sensitivity to contaminants like carbon monoxide are some remaining challenges. Some efforts to improve CO tolerance and decrease the platinum cost without affecting the cell resistance are utilizing less expensive metals such as ruthenium or palladium. Additionally, several platinum alloys, including Pt-Co, Pt-Ni, Pt-Fe, Pt-V, Pt-Mn, and Pt-Cr, keep the performance at the same levels while reducing costs. **Figure 29** represents the cost and loading targets of platinum catalysts for a 100 kW FCEV and **Table 3** shows the main catalyst alternatives along with their related benefits and drawbacks [115].

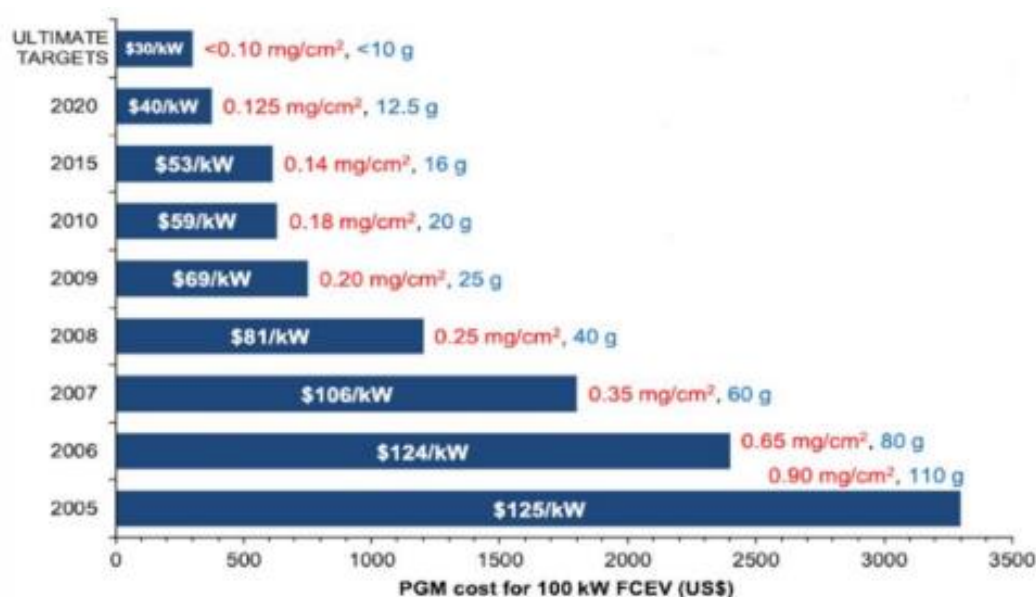
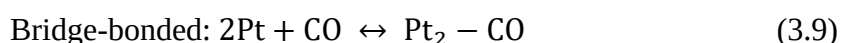
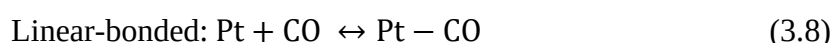


Figure 29. Cost and loading of platinum group metals (PGM) for 100 kW FCEV from 2005 to 2020, on the current Pt raw price of USD $\approx$ 30/g. The values inside the bars show the total fuel cell stack cost for a manufacturing volume of 500,000 units per year. The values outside the bars give the total catalyst loading per unit cell area (mg/cm²) and for a 100 kW FCEV (g).

Table 3. Benefits and remaining challenges for each of the primary categories of electrocatalysts.

Catalyst-type	Benefit	Remaining Challenges
Platinum	Mature technology	Unable to meet long term automotive Pt loading and catalyst layer durability targets
Pt-alloy/de-alloy	Mature technology	Hard to meet long term automotive Pt loading target
	Improved performance over Pt/C	
Core shell	Enhanced MEA durability	Difficult to maintain the quality of the shell
	Improved mass activity over Pt alloy	
	Improved durability over Pt/C	
Shaped control nanocrystal	Highest ESCA	Dissolution of a core is still a concern
	Significantly higher mass activity ($\sim \times 15$) over Pt	Scale up is at an early stage
		Conflicting data on stability
Nano frame/ nano cage	Significantly higher mass activity ($> \times 20$) over Pt	MEA performances have still not been demonstrated
		Scale up is at an early stage
	Highly stable (improved durability over Pt /C)	Ionomeer penetration into the nanocage will likely be difficult
Non-precious metal catalyst	Potentially offer the largest benefits (significant cost reduction)	MEA performance at high current density may be challenging
	Tolerant to common contaminants	Close to meeting targets for non- automotive applications but far automotive targets
		At current volumes PGM is not a main concern for non- automotive applications

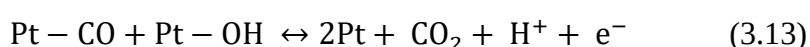
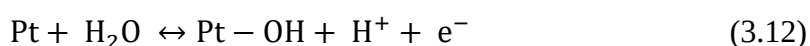
The presence of carbon monoxide (CO) has been shown to significantly degrade the performance of proton exchange membrane fuel cells (PEMFCs). When CO concentrations exceed 10 ppm, the reaction rates decrease, and the overall activity of the catalyst is diminished. This occurs because carbon monoxide forms stronger bonds with the platinum catalyst than hydrogen does, minimizing the Gibbs free energy and making the CO- Pt bond energetically favorable. CO poisoning can be at vacant platinum sites or at sites already occupied by hydrogen atoms through two primary adsorption mechanisms: linear-bonded adsorption and bridge-bonded adsorption. These mechanisms hinder the catalyst's efficiency, reducing the fuel cell's overall performance and durability.



According to linear-bonded adsorption, the two poisoning mechanisms are described by the following reactions:



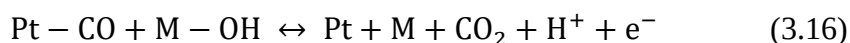
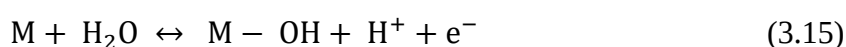
Carbon monoxide (CO) reduces the efficiency of proton exchange membrane fuel cells (PEMFCs) by covering the active platinum sites, slowing down the hydrogen oxidation reaction (HOR). To address this issue, CO that binds to the platinum catalyst can be removed by oxidation, but this only happens at higher potentials, between 0.6 and 0.9 V, while HOR occurs at much lower potentials, up to 0.2 V. The oxidation process can be explained by these reactions:



CO oxidation requires high potentials because of two challenges: the strong bond between CO and platinum (Pt-CO) and the difficulty platinum has in forming hydroxyl species (Pt-OH) at the lower potentials where HOR takes place. This gap makes CO removal challenging and leads to significant CO poisoning of the fuel cell. One solution is to lower the potential required for CO oxidation. This can be achieved by either weakening the Pt-CO bond or encouraging the formation of hydroxyl species. Research shows that combining platinum with another transition metal improves CO tolerance while maintaining efficient HOR activity. The improved performance comes from two mechanisms:

1. **The bifunctional mechanism:** The added metal helps form hydroxyl species (M–OH) at lower potentials, which react with Pt–CO, converting it into CO₂ and freeing up the platinum sites.
2. **The electronic (or ligand) effect:** This mechanism weakens the Pt–CO bond by altering the electronic structure of platinum, reducing CO poisoning even at lower potentials (up to 0.2 V).

These mechanisms make the fuel cell perform better in the presence of CO, ensuring more reliable and efficient operation. The bifunctional mechanism is described by the reactions[116]:



3.2.1.2 Bipolar Plates :

Bipolar plates (BPs) are very important for a fuel cell, accounting for over 70% of its weight and more than 40% of its cost. They are placed after the MEA layers and connect individual fuel cells electrically, allowing them to work together and form a complete, functional stack. They facilitate the different reactant gases to be fed to the specific electrode. They also play a vital role in managing the flow of reactant gases by not only ensuring that these gases are evenly distributed but also including dedicated pathways for effective heat exchanges. The grooved structure of BPs specifically includes three distinct channels, which deliver reactant gases to each cell, circulate liquid coolant, and remove water. These channels, ideally more hydrophilic than the surrounding layers, facilitate efficient water management. Graphite is the standard material for BPs, valued for its excellent corrosion resistance and electrical conductivity. However, it has some drawbacks, such as brittleness which hinders manufacturing, and gas permeability, which can lead to leaks. To address these issues, researchers are exploring alternative materials. Carbon composites offer good electrical and thermal conductivity but lack mechanical strength. Metals like aluminum, stainless steel, and titanium are also being investigated, as they provide strong mechanical, electrical and thermal properties and are easier to construct. However, metals require protective coatings to prevent corrosion, which can generate oxidants, passive layers, or metal ions that might diminish the MEA's integrity. An alternative approach is the use of metal foam instead of graphite for Bipolar plates. Reddy and Kumar suggested the application of metal foam as the flow field and compared it with conventionally used rectangular

channels. The result of this research showed that reducing the permeability of metal foam significantly improved the electrical performance of the fuel cell. For example, when the permeability was around 10^{-6} m, the average current density was approximately 5943 A/m². However, lowering the permeability to 10^{-11} m increased the average current density to 8325 A/m². The design of the flow field in a bipolar plate plays a crucial role in determining fuel cell performance. It can affect pressure losses and the uniformity of gas spreading, as well as electrical current and heat transmission. Straight parallel rows, serpentine, pin-type, interdigitated-type and spiral flow fields are the most common designs used in PEM fuel cells and are presented in the **Figure 30**.

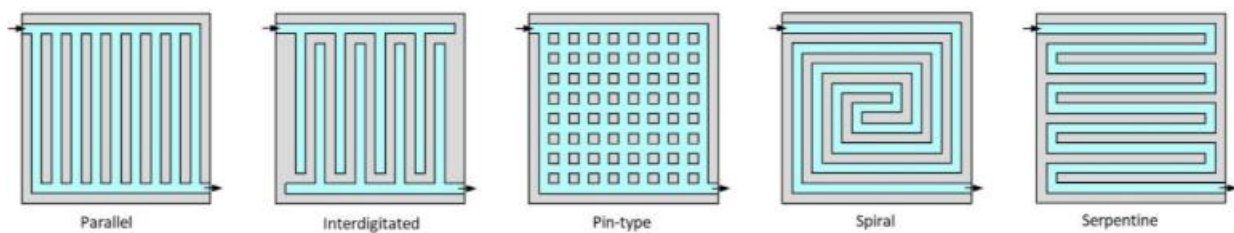


Figure 30. Main flow field designs for bipolar plates.

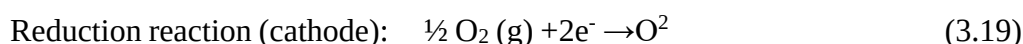
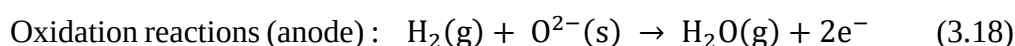
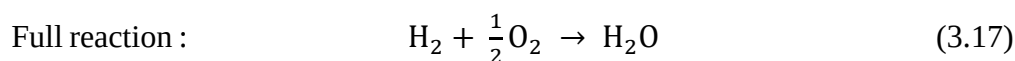
Tsai et al. investigated the impact of flow field design by using metal foam as a flow distributor, comparing five different metal foam flow field designs to a conventional graphite bipolar plate. They found that metal foam performed better, and performance could be further enhanced by using multiple inlets and dividing the metal foam into separate regions. This approach improves gas distribution, further boosting fuel cell efficiency. Additionally, Wilberforce et al. proposed various anode housing (flow field) designs using aluminum foam. Through numerical simulations, they concluded that open-pore cellular foam outperformed traditional flow plate designs by reducing dead zones where water can accumulate and negatively impact performance. Tseng et al. conducted an experimental study on the impact of porosity, hydrophobic treatment, and operating conditions on metal foam flow fields. Their results indicated that metal foam outperformed traditional graphite plate flow channels, with minimal concerns regarding corrosion. On the other hand, Hossain and Shabani highlighted several challenges in using metal foam for proton exchange membrane fuel cells (PEMFCs). One key issue is the potential for corrosion of the metal, which could reduce its conductivity. While metal foam holds promise as a candidate material for PEMFCs, more experimental data is needed to fully validate its effectiveness [115],[106].

3.2.1.3 Gaskets

It's about specific elastomers that should be used to avoid gas leakage due to the small hydrogen molecule size. Proton conductivity in membranes is closely tied to their hydration levels [115].

3.2.2 Solid Oxide Fuel Cell (SOFC)

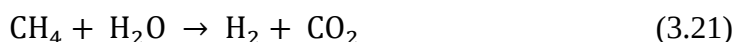
As we referred above, solid oxide fuel cell (SOFC) is another type of fuel cell that is very promising for vehicle applications. It's an all-solid-state energy conversion device that generates electricity and heat by electrochemically combining fuel and oxidant gases through an ion-conducting oxide material. These devices offer several advantages over traditional power generation systems, such as high efficiency, reliability, modular design, adaptability to different fuels like hydrocarbons, biogas, methane, carbon monoxide, natural gas and minimal emissions of nitrogen and sulfur oxides. A solid oxide fuel cell (SOFC) essentially consists of two porous electrodes of anode and cathode separated by a dense oxygen-ion-conducting membrane, which acts as the electrolyte and the interconnection which connects the anode of one cell to the cathode of the next cell. Components need to be chemically, structurally, morphologically, and dimensionally stable in both oxidizing and reducing environments. Additionally, it must exhibit chemical compatibility with other components and possess the necessary ionic or electronic conductivity. Each component needs to be chemically, structurally, morphologically, and dimensionally stable in both oxidizing and reducing environments. When components have the same thermal expansion coefficient, we decrease the risk of thermal stresses during fabrication and operation. Also, when the components are processed sequentially, the fabrication temperature for each successive component must be lower than that of the previous one. This ensures that the microstructure of the earlier components remains unaffected, preserving their intended properties and performance [117],[118]. The reactions that occur on the process of a SOFC are described as follows [2],[117]:



CO and hydrocarbons can also be used in SOFCs at high temperatures, so a water gas displacement reaction is possible:



And the steam reforming reaction is possible (in case of natural gas separation) [106]:



3.2.2.1 Materials for SOFC Components

1. Electrolyte: The most common material for electrolyte in SOFCs is 8–10 mol.% Y_2O_3 stabilized zirconia (YSZ). YSZ may not provide the highest conductivity compared to other dopants, but its widespread availability, affordability, and solid mechanical and electrical properties make it a popular choice for electrolyte material. To function effectively, YSZ must be non-porous to prevent gas leakage among the two FCs sides, uniformly thin to minimize resistive losses, and have an electronic transport number near zero for maximum efficiency. Its conductivity increases with temperature according to Arrhenius equation, and its ionic transport number is nearly one, showing minimal electronic conduction. The thermal expansion coefficient (TEC) of YSZ is around $10^{-11} \times 10^{-6} \text{ 1/K}$. This value of TEC serves as the baseline for SOFC design components. To reduce thermal stresses, the TECs of other parts are adjusted to match YSZ, either by adding dopants or modifying porosity. A high fracture toughness is important for the electrolyte to resist flaws and provide better durability during manufacturing.

For YSZ with 8 mol.% yttria, the fracture toughness is about $3 \text{ MN}\cdot\text{m}^{-3/2}$ at room temperature. Research shows that adding fine particles of partially stabilized zirconia or alumina can boost toughness without influencing its conductivity. To achieve enough ionic conductivity and power density, cells with YSZ as electrolyte need to operate above 800°C . Any reduction in the operating temperature leads to the decrease in interfacial reactions between components and extends the cell's lifespan. To overcome these disadvantages researchers, turn their attention to the development of alternate electrolyte materials, possessing sufficient ionic conductivity at reduced temperatures. A few examples of these materials are oxygen ion-conducting materials, stabilized bismuth oxide (Bi_2O_3) and ceria (CeO_2).

Stabilized bismuth oxide (Bi_2O_3) shows excellent ionic conductivity, but it breaks down into bismuth metal under low oxygen partial pressures (below 10^{-13} atm), making it unsuitable as an SOFC electrolyte. Doped ceria is another option but undergoes a large departure from stoichiometry at high temperatures and in reducing environments, leading to unwanted electronic conductivity. To address these issues, researchers have explored methods such as adding dopants or coating ceria with zirconia to improve its performance. Additionally, several doped perovskites (ABO_3 structures) have emerged as potential electrolytes for intermediate temperatures ($600\text{--}800^\circ\text{C}$). Prominent examples include doped lanthanum gallates, barium cerates, and strontium zirconates.

2. Cathode : The cathode electrode operates in the oxidizing environment of air or oxygen at almost 1000°C and participates in the oxygen reduction reaction (3.19), where oxygen consumes only two electrons and produces oxygen ions. The cathode should have high electronic conductivity, chemical and dimensional stability during fabrication and operation, a thermal expansion coefficient compatible with the other cell components and it have to be porous enough to facilitate oxygen molecules to reach the cathode-electrolyte interface. Cathode materials due to the high operating temperatures of SOFC are only noble metals or electronic-conducting oxides. However, noble metals like platinum or palladium are too expensive for widespread use. Among doped oxides, lanthanum manganite (LaMnO_3) is the most commonly used cathode material. LaMnO_3 is a p-type perovskite oxide whose oxygen stoichiometry varies with processing conditions, temperature and oxygen partial pressure. Even when it is stable in oxidizing conditions, it dissociates under highly reducing conditions. Its p-type conductivity comes from cation vacancies, and electronic conduction occurs through small polaron hopping—electrons transfer between Mn^{3+} and Mn^{4+} valence states. Doping with divalent ions like calcium, strontium, barium, or magnesium enhances conductivity by increasing Mn^{4+} content. For example, strontium doping improves electronic conductivity by replacing La^{3+} with Sr^{2+} .

3. Anode: The anode electrolyte material should have good stability in the reducing environment of the fuel, should be electrical conducting and have sufficient porosity to allow the transportation of the products of fuel oxidation and the fuel away from the electrode- electrolyte interface where the oxidation reaction takes place. The two electrodes that liberate during the oxidation reaction (3.18) move to the cathode through the external circuit. The reducing conditions on the fuel side of a SOFC propose the use of metals as a material for the electrode, with nickel being the most common choice due to its low cost. However, nickel has a higher thermal expansion coefficient ($13.3 \times 10^{-6} \text{ K}^{-1}$) than YSZ, which can lead to mechanical stresses. At the cell's operating temperatures, nickel can sinter, reducing its active surface area and lowering anode conductivity, ultimately affecting cell performance. Manufacturing a YSZ skeleton around the Ni particles prevents nickel sintering, reduces the thermal expansion coefficient of the electrode to align it more closely with the electrolyte, and improves adhesion between the fuel electrode and the electrolyte. The electrical conductivity of Ni-YSZ cermet electrode strongly depends on its nickel content, with a percolation threshold at around 30 vol.% nickel, enabling effective electronic conduction. Some other candidate anode materials cobalt-YSZ, ruthenium-YSZ, and mixed conducting oxides based on Y_2O_3 – ZrO_2 – TiO_2 solid solutions .

4. Interconnection: Interconnections in an SOFC should use materials that gratify the following requirements : 100% electronic conductivity, (unlike the electrolyte, which requires 100% ionic conductivity), be non-porous to prevent fuel and oxidant mixing, have a thermal expansion coefficient compatible with the cathode and electrolyte, and show minimal reactivity with the cathode, electrolyte, and electrical contact material (typically nickel). Alkaline earth-doped lanthanum chromite (LaCrO_3) meets these stringent criteria and is the most widely used interconnect material in SOFC. Lanthanum chromite is often doped with divalent ions like strontium, calcium, or magnesium to achieve the conductivity needed for use as an interconnect in SOFCs. The key difference between LaMnO_3 and LaCrO_3 is the chromite ability to remain stable in both highly reducing and oxidizing environments.

3.2.2.2 SOFC Design and Fabrication Process

Solid Oxide fuel cells are developed in various designs, with the most common being tubular and planar configurations. Each design has unique advantages and challenges, tailored to different applications and performance goals.

1. Tubular Design: In a tubular SOFC, a ceramic tube serves as both the mechanical support and the air electrode (cathode). The other components, including the electrolyte and anode are deposited as thin layers on this tube. During operation, air (oxidant) is introduced near the closed end of the tube through a ceramic injector. It flows along the tube and exits through the space between the injector and the cell. Fuel is supplied on the outer surface of the tube and is electrochemically oxidized as it flows toward the open end, generating electricity. **Figure 31 a)** illustrates the design of the tubular SOFC. Individual cells are connected in series or parallel to form a stack. For series connections, porous nickel felt links the anode of one cell to the cathode of the next through nickel plating on the interconnect. For parallel connections, the anodes of adjacent cells are directly connected. A key advantage of the tubular design is that it doesn't require high-temperature seals to separate the fuel from the oxidant, simplifying construction. However, the longer current path increases resistive losses, reducing efficiency. Fabrication begins with the extrusion of the cathode tube, which is sintered in air at around 1500°C to achieve ~30% porosity. The interconnect is then applied as a thin (85 μm) and narrow (9 mm) strip using plasma spraying, with the rest of the air electrode masked to restrict deposition. The masking material is removed in a post-deposition cleaning step. The YSZ electrolyte is applied as a thin film (~40 μm) using an electrochemical vapor deposition (EVD) process. At this process the reaction of zirconium chloride and yttrium chloride with oxygen

happens at around 1200°C to form the YSZ layer. The anode, 100–150 µm thick, is created in two steps. First, a nickel-YSZ slurry is applied over the electrolyte and sintered at about 1300°C to produce a 40% porous structure. Finally, nickel is electroplated onto the interconnect to ensure proper electrical contact.

2. Planar Design: In the planar SOFC design, cells are built as thin flat plates, with each cell consisting of an anode, electrolyte, cathode, and interconnection as you can see in **Figure 31 b)**. The interconnection has a ribbed structure that allows gases to flow and connects adjacent cells. This design is more efficient than the tubular type, offering higher power density and resistance losses that don't depend on cell size. Using thin components reduces resistance, supports lower operating temperatures, and makes it easier to manufacture parts separately, avoiding complications from firing them together. Planar SOFC design need high-temperature seals at the plate edges to keep fuel and oxidant separate. These seals, often made from materials like cement or glass-ceramics, can be problematic due to issues like cracking, reactions at the interfaces, and mismatched expansion rates. In the planar SOFC design, the YSZ electrolyte fabrication happens through tape casting and sintering to a thickness of 50–120 µm. The electrodes are added using techniques like slurry coating, screen printing, or plasma spraying. The interconnection is made from either LaCrO_3 (via tape casting or hot pressing) or metal alloy with high-temperature and oxidation-resistant [117].

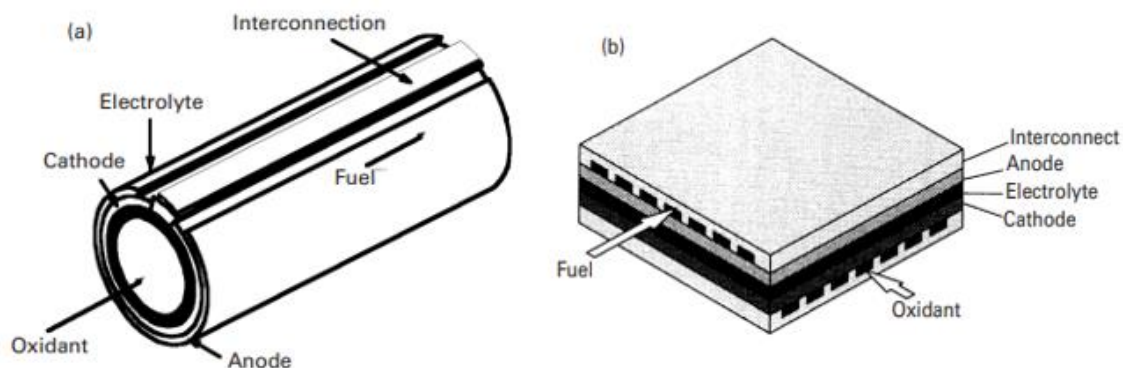


Figure 31. The Different designs of SOFCs: a) tubular b) planar.

3.2.3 PEMFC and SOFC Comparison

PEMFC and SOFC have both been effectively used in automotive drivetrains, but they have key differences. PEMFC operates at lower temperatures and requires pure hydrogen, making it sensitive to fuel impurities. In contrast, SOFC works at higher temperatures and can use a variety of hydrogen-containing fuels. SOFC's high operating temperature allows it to internally reform fuels into hydrogen, tolerating impurities that would damage PEMFCs. The SOFC's

efficiency ranges between 35–43 % and the PEMFC's ranges among 53–60%, but SOFC can achieve higher efficiency utilizing the heat generated during operation. PEMFCs rely their use on an expensive catalyst, while SOFCs operate without requiring a catalyst. This happens due to the high operating temperatures, typically in the region of 600–1000°C. Specifically high temperatures provide sufficient energy for the reactions to occur without relying on expensive materials, making this type more cost-effective. Furthermore, SOFC had higher power output (2000 kW) when compared to PEMFC (100 kW) [1],[118].

3.3: Fuel cell technology in the automotive section

A lot of different studies have proved many advantages with the application of fuel cells for powering automotive systems. Some of them are:

- The efficiency of a FCEV (can reach 60%) is higher than that of ICE-powered vehicles. That has to do with the fact that electricity is generated directly through the chemical reactions of the fuel, without the need for combustion. In Carnot thermal cycles, the efficiency of electricity generation depends on the limited efficiency of the combustion process.
- A fuel cell emits much smaller amounts of pollutants and greenhouse gases e.g. carbon dioxide and monoxide, nitrogen oxides, etc. Their only by-products are water and heat.
- Wide range of operating power capabilities for vehicles (20 to 250 kW).
- Autonomy ranges are comparable with market references (over 400 km).
- Low refueling time (< 5 min).
- Noise and vibration during their operation are greatly reduced, that is, they are negligible due to the absence of moving parts.
- The modular structure of fuel cell systems makes it easy to detect and replace a damaged or malfunctioning cell within the stack. This reduces maintenance costs as the repair or replacement process is simplified.

These reasons outline the need for the expansion of the FCEVs development. According to a 2019 report by Market Research Future (MRFR), the global automotive hydrogen and fuel cell market is projected to grow at an impressive compound annual growth rate (CAGR) of 25% through 2025. The rising demand for heavy commercial vehicles and passenger cars is a key driver of fuel cell adoption, positioning them as a greener alternative to traditional energy sources. Toyota, Honda, and Hyundai were the first to introduce mass-produced

hydrogen cars, quickly followed by other major automakers. In addition to passenger vehicles, hydrogen-powered trucks and heavy-duty vehicles (HDVs) are now being developed to help decarbonize the transportation sector. Specifically, FCEVs are positioning themselves to dominate the market for long-distance and heavy-duty transport. In Europe, the rollout of hydrogen buses is already underway, while hundreds of units operating in various Chinese cities. The “Global EV Outlook 2023” states that in the year 2023 the number of FCEVs has increased by 40% compared to 2021, reaching over 72,000 vehicles globally, of which 80% are light-duty vehicles (LDVs) and 20% are heavy-duty vehicles. In 2022 Republic of Korea, the USA, China, and Japan were leading in the FCEV market, respectively, with 40%, 21%, 19%, and 11% of total fuel cell vehicles in their stock as shown in the first diagram of **Figure 32**. The second diagram illustrates the distribution of FCEV stock classified according to application. China is the country with the main role in HDV, with 5400 buses, and 7000 trucks [3],[115].

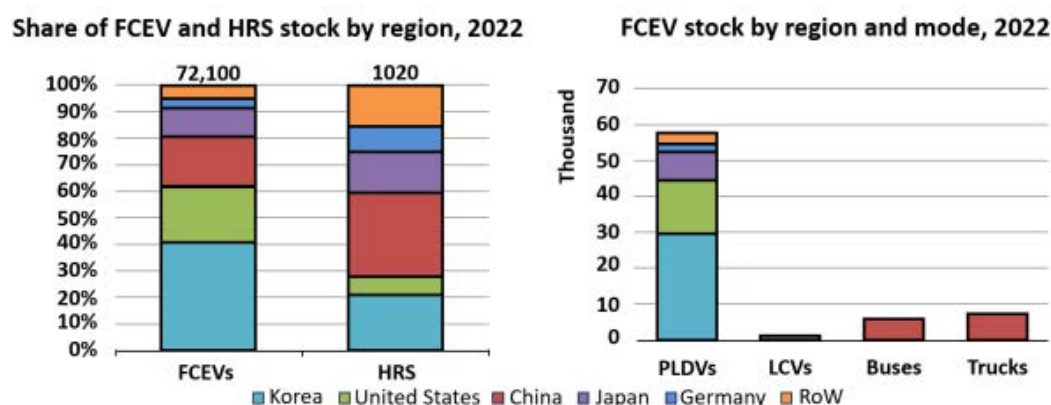


Figure 32. FCEVs and hydrogen refueling station stock by region, 2022. HRS: hydrogen refueling PLDVs: passenger light-duty vehicles LCVs: light commercial vehicles; RoW: rest of the world.

3.3.1 Global hydrogen and fuel cell vehicle policy

Countries around the world are adopting policies to promote hydrogen and fuel cell (H2FC) technologies, driven by goals like improving air quality, combating climate change, enhancing energy security, and boosting economic growth.

- **United States:** The focus is on reducing transportation emissions, as the sector accounts for 37% of national energy use. PEM fuel cells, known for efficiency and low emissions, are prioritized for vehicles, while stationary applications have less attention.
- **China:** The "Made in China 2025" strategy addresses air quality and economic growth, emphasizing a robust hydrogen industry to support fuel cell vehicles (FCVs). Hydrogen

production is expected to transition from industrial by-products to water electrolysis in the future.

- **Japan:** Japan's hydrogen plan includes three phases to establish a hydrogen-based society by 2040, focusing on fuel cell vehicles, hydrogen supply chains, and carbon-free production.
- **Europe:** Countries like the UK, France, and Norway are integrating hydrogen into strategies for cleaner transportation and industrial decarbonization.
- **GCC:** Gulf nations, including Saudi Arabia and the UAE, Oman, Qatar, Kuwait, and Bahrain, have historically relied on fossil fuel exports but are increasingly recognizing the importance of electric and hybrid vehicle transitions. In these regions, hybrid automotive systems incorporating engines, motors, batteries, and fuel cells are being explored, with fuel cells viewed as a vital component of hybrid-electric vehicles.

Hydrogen production and infrastructure are foundational to the FCV industry worldwide. The hydrogen industry chain integrates four sectors: production, transportation, refueling, and applications, ensuring hydrogen availability for FCEVs and is the backbone of the growing fuel cell vehicle industry, paving the way for cleaner and more sustainable mobility.

3.3.2 Classification of fuel cell electrical vehicles

Luo et al. divided fuel cell electric vehicles (FCEVs) based on their energy systems, as illustrated in **Figure 33**. In fuel cell hybrid electric vehicles (FCHEVs), supplementary energy units include batteries, supercapacitors, superconducting magnetic energy storage systems (SMES), photovoltaic (PV) panels, and flywheel. They identified seven main topologies: i) Full FCEVs (relying on fuel cells), ii) Fuel cell + battery hybrid electric vehicles, iii) Fuel cell + supercapacitor hybrid vehicles, iv) Fuel cell + battery + supercapacitor hybrids, v) Fuel cell + battery + PV panel hybrids, vi) Fuel cell + flywheel hybrids, and vii) Fuel cell + SMES hybrids.

Full FCEVs depend entirely on fuel cells for power. However, during rapid acceleration or sudden energy demand, high energy and power density are needed. These not so commonly used systems have serious disadvantages like low power response and low power density. However during rapid acceleration or sudden energy demand, high energy and power density are needed. To support this, batteries are often included in FCEVs to handle peak power demands and recover energy during braking. In some designs, supercapacitors replace batteries, acting as auxiliary energy systems, which store excess energy when the fuel cell output exceeds demand and help prolong the lifespan of both the batteries and fuel cells [119].

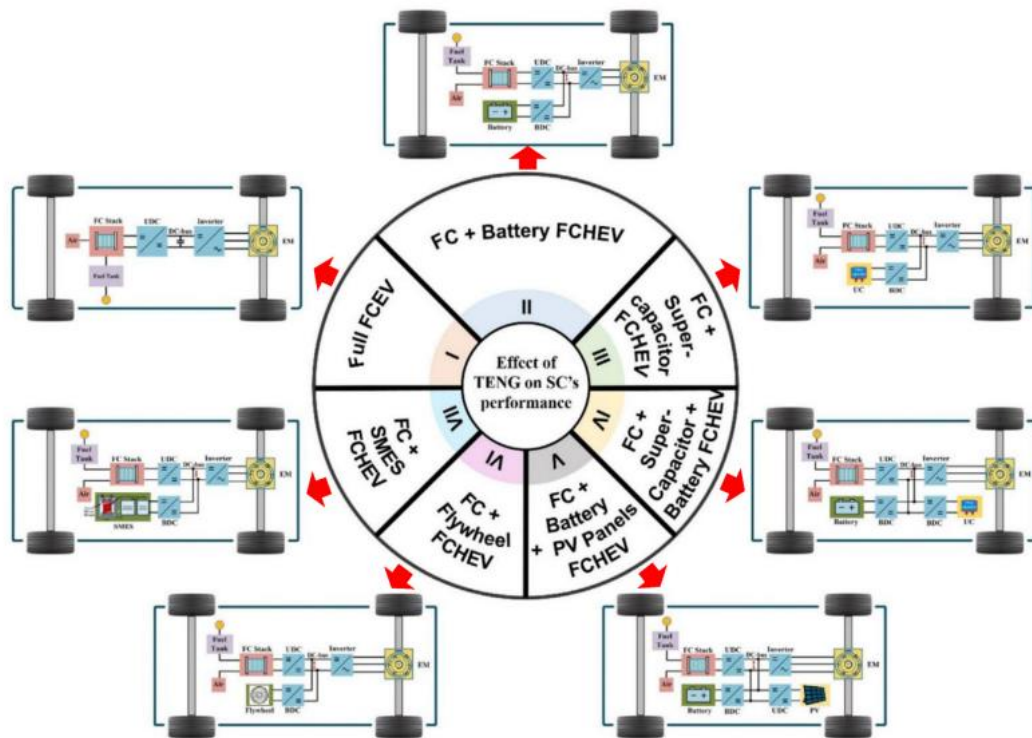


Figure 33. Classification of FCEVs based on their energy unit.

3.3.3 Fuel Cell Hybrid Electric Vehicles (FCHEVs)

Fuel cell hybrid vehicles overcome the disadvantages of traditional fuel cell vehicles by incorporating onboard energy storage systems, such as batteries and/or supercapacitors. In this hybrid configuration, the fuel cell handles the baseline power demand, while the energy storage system manages dynamic energy needs, including peak power demands, rapid adjustments, and startup energy. This system allows the fuel cell to consistently operate at its maximum efficiency, optimizing performance and extending its lifespan. Experimental models are also equipped with additional energy accumulators to further enhance their functionality and versatility. FCEVs typically includes a three-phase traction motor to drive the vehicle, an energy storage system composed of batteries and supercapacitors, a direct current (DC) bus for energy transfer, an inverter, which manages energy output to the traction motor and regulates SCAP contributions and auxiliary devices to support system operations. Fuel cell hybrid vehicles can be classified into passive and active systems:

- **Passive Systems:** In these systems, the fuel cell is directly connected to the battery via the DC bus, meaning their voltages are inherently coupled. This design eliminates the need for a DC/DC converter after the fuel cell, reducing system costs.

- **Active Systems:** These systems use a DC/DC converter to step up the fuel cell voltage to match the typically higher voltage of the battery system. For even greater control and flexibility, an additional DC/DC converter can be integrated into the battery's connection to the DC link, allowing independent voltage management for each component.

However, Active hybrid systems are more complex to design and control, they are highly appealing due to their significantly greater efficiency. Additionally all the previously mentioned system layouts require an extra DC/DC converter to provide power to the balance of plant (BoP) and auxiliary systems. The different configurations are shown in **Figure 34** [115].

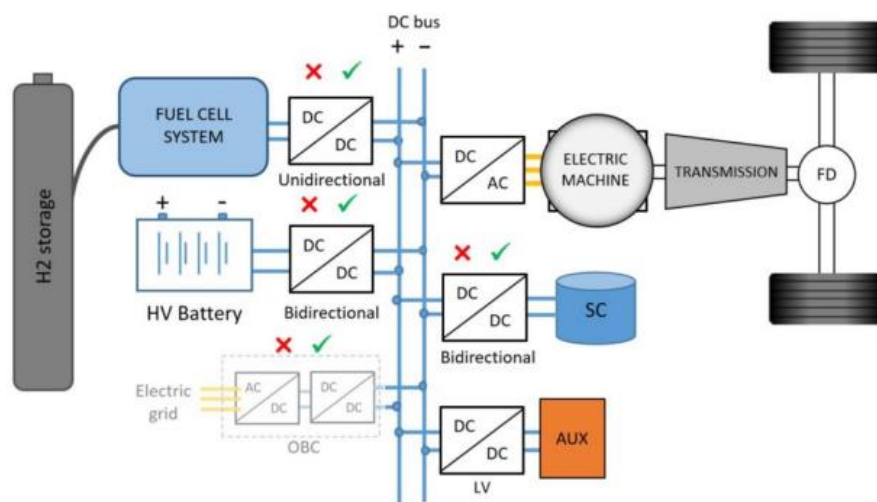


Figure 34. Generic fuel cell electric vehicle (FCEV) powertrain topology, including fuel cell system (FCS), HV battery, electric drive, supercapacitor (SC), transmission, LV auxiliary loads, onboard charger, and related power electronics converters [115].

3.3.3.1 Control Strategies to make FCHEVs more efficient

The performance of the hybrid energy system is heavily influenced by the control strategies employed. Common strategies include:

1. **Peaking Power Source Strategy (PPSS):** In PPSS various components such as controllers, wheels, traction motors, and pedals are electronically connected to gather signals. The vehicle controller determines the required power and torque based on input from the accelerator and brake pedals. When a driver demands power, the system dynamically adjusts the energy flow between the fuel cell (FC) and the Peaking Power Source (PPS) (e.g., batteries or supercapacitors) to meet the vehicle's needs. The power can come entirely from the FC, the PPS, or both, depending on the driving conditions that means if the driver suddenly accelerates, the PPS responds

quickly to support the FC and ensure the vehicle's smooth operation. The traction system ensures that the output power aligns with the demand for a responsive and efficient driving experience.

2. **Operating Mode Control Strategy (OMCS):** OMCS manages power distribution between the fuel cell and the battery based on vehicle demand. During discharge mode, if the power demand (P_{demand}) is less than the nominal fuel cell power (PFC) the FC meets the need. If power demand exceeds the nominal PFC, both the FC and battery supply energy. In charging mode the FC provides power for P_{demand} while charging the BAT. In fast charge mode, where P_{demand} is much smaller than the nominal PFC, the FC also powers auxiliary systems requiring extra energy. OMCS ensures efficient energy management during different driving conditions.
3. **Fuzzy Logic Control Strategy (FLCS):** The FLCS uses intelligent algorithms to optimize the energy flow in the vehicle. Its goal is to enhance overall efficiency while maintaining the performance of the energy storage system. When the State of Charge (SOC) for both the supercapacitor (SCAP) and battery is low (LSOC), the DC power (PDC) from the fuel cell is maximized (DC_{max}) to recharge the system. On the other hand when the SOC levels are high, the PDC is adjusted based on P_{demand} either minimized (DC_{min}) or maintained at a moderate level (DC_{middle}). This method aims to keep balances the SOC of SCAP and BAT to ensure they remain at optimal levels while meeting power demands
4. **Equivalent Consumption Minimization Strategy (ECMS):** The ECMS manages energy resources by optimizing fuel and electrical energy use. The energy consumption of SCAP and BAT is translated into an equivalent hydrogen consumption to account for all energy sources uniformly. ECMS ensures that energy from SCAP and BAT can substitute for hydrogen energy from the fuel cell when needed, effectively blending multiple energy sources. By focusing on minimizing total energy consumption while maintaining performance, ECMS provides an efficient way to manage energy in hybrid fuel cell vehicles [2].

3.3.4 Synthetic Comparative Analysis of FCEVs and BEV Technologies:

While fuel cell vehicles (FCEVs) are more efficient than traditional internal combustion engine (ICE) vehicles, their efficiency still falls short of battery electric vehicles (BEVs). ICE vehicles achieve 25% tank-to-wheel efficiency, while FCEVs reach about 60% and BEVs lead

with 80%. Fuel cell electric vehicles low well-to-wheel performance (**Figure 35 a**) denotes that BEVs are the more efficient option and should be prioritized where possible. Batteries are better suited to typical driving conditions, as fuel cells tend to degrade faster under variable power demands. Fuel cells perform better under steady power loads, particularly at partial loads where their efficiency peaks. For small-to-medium vehicles, battery electric vehicles (BEVs) generally have lower capital and operational costs compared to fuel cell electric vehicles (FCEVs). But hydrogen vehicles could still play a complementary role, as FCEVs offer an opportunity to utilize excess renewable energy, helping to bridge the gap between the intermittent supply of renewables and energy demand. For applications requiring high power, extended range and greater autonomy hydrogen has the potential to be a game changer factor (**Figure 35 b**). Thanks to its higher energy density compared to lithium-ion batteries, hydrogen enables greater range without significantly increasing vehicle weight. Aghabali et al. demonstrated that the power-to-weight ratio of typical 400 V or 800 V lithium-ion batteries can impose limitations in such scenarios. Also, the high weight and the acceleration capability of BEVs leads to wear and tear on road surfaces. Fuel cell systems offer several advantages for heavy-duty vehicles (HDVs). One major benefit is that fuel cells are well-suited to the operating cycles of HDVs. Their predictable routes mean fewer refueling stations are needed, which keeps infrastructure costs lower. Additionally, HDVs can justify higher upfront costs because their focus is on reducing operational expenses over time. Compared to battery-powered HDVs, fuel cell vehicles provide similar driving ranges with less weight impact and more room for cargo. For instance, Verbruggen et al. found that a 40-ton truck with a 600 km range powered by battery pack with energy density of 150 Wh/kg and energy consumption of 1.72 kWh/km, lost about 4 tons of cargo capacity. In contrast, a fuel cell truck could achieve an 800 km range with just two hydrogen tanks (40–60 kg each at 350 bars), barely affecting its payload capacity. Other advantages of fuel cell HDVs include faster refueling times compared to battery electric vehicles (BEVs) and the absence of resource limitations for platinum, unlike potential lithium supply constraints for BEVs. These advantages make fuel cell technology a compelling solution for HDVs, especially for applications that demand long ranges and heavy payloads [115].

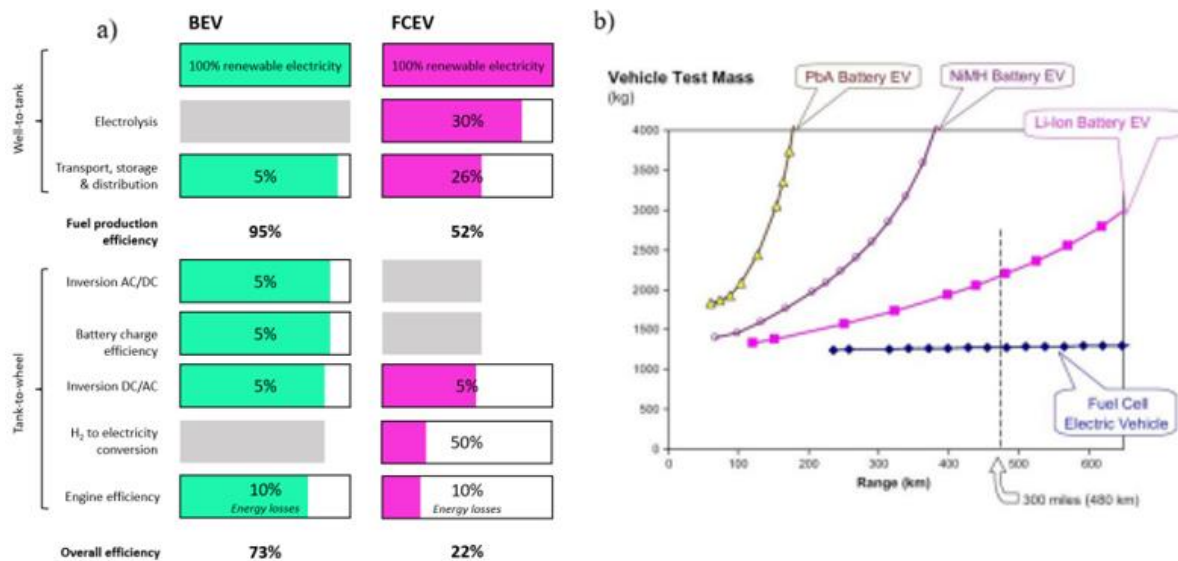


Figure 35. a) comparison of the efficiency of two types of powertrain b) Calculated mass of fuel cell electric vehicles and battery electric vehicles as a function of the vehicle range, the power trains of all vehicles are adjusted to provide a zero to 97 km/h acceleration time of 10 s.

3.3.5 Application of fuel cells in private transport

This sector is considered to be the largest possible market for fuel cell technologies due to the ever-increasing number of vehicles worldwide. As we reported before there are several challenges that we need to overcome for the FCEVs' commercialization. A few of them worth mentioning are the necessity for relatively small and lightweight power units, a considerable fueling infrastructure and an increase in maintenance procedures that the common buyer would have to commit to. One of the biggest challenges for hydrogen adoption is the lack of a widespread refueling infrastructure. To address this, many recent prototypes have been equipped with onboard reformers that use methanol or gasoline. While this approach offers a potential solution, it also comes with trade-offs, such as increased hardware complexity, higher maintenance demands and increased costs [3]. The currently major leading companies in the FCEV market are Hyundai, Toyota, and Honda. In 2019, Hyundai Nexo led the fuel cell electric vehicle (FCEV) market, accounting for 63% of global sales, followed by Toyota Mirai at 32% and Honda Clarity Fuel Cell at around 5%. Hyundai has ambitious plans to expand further, aiming to produce 500,000 FCEVs annually by 2030. All these manufacturers rely on PEM fuel cells for their vehicles. Companies like Peugeot, Citroen, and Opel are joining the market with new fuel cell van projects.

3.3.5.1 Audi concept

The Audi h-tron quattro concept showcases a combination of a 110-kW fuel cell stack, a 1.8 kW power-optimized battery stack, and a 100-kW electric motor. It boasts an impressive 600 km driving range with a refueling time of just 4 minutes. The features of this FCEV can be seen in **Figure 36**. Hydrogen is stored onboard at 700 bar, and the 60 kg battery pack contributes to energy recovery during braking. A three-way converter connects the battery, fuel cell, and power electronics, enabling high output voltage without significant drops. The vehicle's chassis houses 330 individual fuel cells, which operate between 220 and 280 V and at temperatures of up to 95°C. This fuel cell stack represents Audi's fifth-generation advancements in hydrogen technology.

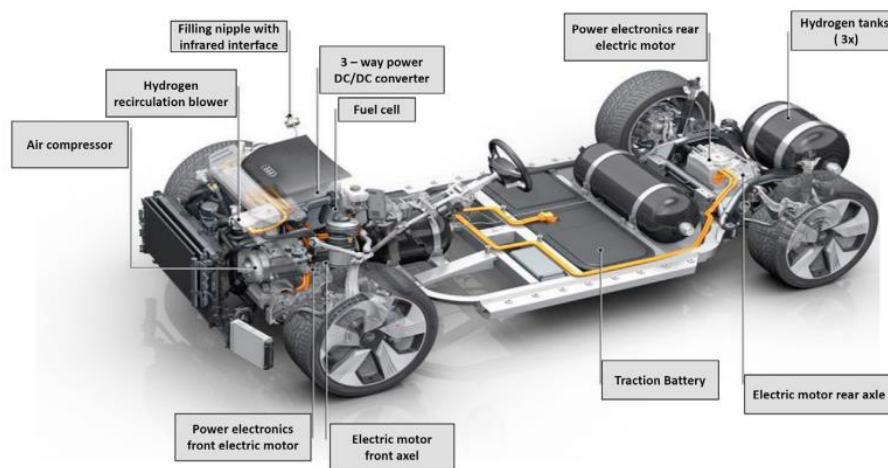


Figure 36. Audi modelled fuel cell electric vehicle.

3.3.5.2 Toyota Mirai

The Toyota Mirai, launched in 2014, has seen over 10,000 units produced. However, its adoption has been limited, partly due to lagging infrastructure development, which failed to keep pace with Toyota's plans for growth. Another significant barrier is its price: starting at \$59,455, the Mirai is considerably more expensive than other Toyota electric or hybrid models. This high cost stems from the use of exotic materials, such as carbon fiber for its hydrogen tanks, and the premium components typical of a high-end vehicle. Mirai features a next-gen fuel cell system with 3.1 kW/L power density, doubling that of the FCHV-adv while delivering over 100 kW output in a more compact design. It uses a lightweight fuel cell stack and two 70 MPa hydrogen tanks under a custom body. Seating up to four people, the FCV was set for a 2015 launch with a 95% lower fuel cell system cost than the 2008 FCHV-adv. The main components of the Toyota Mirai are illustrated in **Figure 37**.

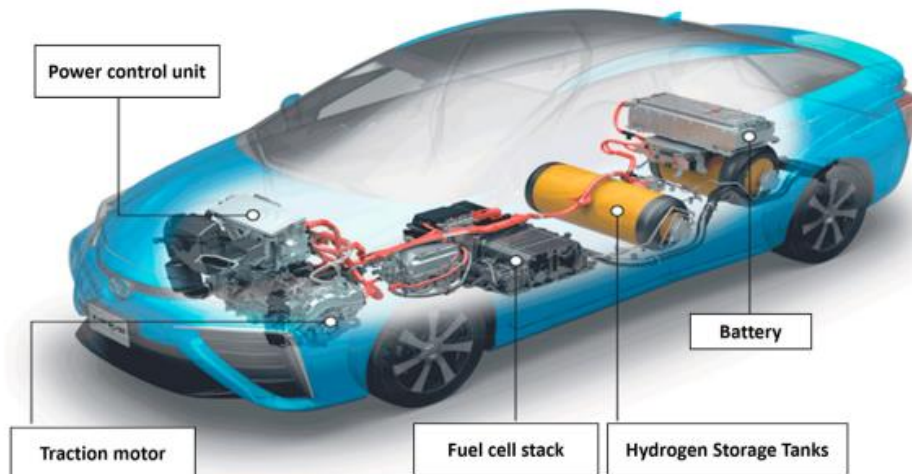


Figure 37. Components in Toyota Mirai.

3.3.5.3 Hyundai 2019 Nexo

Hyundai's Unique Selling Proposition (USP) for the Nexo lies in its innovative 59-liter triple-tank system, which can store 6.4 kg of hydrogen onboard. This setup, as shown in **Figure 38**, gives the Nexo "Blue trim" version an impressive driving range of 612 km. However, like other fuel cell car manufacturers, Hyundai faces challenges such as the limited availability of hydrogen refueling infrastructure. For instance, in the U.S., only 59 hydrogen refueling stations were expected to be operational by the end of 2020. Additionally, hydrogen costs remain a significant barrier. In California, hydrogen prices range from \$10 to \$16 per kilogram, making it far less economical than alternative fuels like natural gas, which costs about \$5 per kilogram. [3]. Its cost in germany rises up to 77.008,4 €.



Figure 38. Hyundai Nexo 2019 with 3 small hydrogen tanks.

Key specifications of recent fuel cell electric vehicle models are summarized in **Table 4**.

Table 4. Specifications for the latest Fuel cell electric vehicle models currently in production

FCEV	Launch date	Mass (kg)	Fuel cell/motor power (kW)	Power density (kW/L)	Acceleration time (s) 0 –60 mph (100 km/h)	Fuel tank capacity (kg) (wt%)	Fuel pressure (MPa)	Estimated range (km)	Fuel economy (kg hydrogen/100 km)	Fuel consumption (mpg gasoline equivalent)
Hyundai Nexø	2018	1873	95/120	3.10	9.5 (10)	6.33 (7.18 wt %)	70	370–595	0.84	57–61
Honda Clarity	2016	1875	103/130	3.12	9.2 (9.7)	5.46 (6.23 wt %)	70	366–589	0.97	67
Hyundai ix35 FCEV or Tucson FCEV	2014	1980	100/100	1.65	12.5(13.2)	5.64 (6.43 wt %)	70	369–594	0.95–1.0	66
Toyota Mirai	2014	1850	90/114	3.10	9(9.5)	5.0 (5.70 wt%)	70	312–502	0.76	67

3.3.5.4 Nissan's SOFC vehicle case

In 2016, Nissan introduced the world's first solid oxide fuel cell (SOFC) vehicle using bioethanol, achieving an efficiency of 55% . This innovative vehicle features an SOFC system integrated with a battery, a bioethanol fuel tank, a reformer, and a motor, as illustrated in **Figure 39**. The process begins with fuel being pumped from the tank into the reformer, where hydrogen is extracted from the bioethanol. This hydrogen is then delivered to the fuel cell's anode to generate electricity. The generated energy is either used directly to power the motor or stored in the battery. Additionally, the vehicle recovers energy through a regenerative braking system, further enhancing its overall efficiency and performance [120],[121]. The ethanol fueled in this Nissan vehicle is produced only from renewable sources and for this reason it was named e-Bio Fuel-Cell Vehicle. This hybrid system combines a 5-kW solid oxide fuel cell (SOFC) system, a 30-liter fuel tank, and a 24-kWh lithium-ion battery. While its top speed reaches 120 km/h, slightly lower than the 150 km/h of Nissan's PEMFC-powered X-Trail, it compensates with an impressive range of up to 600 km and an acceleration time of 14 seconds. The metal supported SOFC stack has a specific power of 0.0385 kW/kg and a total weight of 130 kg. On this hybrid system the Li-ion battery has a dual role, starting the SOFC system and providing energy during operation. The lithium-ion battery pack, weighing 267.5 kg, boasts an energy density of 157 Wh/kg. Measuring 290 mm x 216 mm, it consists of 48 modules, each housing four cells. Each cell has a voltage rating of 3.75 volts and utilizes lithium manganese oxide-lithium nickel dioxide at the cathode and graphite at the anode. Powering the vehicle is an 80-kW synchronous AC electric motor with a torque output of 280 Nm, providing reliable performance and efficient operation for this groundbreaking hybrid vehicle [121],[122].

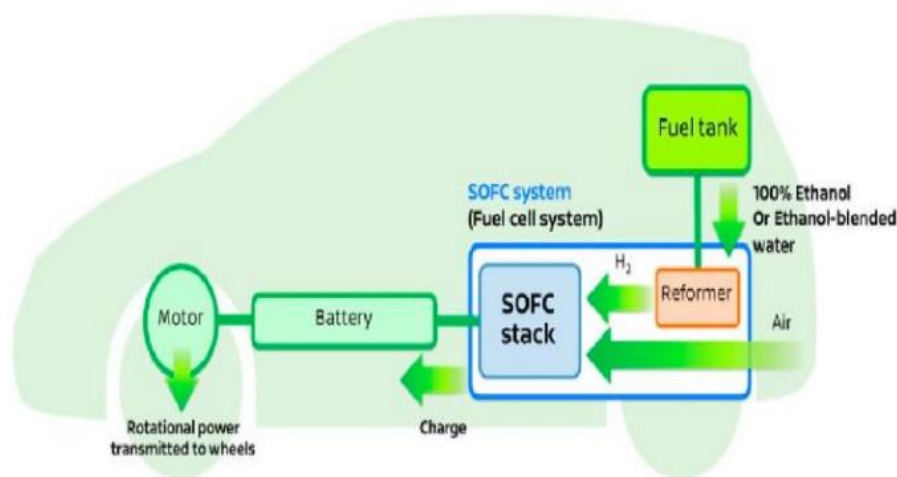
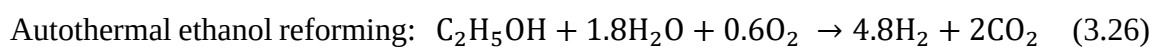
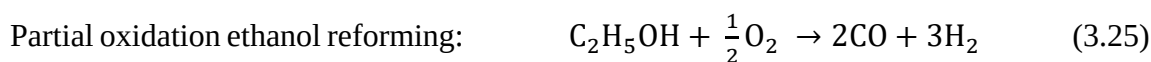
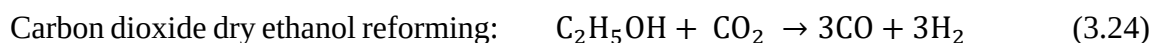
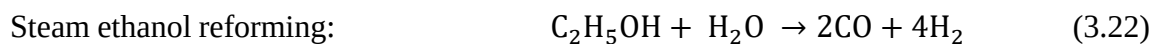


Figure 39. Schematic diagram of Nissan SOFC vehicle [122].

In particular, the ethanol used comes from biomass. The carbon dioxide consumed during biomass production equals the amount emitted during ethanol use, so the company promises a CO₂ neutral car with zero additional emissions. Ethanol cannot be fully oxidized due to the difficulty of breaking its strong carbon-carbon (C-C) bonds, instead, it undergoes partial oxidation, forming intermediate compounds and producing only 4e⁻, limiting its direct efficiency. To optimize fuel utilization, Nissan incorporated a reformer into the vehicle. This reformer converts ethanol into a hydrogen-rich mixture, which is then used by the solid oxide fuel cell (SOFC) system to generate electricity efficiently. The hydrogen generated undergoes electrochemical reactions in the SOFC to produce power. Generally, ethanol can be reformed through several possible routes that can be divided into 1) steam ethanol reforming (SER), 2) carbon dioxide dry ethanol reforming (DER), 3) partial oxidation ethanol reforming (OER) and 4) autothermal ethanol reforming (AER). These methods involve different chemical reactions, that are presented below :



cold start capabilities, safety concerns, and underdeveloped energy management systems (EMS). While these challenges continue to be present, city buses powered by fuel cell systems and hydrogen have been successfully deployed in countries such as Japan, Germany, and the UK. The ZeEUs e-bus Report states that the European fuel cell bus industry reached 2% of urban buses and this percentage will grow to 10% by 2030, that promises exciting opportunities for the future of sustainable transport. **Figure 41** illustrates a fuel cell bus.

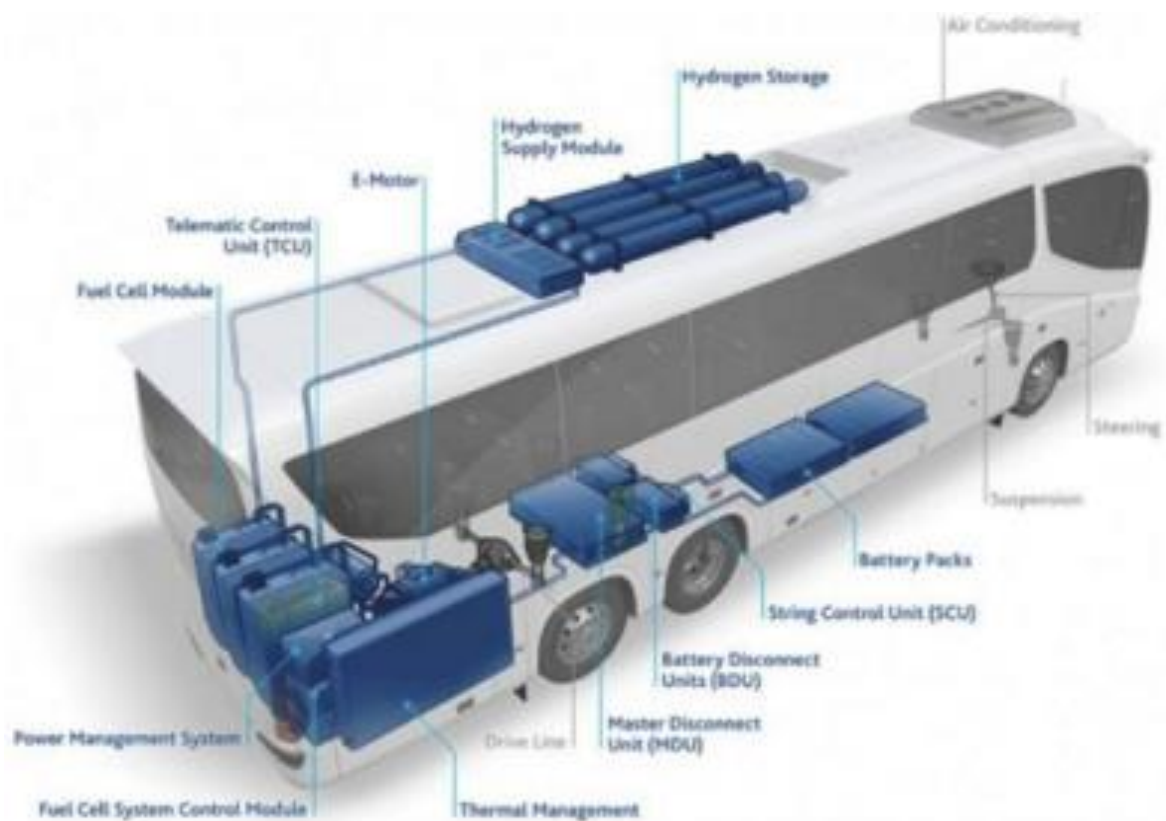


Figure 41. Schematic of a fuel cell bus.

London is leading in the effort for the mass evolution of hydrogen fuel buses in the UK. “Trasport For London” is a project that has managed to gather 13.8 million € for infrastructure and 20 double-decker buses, that will be serve people’s transportation on three bus routes in London's "Ultra Low Emission Zone". Flixbus (Europe’s major long-distance bus travel operator) and Frudenberg are working on an upcoming project that aims to expand the growth of fuel cell buses in the next following years. As Flixbus denotes, the acceleration of the new buses should match today’s standard diesel buses, and the vehicles should cover at least 500 km before refueling (which should take no longer than 20 min). **Figure 42** shows the components of the Flixbus fuel cell bus [3] .

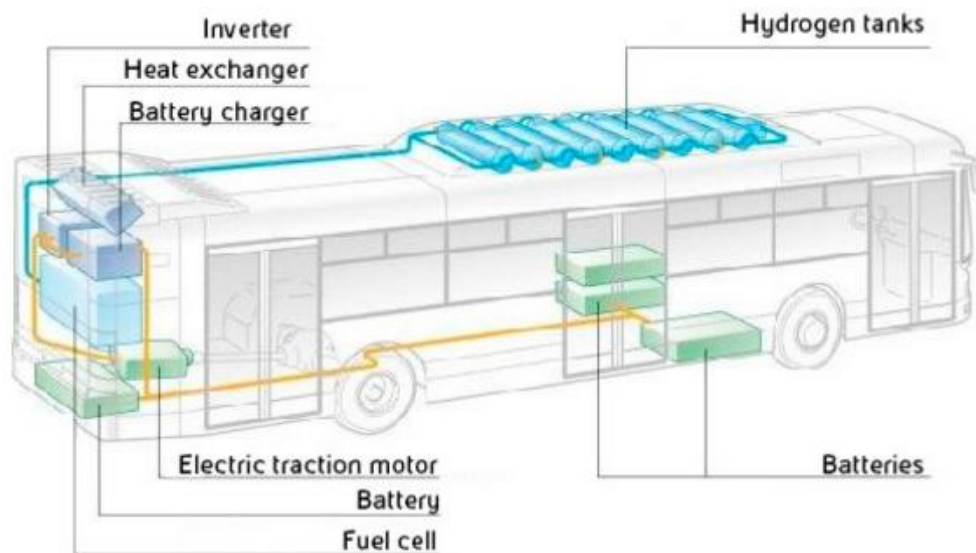


Figure 42. Flixbus Fuel Cell bus components.

3.3.7 The BoP of Fuel Cell Systems in FCEVs

The operation of a fuel cell stack relies on several auxiliary systems and components collectively known as the Balance of Plant (BoP). The BoP ensures the smooth functioning of the fuel cell by supporting its core operations and typically consists of three main systems:

1. **Air Supply System:**

- Components: Compressor, humidifier, and air filter.
- Function: Supplies air to the cathode of the fuel cell, ensuring adequate oxygen for the electrochemical reaction.

2. **Hydrogen Supply System:**

- Components: Hydrogen tank, pressure control valve, recirculator, purge valves.
- Function: Provides hydrogen to the anode, maintaining the necessary fuel supply for the reaction.

3. **Temperature Management System:**

- Components: Pump, thermostatic valve, radiator, and heater.
- Function: Regulates the temperature of the fuel cell stack by circulating coolant through channels in the bipolar plates, ensuring optimal operating conditions.

A schematic representation of the BoP, including its subsystems and components, is illustrated in **Figure 43** to provide a clear understanding of how these elements work together to support fuel cell operations.

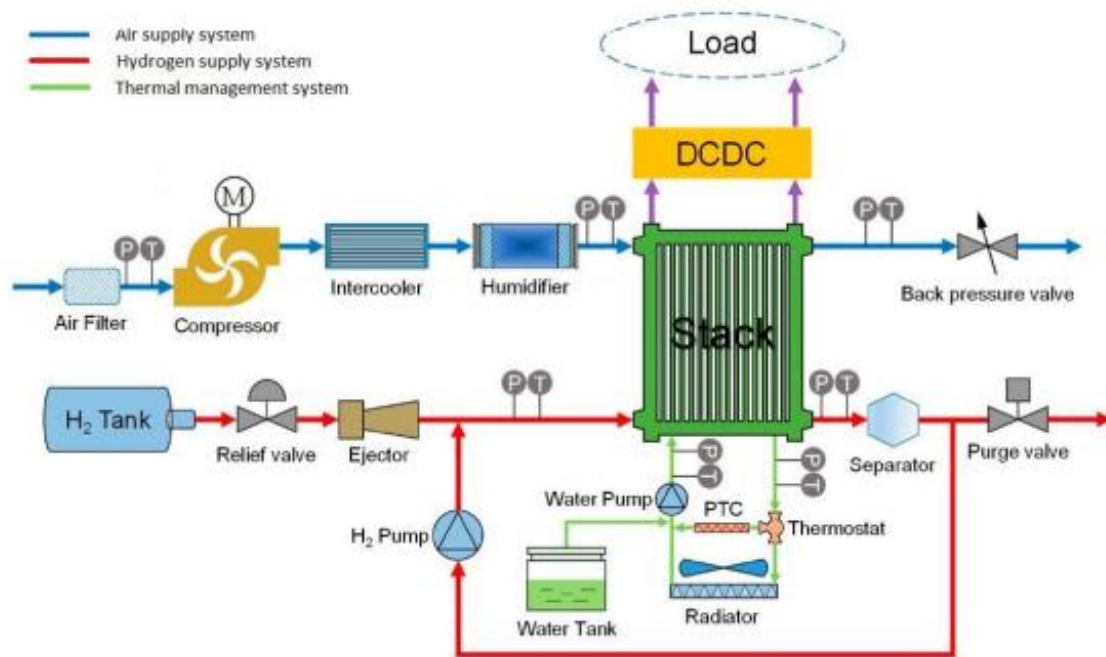


Figure 43. Schematic diagram of the BoP of the PEM fuel cell stack.

1. Air supply system:

Fuel cell electric vehicles (FCEVs) typically use ambient air as the source of oxygen for the reaction with hydrogen in the fuel cell. To enhance system performance, this process often operates under pressurized conditions, usually in the range of 1.5–2.5 bar. Increasing air pressure benefits the fuel cell system in several ways:

- According to the Nernst equation pressurizing the air inlet increases the cell voltage, which enhances the power output. However, at pressures beyond 4 bar, this benefit diminishes due to mass transport limitations.
- It reduces the stack volume and enables a more compact stack design, saving space.
- Increased pressure raises oxygen concentration, reducing polarization losses and improving the reaction rate, thereby boosting efficiency.
- Higher pressure improves the movement of gases and water within the system, which reduce the membrane degradation.

One challenge with the supply of oxygen is oxygen starvation, which can happen when the fuel cell doesn't get enough oxygen, often during rapid changes in driving conditions like quick accelerations or stops. If even a single cell in the stack experiences oxygen starvation, the other cells will impose it to operate at the same current. This causes it to enter voltage reversal conditions (electrolytic mode), where energy from other cells drives the reaction in reverse.

Such conditions can degrade the catalyst and severely damage the cell. To address this issue, and have an adequate supply of oxygen, maintaining an excess air supply ($\lambda > 1$) is an effective strategy. The air excess ratio (λ) is defined as the ratio of the actual oxygen flow entering the stack to the oxygen flow consumed in the reaction. This ensures an adequate supply of oxygen, preventing starvation and protecting the fuel cell components. 3.27:

$$\lambda = \frac{\dot{m}_{air}}{\frac{i \cdot n \cdot M_{air}}{4 \cdot F \cdot x_{O_2}}} \quad (3.27)$$

where $\dot{m}_{air}$ (kg/s) is the air mass flow flowing through the cathode, i (A) is the stack current, n is the number of cells in the stack, M_{air} [g/mol] is the molar mass of air and F (C/mol) is the Faraday constant.

While increasing the air excess ratio λ , helps prevent oxygen shortages in a fuel cell, it comes with a trade-off: the air compressor has to work harder, consuming more power. This increased power consumption reduces the overall net power output of the system. For optimal performance in PEM fuel cells, the air excess ratio is typically kept around $\lambda \approx 2$. Achieving the necessary pressure for this ratio usually requires a compressor with a compression ratio of 2–3. The performance of the air compressor is crucial since it strongly impacts both fuel cell and system efficiency. In fact, the air compressor is the most energy-demanding component of the Balance of Plant (BoP), accounting for up to 30% of the fuel cell's output power. To get over these challenges three main layouts for the air compression stage are commonly used in fuel cell systems. These 3 systems are shown in **Figure 44**:

1. **Single-stage connection:** A single compressor is used, with a throttle valve placed after the fuel cell stack to fine-tune and increase pressure if needed.
2. **Turbocharger:** This setup pairs a compressor with an expander (turbine). The turbine recovers 20–50% of the power used by the compressor, making the system more energy-efficient.
3. **Two-stage serial compressors:** In this configuration, a second compressor is added to further boost the pressure generated by the first compressor, allowing for higher compression levels when needed.

Finding the right balance between air compression and energy consumption is key to maximizing the efficiency and performance of fuel cell systems.

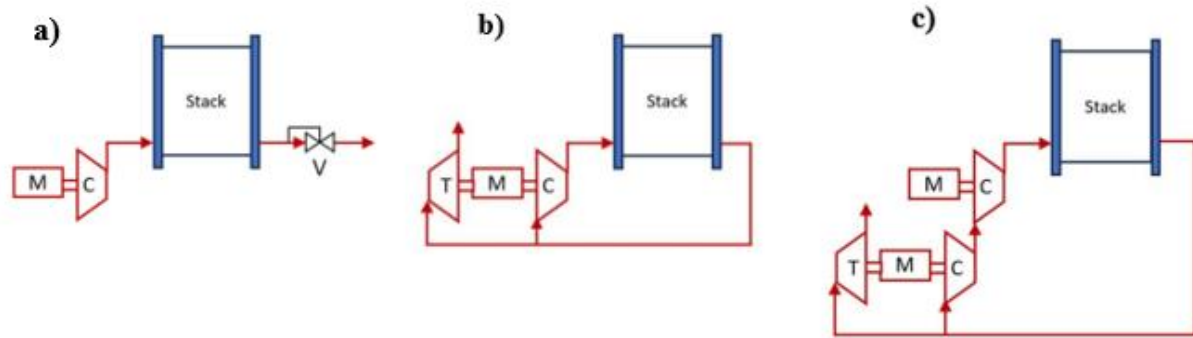


Figure 44. a) Single-stage compressor (either positive displacement or centrifugal), b) combined compressor and expander and c) two-stage serial turbocharger (M: motor C: compressor and T: turbine).

The second layout (turbocharger layout) is the most promising option to use as air compression in fuel cell system, because it is light, compact and has excellent efficiency. Layouts like this are also used in ICE vehicles, but in other operating conditions: for example, in PEM fuel cells, the exhaust stream is at 80–120 °C, while in typical ICE turbines, the exhaust stream is at about 950 °C.

Water management is also a very important segment of fuel cell operation and is greatly affected by the working condition of the air supply system. Specifically, a higher tendency for water accumulation occurs in low air flow rates. This accumulation leads to flooding and oxygen starvation. High air flow rates increase the air pressure, enhance the stack voltage and facilitate water removal. But membrane drying-up problems may arise after long operation. To address these issues the system has to use a humidifier which will be equipped in the air supply system next to the compressor.

The restricted available space for transporting water to humidification on FCEVs needs the installation of a humidification system with internal or external water recirculation as this is used in the Toyota Mirai. The most common humidifiers are water bubbles, that control the temperature of the liquid and hence the relative humidity (RH) of the passing gases. The air supply system should include a filter, because the bad air quality may reduce fuel cell efficiency due to particle and compound accumulation in the stack membrane.

2. Hydrogen Supply System :

Hydrogen as we mentioned before has a very low volumetric density, which poses a significant challenge for onboard storage. To achieve driving ranges comparable to internal combustion engine (ICE) vehicles, hydrogen storage systems must balance weight, volume, safety, and cost. To address these challenges, the 3 storage solutions: Compressed Hydrogen Storage, Cryogenic Liquid Hydrogen, Metal Hydrides we referred to on 3.1.5 were introduced. Hydrogen pressure at the fuel cell inlet is 1.1-3 bar at a temperature 40 – 85 °C. This is controlled by an electric pressure control valve to ensure consistent operation. For optimal performance, the fuel cell stack requires a slight surplus of hydrogen at the anode, known as an over-stoichiometric ratio, typically $\lambda_{H_2} \approx 1.2$. This ensures that the system always has enough hydrogen for the electrochemical reaction to proceed smoothly. If there is not enough hydrogen on the anode, a condition called hydrogen starvation occurs which is more harmful than oxygen starvation. This can be highly damaging to the fuel cell, resulting in Voltage reversal that reverses the normal operation of the cell, Catalyst degradation, causing the carbon carrier to collapse, Corrosion and structural damage which leads to perforation of the carbon paper and bipolar plates, permanent damage, meaning that the cell may become irreparable and need to be scrapped.

To avoid wasting valuable hydrogen and to improve water management, fuel cell systems often operate in Dead End Anode (DEA) mode, where the hydrogen supply is recirculated instead of vented. This recirculation ensures that unreacted hydrogen is reused efficiently. However, pressure losses in the fuel cell require precise control of the hydrogen recirculation process. This is typically achieved using two approaches. The first approach is active recirculation where a blower is used to manage hydrogen flow and maintain pressure. Even though this approach is effective, the blower is a major energy consumer within the fuel supply system. It ranks second or third in energy consumption among Balance of Plant (BoP) components (just after the air compressor and coolant pump) and typically uses around 0.9 kW in an 80 kW fuel cell system. The second is Passive Recirculation. In this a jet pump can be used as a simpler, more efficient alternative. Unlike a blower, the jet pump requires no external power, reducing overall energy consumption and improving system efficiency. This approach is valued for its low cost, high reliability, and straightforward design, making it a preferred choice in many systems. **Figure 45** shows the two approaches.

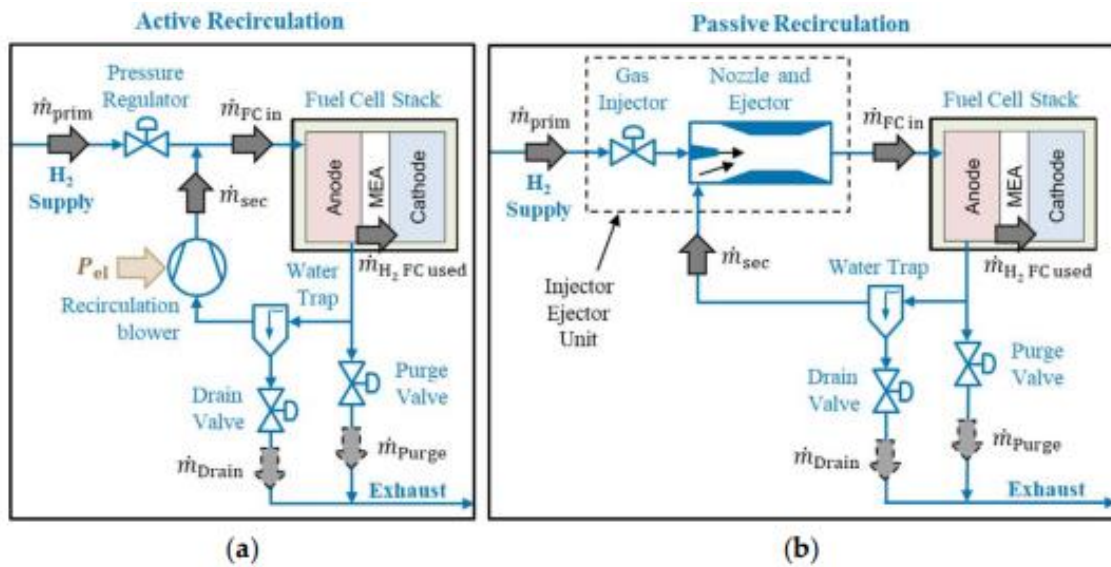


Figure 45. Anode subsystem of a PEM fuel cell: a) active recirculation and b) passive recirculation.

As shown in the next figure the first hydrogen flow passes through a nozzle, ensuring the kinetic energy for suction. The secondary flow is recirculated, enters the suction chamber, encounters the first flow in the mixing chamber and exits the jet pump through a diffusor.

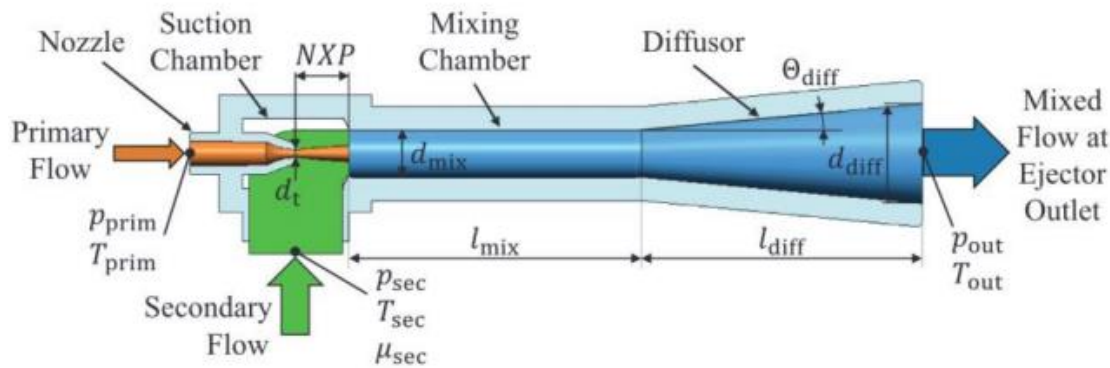


Figure 46. Jet pump work principle.

Managing the hydrogen supply in fuel cell systems is a complex task due to the intricate fluid interactions involved. This complexity makes controlling the hydrogen supply more challenging. Yin et al. reviewed numerous studies focused on optimizing the ejector recirculation system, which is currently the most widely used technique in fuel cell electric vehicles (FCEVs). However, some vehicles, like the Toyota Mirai, use active recirculation with a blower instead. The hydrogen supply system is closely linked to the air supply system, and this relationship plays a critical role in water management within the fuel cell stack. Issues such as the diffusion of air nitrogen into the anode or the presence of fuel impurities can degrade the stack and lower its voltage. Additionally, operating in Dead End Anode (DEA) mode can lead

to the accumulation of water and impurities in the membrane, further contributing to voltage drops. To mitigate these issues, the hydrogen supply pressure at the anode is typically kept higher than the air supply pressure at the cathode. This pressure difference helps reduce nitrogen migration and limits water vapor permeation through the membrane. One widely used solution for managing impurities and excess water is purging the anode channel. Different purging strategies, focusing on determining the optimal conditions to trigger hydrogen purges have been tested. In humid environments, the right triggering thresholds for purging significantly impact the stack's efficiency, whereas in dry conditions, purging thresholds have less influence on performance. By balancing these control strategies, fuel cell systems can achieve improved efficiency and durability, addressing the challenges of hydrogen supply and stack water management.

4. Temperature Management System:

In a fuel cell the average efficiency is approximately 60% (the input energy is converted to electrical power) and the remaining 40% is dispersed as waste heat, produced in proportion to the power output. This heat must be carefully managed to maintain optimal performance. Heat transfer in proton exchange membrane (PEM) fuel cells is particularly complex due to the presence of a non-isothermal two-phase flow involving liquid water and vapor. The major heat contributors are: The irreversibility of electrochemical reactions cause the overpotentials in the catalyst layers (CLs) account for up to 60% of the total heat generation. The entropic heat that is generated from entropy changes during electrochemical reactions, contributing up to 30% of the total heat. The last one is the Joule heating resulting from ionic and electrical resistance within the system, it contributes up to 10% of the total heat.

The heat significantly influences the fuel cell's performance, as its efficiency is highly dependent on maintaining the right operating temperature and ensuring even temperature distribution across the membrane. Proper temperature management is also closely tied to water management, as both factors directly affect the cell's overall efficiency and stability. Effectively balancing temperature and water conditions within the fuel cell ensures optimal performance and extends the system's operational lifespan. Optimal working conditions are very important for the right operation of the fuel cell. These conditions have two main demands:

- 1. Keeping a nearly constant temperature around 80°C:** The hydration of the fuel cell membrane is highly sensitive to temperature, as it depends on saturated steam pressure, which increases exponentially with temperature. High temperatures can dry out the

membrane, leading to increased ionic resistance, higher ohmic losses, and material degradation, while low temperatures encourage the formation of liquid water, increasing the risk of electrode flooding, oxygen starvation, and significant mass concentration polarization. This can also slow down reaction kinetics in the catalyst layer (CL) and reduce the membrane's ability to conduct protons effectively.

2. Ensuring isothermal conditions across the cell area: Uneven temperature distribution within the stack can cause local phase changes in water that influence relative humidity. This leads to differences in electrochemical reaction rates across the system, resulting in inefficient use of catalysts and reactants. It can also create hot spots, reducing the fuel cell's efficiency and ruining its components over time.

Under stoichiometric conditions, the reactant gas flow removes a small portion of the heat (<5%). While this may suffice for small fuel cells (<100 W), automotive applications require more robust heat dissipation solutions due to the higher power demands. Removing waste heat from PEMFCs is particularly challenging compared to internal combustion engines (ICEs) because fuel cells with polymer membrane electrolyte operate at a much lower temperature, 80 °C vs 400 °C. To maintain optimal temperatures, different cooling methods are employed:

- **Air Cooling** : The simplest approach, ideal for small systems (< 2 kW). Heat is removed via airflow over bipolar plates, with dedicated channels for thermal dissipation. Fans are used to force air through the channels. While simple, air cooling has limited capacity and is unsuitable for larger or more demanding systems.
- **Liquid Cooling**: The most common method for PEM fuel cells, especially in automotive applications, due to its high cooling capacity, efficiency, and flexibility. A liquid coolant (typically deionized water or an antifreeze mix like ethylene glycol and water) is circulated through cooling channels in the bipolar plates using a pump. Despite its advantages, liquid cooling comes with challenges such as power consumption by the pump, potential leaks, and risks of corrosion

Many factors like channel layout, size, and coolant flow rate can affect thermal exchange efficiency. Specifically small channels can increase power consumption, while overly large manifolds may lead to non-uniform cooling. Also, an optimized flow rate is critical to ensure effective heat removal without overburdening the pump. In automotive applications, designs vary between manufacturers. The Toyota Mirai and Hyundai Nexo use one cooling unit per fuel cell, ensuring precise heat management but the Honda Clarity employs one cooling unit

for every two cells, balancing efficiency and complexity. **Figure 47** shows the design of the coolant channels in the Honda FCX Clarity Fuel Cell [115].

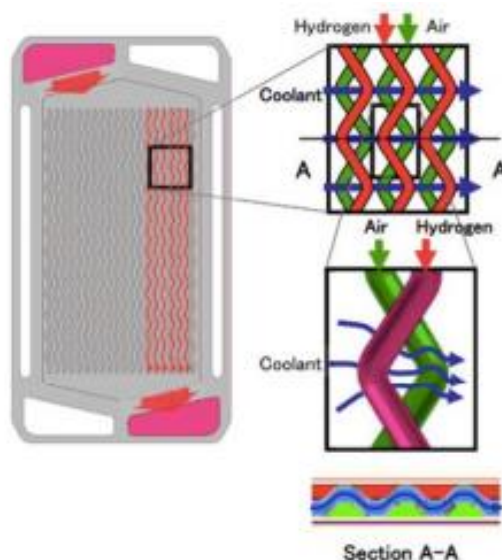


Figure 47. Coolant channels in the Honda FCX Clarity Fuel Cell.

3.4 Bioethanol as Fuel for Fuel Cells

Bioethanol has emerged as a promising biofuel alternative, addressing environmental concerns associated with fossil fuels. Bioethanol can be produced from diverse biomass resources, including agricultural waste, forestry residues, municipal solid waste, dedicated energy crops starchy materials, and lignocellulosic biomass. Agricultural residues such as wheat and rice straw, corn stalks, and sugarcane bagasse are widely available. Forestry waste includes logs and tree roots left after timber harvesting, while municipal solid waste contains significant cellulosic material from paper and cardboard. Additionally, sugar-rich crops like switchgrass and fast-growing trees such as poplars and willows offer a renewable and sustainable source of biomass. While bioethanol production is well-established from sugar and starch-based feedstocks, large-scale commercial production from lignocellulosic materials is still in its early stages, requiring further research and technological advancements. The production process may vary based on the type of feedstock but generally follows key steps:

1. **Milling/Grinding:** Reducing particle size for better processing.
2. **Saccharification:** Converting cellulose and starch into fermentable sugars using enzymes.
3. **Fermentation:** Adding microorganisms (yeast, bacteria, or fungi) to convert sugars into ethanol and CO₂.
4. **Purification:** Distilling and separating ethanol to increase its concentration for use as fuel.

The conversion process differs for sugar, starch, and cellulose-based feedstocks. Specifically sugar-based feedstocks (e.g., sugarcane, sugar beet) ferment directly into ethanol, starch-based feedstocks (e.g., corn, wheat) require enzymatic hydrolysis to break down starch into fermentable sugars before fermentation and cellulose-based feedstocks (e.g., agricultural residues, wood) undergo pretreatment to break lignin structures, followed by saccharification and fermentation. Ethanol (C_2H_6O), also known as ethyl alcohol, is a flammable, colorless liquid commonly used in alcoholic beverages, fuel, and industrial applications. Bioethanol shares the same chemical properties as ethanol and is often blended with gasoline to enhance fuel performance. The octane number of ethanol is higher than that of conventional petrol. Its high-octane number makes it an effective oxygenate additive, replacing toxic compounds like methyl tertiary butyl ether (MTBE). However, its lower energy yield compared to gasoline suggests its optimal use may be in biodiesel production rather than as a direct gasoline substitute [125].

Ethanol is at the center of attention as a transportation fuel, particularly in the U.S. and Brazil. In the USA ethanol use surged from 1.7 billion gallons in 2001 to 13.2 billion gallons in 2013. This growth has been driven by government policies, including the U.S. Environmental Protection Agency (EPA) allowing up to 15% ethanol in gasoline for vehicles produced after 2001. Furthermore Brazil's bioethanol industry is a major success story, driven by its vast sugarcane resources and supportive government policies. Since the 1970s, Brazil has mandated ethanol blending in gasoline, currently set at 25%. The country's ability to utilize by-products efficiently has kept production costs low, making bioethanol a competitive alternative fuel. The adoption of flex-fuel vehicles, capable of running on both ethanol and gasoline, has further boosted the industry. Ethanol helps lower fuel costs and reduces greenhouse gas emissions compared to gasoline. However, it has a lower energy density about two-thirds that of gasoline, that is a key drawback. Despite this, ethanol remains a promising fuel alternative as fossil fuel prices continue to rise, making ethanol a more stable and cost-effective option. Efforts are ongoing to transition from first-generation biofuels (sugar and starch-based) to second-generation biofuels derived from agricultural waste and woody biomass. Advanced technologies, including biomass co-firing in coal power plants, are being explored to integrate bioethanol into large-scale energy production.

Beyond its use in combustion engines, ethanol is also being explored as a fuel for direct ethanol fuel cells (DEFCs). DEFCs offer a higher energy output than direct methanol fuel cells (DMFCs), producing 8.0 kWh per kilogram compared to methanol's 6.1 kWh per kilogram. Additionally, ethanol is less toxic than methanol and is widely available through agricultural

production, ensuring a stable and affordable supply. The goal of DEFCs is to completely oxidize ethanol into carbon dioxide, generating 12 electrons per reaction—double that of methanol. However, DEFCs currently face challenges, such as incomplete oxidation due to ethanol's molecular structure, catalyst limitations, and membrane efficiency. Research is ongoing to enhance performance and improve energy conversion, making ethanol a more viable fuel source for the future [126],[127] .

Chapter 4

4.1 Economic analysis of FCVs (in comparison with ICE vehicles)

Hydrogen-based fuel cell vehicles (FCVs) are seen as a promising alternative to fossil fuel-powered internal combustion engine vehicles (ICEVs), offering the potential to reduce transportation-related environmental impacts. However, the limited availability of hydrogen infrastructure restricts their use to regions with supporting projects. Despite several advantages of HFC, high cost is still the major bottleneck of HFC-based transport. According to the NREL (National Renewable Energy Laboratory), the current cost of a medium size HFC-powered passenger vehicle is approximately \$53,1k and is expected to reduce to \$33,1k by 2050. The current cost of a hydrogen fuel cell is around \$160 per kW and is expected to go down to \$40 per kW by 2050. For example, the Honda FCX Clarity was estimated to cost between USD 120.000 and 140.000 to manufacture. A significant driver of these costs is the platinum used in the catalyst layer of the fuel cell stack. Additionally, the use of platinum and other rare materials in the stack raises concerns about the environmental impact of fuel cell production. The techno-economic life cycle of a fuel cell stack. includes two main stages: manufacturing and end use. Manufacturing costs cover design, materials, component fabrication, labor, and equipment needed for assembling both custom-made and commercial fuel cells. The total cost of an 80 kW-net Argonne fuel cell stack system is estimated at \$30 per kW. The electrodes, which include the cathode, anode, and catalyst, make up about 51% of the total stack cost. Meanwhile, stack assembly and conditioning account for around 7%. This means that key components like bipolar plates, electrodes, and seals are among the most expensive parts of the fuel cell, as shown in **Figure 48 a)**.

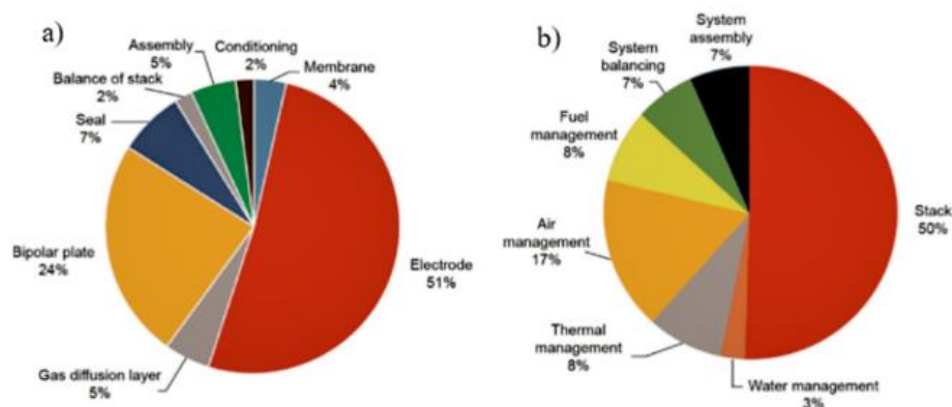


Figure 48. Cost of 80 kW net PEM fuel cell stack **a)** stack cost **b)** Stack system cost [3].

The cost of an 80 kW PEM fuel cell stack system, at mass production volume, was estimated at \$59 per kW. As shown in **Figure 48 b)**, the stack up 50% of the total system cost. The most expensive components were the stack itself, along with air, fuel, and thermal management. Together with other system components, the stack and balance accounted for 14% of the total cost. Fuel cell manufacturing technology has significantly improved, with ongoing material innovations aimed at reducing weight while enhancing performance. For example, platinum loading on the anodes and cathodes ranged from 0.1 to 0.15 mg/cm², with variations between 0.12 and 0.3 mg/cm². The overall system cost is largely influenced by platinum prices, which reached a peak of \$2000.t.oz⁻¹, as illustrated in **Figure 49**. However, platinum prices fluctuate significantly, varying by approximately $\pm 40\%$, ranging from \$800 to over \$2000 t.oz⁻¹.

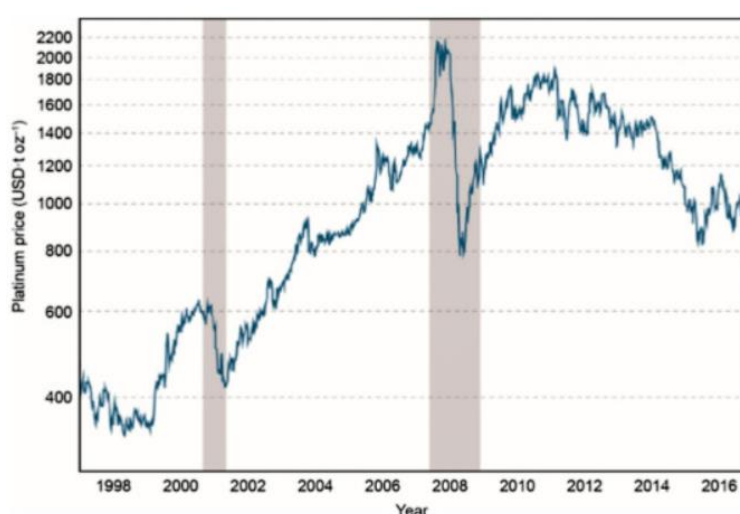


Figure 49. Cost of platinum from 1996 [3].

The fuel cell cost was about \$24,355, while the internal combustion engine cost \$15,805, and the hybrid vehicle cost \$24,050, as we notice at **Table 5**. The cost of the fuel cell system is comparable to that of hybrid vehicles but higher than internal combustion engines when considering materials, manufacturing, and cell costs. It can also be concluded that the efficiency of fuel cells (60–70%) is significantly higher than that of internal combustion engines (10-16%). Although the total net cost of a fuel cell is higher than an ICE, their efficiency balances their gross difference, and this is the main reason why the cost alone should not be the primary factor influencing end-user acceptance. However, many studies on fuel cell costs focus only on manufacturing expenses, overlooking repair and maintenance costs, which are crucial for stack longevity and user acceptance.

Table 5. Comparing the cost of fuel cell vehicles, internal combustion engines and hybrid vehicles [3].

Tye of vehicle	Engine type	Power (hp)	Efficiency (%)	Fuel cost (USD.kg ⁻¹)	Driving range (mi)	Cost (USD)		
						Propulsion system	Chassis and body	Transmission
Proposed fuel cell vehicle	Fuel cell systems	112	60–70	2–3	300.0	13964.0	7902.5	316.1
Honda Civic Sedan	Internal combustion engine	140	10–16	0.98–1.05	475.0	4741.5	7902.5	1580.5
Honda Civic Hybrid	Hybrid	110	10–16	0.98–1.05	580.8	7215.0	12025.0	2405.0

Another cost analysis revealed that the economic viability of both fuel cell powertrains and conventional internal combustion engine powertrains is highly dependent on fuel prices. De Miranda et al. conducted an economic analysis of a plug-in hybrid electric-hydrogen fuel cell city bus in Brazil. The capital cost accounted for around 65% of the total ownership cost, followed by hydrogen costs at 22% and maintenance at 13%. Notably, the capital cost of a plug-in hybrid electric-hydrogen fuel cell city bus was approximately 386% higher than that of a diesel bus. Subsequently, they found that owning a plug-in hybrid electric-hydrogen fuel cell bus in Brazil costs 133% more than a diesel bus, mainly because of its high purchase price. Whiston et al. estimated that the total ownership cost of HFCHEVs was \$0.26/km in 2017 and projected it to decrease to \$0.12/km by 2035, making it competitive with ICEVs. Jeong and Oh found that hydrogen production costs, fuel cell size, and fuel cell price significantly impact the lifecycle cost of HFCHEVs. Jones et al. conducted an economic analysis of thirteen vehicles to evaluate the competitiveness of hydrogen fuel cell electric vehicles (HFCEVs) in the UK in 2017. The study showed that, with tax benefits and subsidies, the lifetime cost of HFCEVs was almost the same as some diesel internal combustion engine vehicles (ICEVs). An HFCEV bus and truck showed 101.7 and 203 %, respectively, higher total cost of ownership than a conventional gasoline vehicle powertrain, according to Li and Taghizadeh-Hesary. Li et al. developed a lifecycle cost model for an HFCEV and compared it with a conventional vehicle

in China. Thanks to local government subsidies, the HFCEV's average lifecycle cost was about 25.8% lower than that of a conventional vehicle.

A recent study in Brazil using the ADVISOR model showed that subsidies and fuel credits could reduce the HFCEV cost by 27.2%, while mass production could cut it by up to 38%. Thus, introducing subsidies, fuel credits, and higher production volume can lower the total cost of ownership. The total cost of owning an HFCEV is still much higher than an ICEV, mainly due to the high production cost of hydrogen and fuel cell vehicles. **Figure 50** compares HFCEVs to conventional ICEVs in terms of fuel economy, GHG emissions, and total cost of ownership, based on data from various light-duty vehicle studies [127].

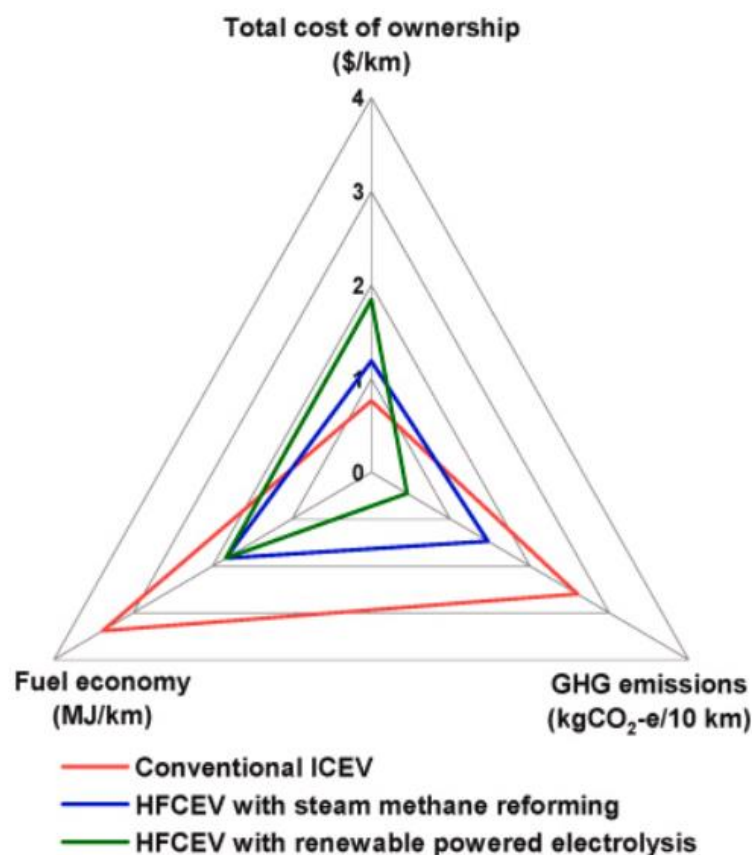


Figure 50. Benchmarking of HFCEV with conventional ICEV.

4.2 Cost Breakdown of SOFC - PEMFC Vehicles

4.2.1 PEMFC

The Department of Energy (DOE) since the late 1990s has evaluated the cost of PEM fuel cell based on near-term technology but modeled at high production volumes. In 2005, the cost of an 80-kW direct hydrogen fuel cell system was assessed relative to the DOE 2005 target of \$125/kW. This system includes the fuel cell stack and balance-of-plant (BOP) components for

water, thermal, and fuel management. **Figure 51 a)** shows the breakdown of the total cost of \$108/kW between the stack, BOP, and assembly. All \$/kW costs are given on a dollar per net power basis. Key assumptions in this projection are summarized in **Table 6**.

Table 6. Key Model Parameters.

Parameter	Units	2005	2004
Power Density	mW/cm ²	600	350
Cell Voltage	Volts	0.65	0.7
Net Power	kW	80	80
Gross Power	kW	90	88
Production Volume	Units/year	500,000	500,000
Platinum Loading	mg/cm ²	0.75	0.3
Platinum Cost	\$/troz	900	450

Figure 51 b) shows the split between the stack and BOP costs with the stack contributing approximately 63%. After the stack, the compressor-expander module (CEM), membrane humidifier, and carbon materials are the most important cost contributors.

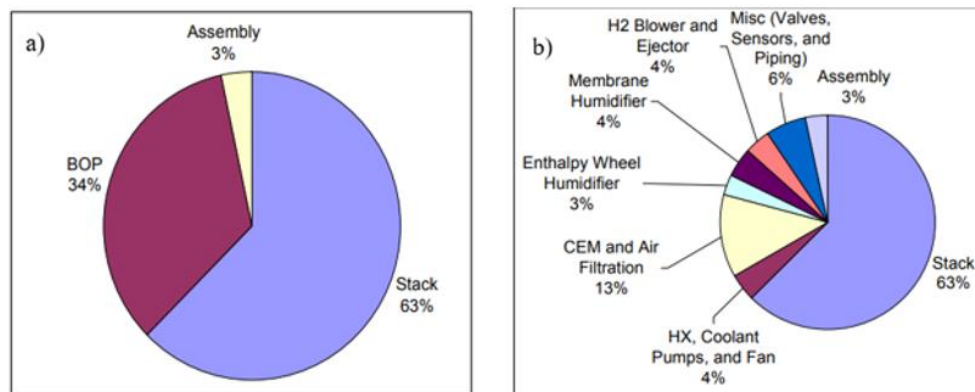


Figure 51. a) Breakdown of System Cost for an 80 kW Direct Hydrogen Fuel Cell System (\$108/kW, \$8,640) Produced at 500,000 Units per Year, b) Breakdown in Stack and BOP Component Cost Contributions for an 80 kW Direct Hydrogen Fuel Cell System (\$108/kW, \$8,640).

The electrode makes up the largest portion of fuel cell costs due to the high platinum loading and price. Meanwhile, other components have become cheaper thanks to material reductions in cost and amounts. **Figure 52:** shows the breakdown in the stack costs for a 2005 80 kW Direct Hydrogen Stack. The top cost drivers for the stack and system were power density, platinum cost, and platinum loading. Power density affects the overall stack size, while platinum cost and loading drive electrode expenses, the biggest stack cost. Though single-cell power densities are high in studies, they're reduced in stacks to prevent overheating and

degradation. Any cost savings from other components or improved power density are often canceled out by rising platinum costs and loading [128].

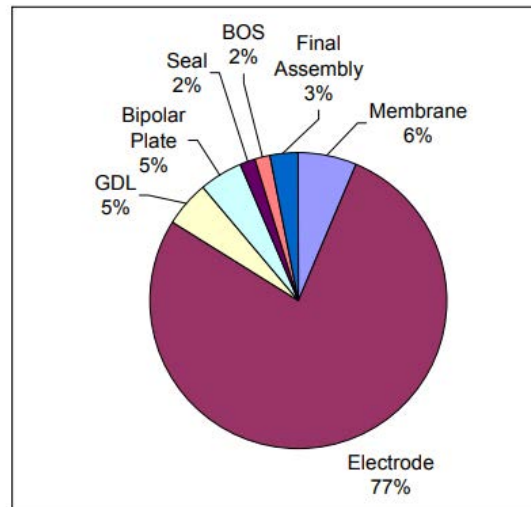


Figure 52. Cost Breakdown for a 2005 80 kW Direct Hydrogen Stack (\$67/kW, \$5,360).

4.2.2 SOFC

The railroad industry operates on low margins and high volume, making cost a key factor. Switching to SOFCs instead of traditional diesel engines must be financially justified. If we assume the same maintenance cost for Diesel IC and SOFC, the cost comparison will take place under the following assumptions in **Table 7**.

We also assume biodiesel as the fuel for both engines. With current biodiesel prices at \$0.66 per liter (\$2.50 per gallon), assuming fuel costs remain constant over 40 years, capital costs are the main factor in the cost analysis. The cost (present value) of a diesel IC power plant is \$3.2 million, while the SOFC power plant costs \$4.9 million. Fuel costs are unlikely to stay constant over that period. **Figure 53** illustrates the cost of both power plants based on annual fuel cost increases. The analysis shows that if fuel costs rise by 9% or more annually, the SOFC power plant is expected to become more cost-effective. **Table 8** presents the cost breakdown for each type of power plant over a 40-year period at an IRR of 8%, with scenarios assuming no fuel cost increases and a 9% annualized fuel cost increase [129].

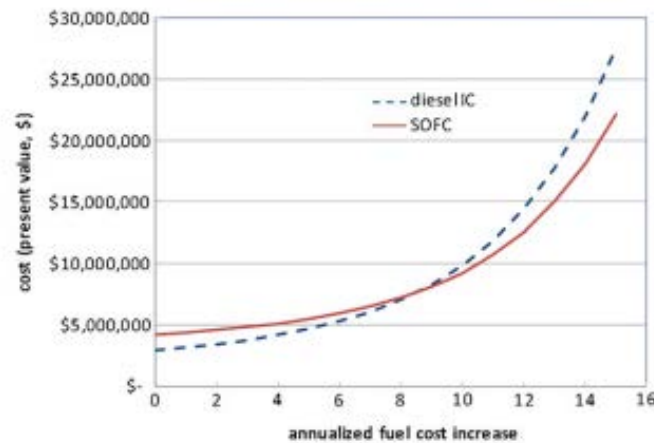


Figure 53. SOFC Cost vs. annualized fuel cost increases for SOFC and diesel IC locomotive power plants over a 40-year period, assuming 900 MWh/year, and 8% IRR [129].

Table 7. Assumptions used in cost comparisons.

	Diesel IC	SOFC
Efficiency	35%	58%
Initial capital cost	\$250kW ⁻¹	\$675kW ⁻¹
Power production between major maintenance	36,000 MWh	32,000 MWh
Rebuild cost	\$75kW ⁻¹	\$175kW ⁻¹

Table 8. Diesel IC and SOFC cost breakdown (costs in millions).

	Diesel IC (no fuel cost increases)	SOFC (no fuel cost increases)	Diesel IC (9% annual fuel cost increase)	SOFC (9% annual fuel cost increase)
Capital cost	\$1.0	\$2.7	\$1.0	\$2.7
Maintenance cost	\$0.014	\$0.046	\$0.014	\$0.046
Fuel cost	\$2.0	\$1.4	\$7.3	\$5.3
Total	\$3.0	\$4.2	\$8.3	\$8.1

4.3 Environmental benefits of fuel cell vehicles

While fuel cell vehicles still remain more expensive than fossil-fueled vehicles, their environmental impact is considerably smaller. The primary advantage of FCVs over fossil-based technologies is their significant reduction in emissions. In most cases, levels of nitrogen oxides (NO_x), volatile organic compounds (VOCs), particulate matter (PM_{2.5} and PM_{2.5-10}), ammonia (NH₃), and carbon monoxide (CO) would decrease substantially. Transitioning to

hybrid or hydrogen vehicles powered by natural gas, wind, or coal would lower greenhouse gas (GHG) emissions by 6%, 14%, 23%, and 1%, respectively. Looking forward to 2100, emission scenarios vary widely, as illustrated in **Figure 54** [130].

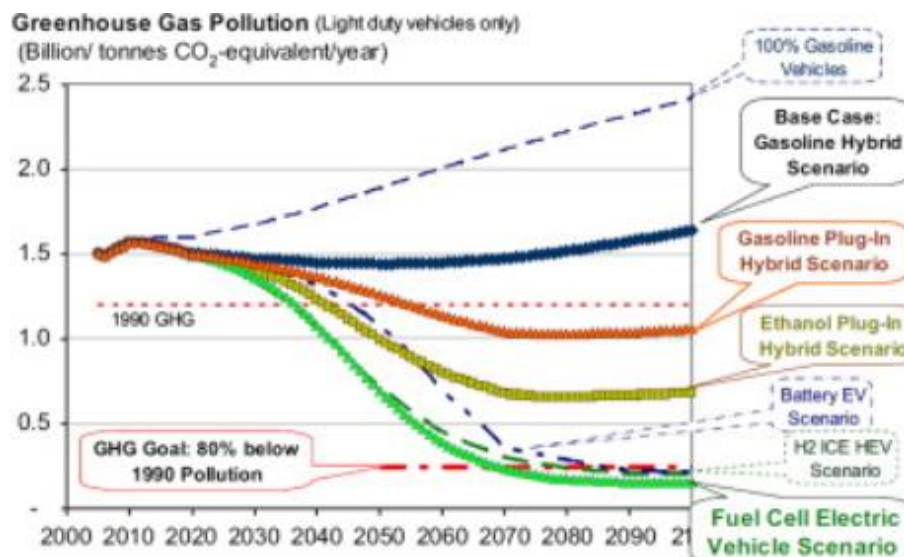


Figure 54. The greenhouse gas pollution over the century for a reference case with no alternative vehicles, the four main vehicle scenarios and two secondary scenarios; the upper dotted horizontal line corresponds to the 1990 light duty vehicle GHG pollution, and the lower line represents an 80% reduction below the 1990 level [130].

4.4 Barriers to commercialization and public adoption

Bringing new technology to market is always challenging, but fuel cells face unique hurdles like high costs, technical limitations, and infrastructure gaps. Unlike other innovations, they face little resistance but if they achieve to match IC engines in performance and price, they'd be widely accepted as a cleaner alternative. Despite decades of investment, fuel cells and hydrogen infrastructure still fall short, leaving their viability uncertain. One main challenge FC need to face is their complexity, involving intricate chemical and physical interactions at the atomic level.

4.4.1 Cost of fuel cell itself

Fuel cell costs fall into three categories: materials, labor, and manufacturing equipment. While mass production can lower labor and capital costs, material expenses depend on technological advances and market conditions. Despite having no moving parts, fuel cells remain more expensive and less durable than IC engines, requiring government subsidies to scale production. Reducing costs requires developing cheaper materials and optimizing design for higher efficiency. Durability and reliability are major challenges. The U.S. DOE set a 5,000-

hour lifespan target for automotive fuel cells, but end-users also need reliability—fewer unexpected repairs and maintenance disruptions. Fuel cells degrade over time due to water and heat issues, leading to material breakdown, corrosion, and inefficiencies. Proper water and thermal management, along with optimized design, can extend lifespan without major material changes. Addressing these challenges is key to making fuel cells a viable scalable technology.

4.4.2 UNEVEN FLOW

In a fuel cell stack, the total power output is ideally the sum of all individual cells. However, the overall lifespan, durability, and reliability depend on the weakest cell. When fuel cells are connected in series or parallel, issues like water buildup, hotspots, catalyst degradation, material wear, and sealing problems can arise. One major challenge is uneven flow distribution, which affects flow rates, pressure drops, and temperature.. A general procedure for development of fuel cells is shown in **Figure 55**. A successful small fuel cell operates effectively under its designed conditions, with materials, sealing, and catalysts performing as intended. Issues like degradation and water flooding do not affect its durability or reliability. Once proven at a small scale, the fuel cell can move to the next phase of scaling up, where identical individual cells are stacked using optimized flow field designs. Scaling-up challenges such as reliability, robustness, and durability are mainly caused by uneven flow distribution, even though failures often appear to be due to materials, catalysts, water, or thermal issues.

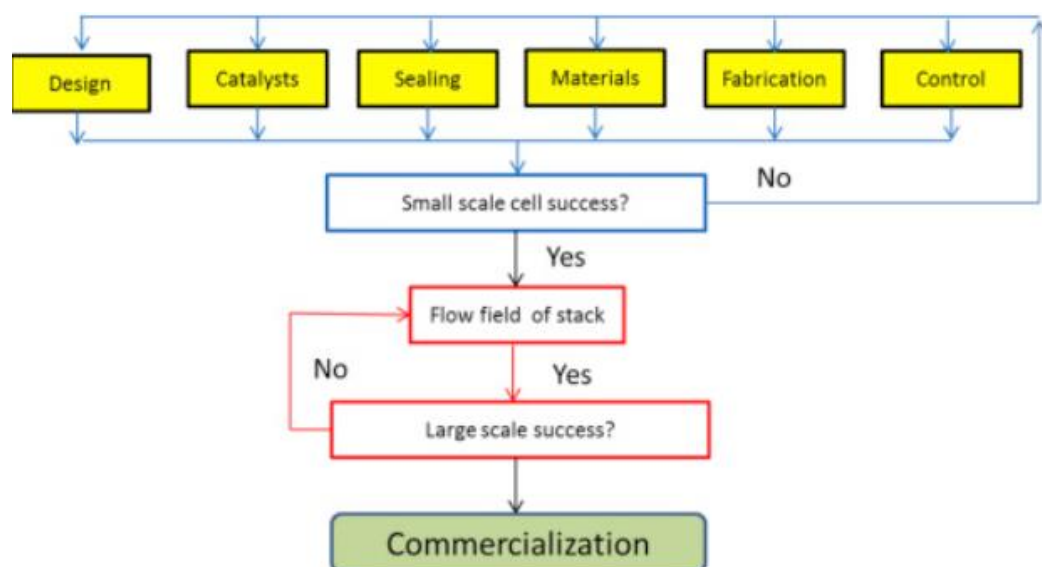


Figure. 55. Flow chart of fuel cell scaling-up.

The performance of a single fuel cell doesn't always match the overall reliability and durability of the entire stack. If one cell fails, the whole stack can stop working. In most cases,

failures happen due to issues with materials, chemistry, water management, or hotspots. **Figure 56** shows a fault tree analysis, highlighting that a cell usually fails when it doesn't function as expected due to changes in flow rates. These changes can cause cells to react too fast or too slow, leading to temperature and water imbalances, which may create hotspots or flooding. Hotspots can exceed material limits, causing faster degradation, while uneven temperatures lead to mechanical stress and failure. Catalysts can fail due to flooding, and seals may break under extreme pressure. Obstruction in some cells can worsen these issues, damaging materials and reducing efficiency. Overall, fuel cell failures happen when certain cells don't function as designed, leading to uneven reactions that reduce performance, reliability, and durability.

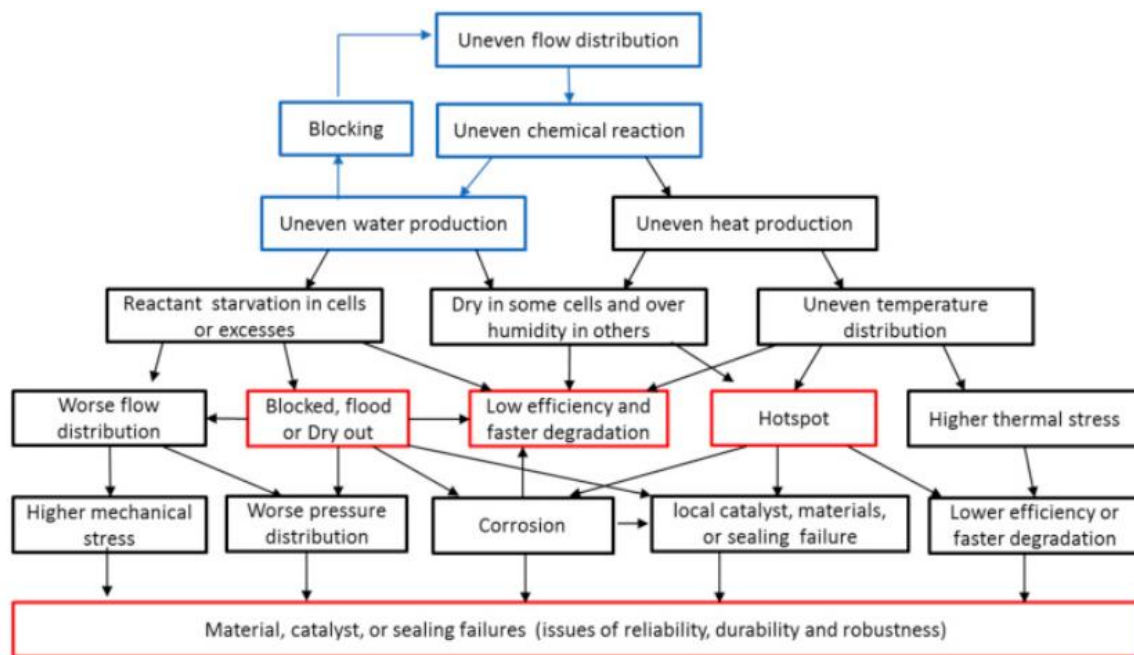


Figure 56. Fault tree analysis of fuel cells due to uneven flow distribution.

Subsequently, a main reason for the slow commercialization is the difficulty to achieve uniform flow distribution within the stack. Uneven flow causes significant differences in temperature and water levels, leading to performance issues and material degradation. As fuel cell stacks scale up, these problems become more severe due to the superposition effect across multiple manifold levels. Therefore, optimizing flow field design is crucial for improving performance, reducing costs, and making fuel cells commercially viable [131].

4.5 Pt -Pd SBCNCs Catalysts for PEMFCs

Proton exchange membrane fuel cells (PEMFCs) have garnered significant attention as clean and efficient energy conversion systems over the past three decades. However, their widespread adoption is hindered by the high cost and limited durability of conventional Pt/C catalysts. To address this, researchers have developed Pt-based alloy catalysts, such as Pt-Ni, Pt-Co, Pt-Cu, and Pt-Pd, which use less Pt while improving catalytic performance. Among these, Pt-Pd alloys stand out due to their structural compatibility, excellent stability, and high catalytic efficiency. Traditionally, synthesizing Pt-Pd catalysts with intricate shapes, such as nanotubes or nanocubes, involved complex multi-step processes like seed-mediated growth. These methods are challenging and not ideal for achieving geometrically advanced structures.

4.5.1 Experimental Procedures

The experiment performed by Rifeng Wua , Panagiotis Tsiakaras, Pei Kang Shen introduces a straightforward, one-pot method for synthesizing symmetry-broken concave nanocubes (SBCNCs) of Pt-Pd. The process involves a solution containing 0.15 mmol disodium tetrachloropalladate (Na_2PdCl_4) and 0.05 mmol chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) in a 3:1 molar ratio, mixed with dimethylformamide (DMF), combined with 40 mg sodium iodide (NaI) and 50 mg polyvinylpyrrolidone. The mixture was heated in a Teflon-lined autoclave at 130°C for five hours. Once Cooled, the final product was purified through multiple ethanol and acetone washes and collected via centrifugation. The synthesized Pt-Pd catalysts were combined with carbon (Vulcan-72) in cyclohexane, then ultrasonicated for two hours. The resulting mixture was purified with ethanol, dried at 80°C, and further heated at 200°C for an hour before being cooled for final use. The catalyst loadings were assessed using ICP-AES spectroscopy. Electrochemical tests were carried out in a three-compartment electrochemical cell using a Pine rotational disk electrode system with a bipotentiostat. The setup included a catalyst-coated glassy carbon (GC) as the working electrode, a Pt mesh as the counter electrode, and a reversible hydrogen electrode (RHE) as the reference electrode . CV curves were recorded at 25°C in a nitrogen-saturated 0.1 M HClO_4 solution, scanning between 0.05 and 1.1 V RHE at 50 mV/s. ORR measurements took place in an oxygen-saturated 0.1 M HClO_4 liquid solution at 1600 rpm with a scan rate of 10 mV/s. Acceleration durability tests involved cyclic sweeps from 0.6 to 1.1 V versus RHE at 100 mV/s, with ohmic iR-drop correction applied.

4.5.2 Experiment Results

The bright-field Transmission electron microscopy (TEM and High resolution-TEM (HAADF-STEM images ,**Figure 57 a), b), and c)**) reveal that the majority of nanocrystals have a well-defined, symmetry-broken concave nanocube shape. They are evenly distributed, with an average edge length of 16.6 ± 2.4 nm.

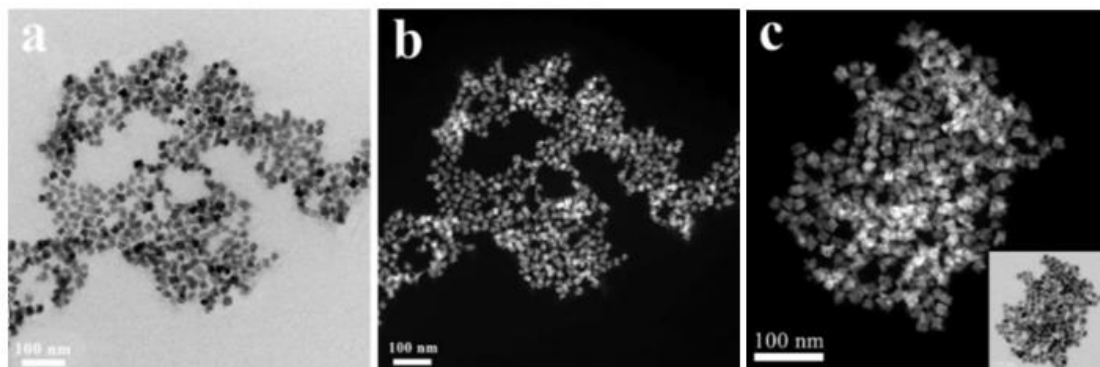


Figure 57. a) The typical low-magnification bright-field TEM, b) and c) low and medium-resolution HAADF-STEM image of the Pt-Pd symmetry-broken concave.

The Pt-Pd nanostructures were analyzed using EDS line scan profiles and elemental mapping ,revealing that Pd is concentrated in the core (**Figure 58 a_I and a_{II}**), while Pt is enriched on the surface, indicating a core-shell structure. The Pt/Pd atomic ratio was found to be 32.4:67.6, consistent with ICP-MS data. Powder X-ray diffraction (XRD) patterns (**Figure 58 b**) showed that Pt and Pd peaks were very hard to distinguish due to a high lattice match (99.23%), but diffraction peaks indexed to FCC structures were observed. In comparison with commercial Pt/C, there are slight shifts of peak positions to higher angles of Pt-Pd SBCNCs and Pt-Pd NCs, confirming the formation of a Pt-Pd alloy. X-ray photoelectron spectroscopy (XPS) analysis (**Figures 58 c and d**) showed that both Pt and Pd are in a zero-valence state on the nanocrystal surface. A positive shift in the Pt 4f binding energy compared to commercial Pt/C indicates lattice strain and charge transfer, which enhance the catalytic properties. The Pt-rich surface was further confirmed by XPS survey maps. To explore the formation mechanism, experiments with different halide ions were conducted. Without I⁻ ions, octahedral Pt-Pd nanostructures were obtained. With I⁻ ions, concave nanocubes (14.1 ± 1.1 nm) were formed. When I⁻ was replaced with Br⁻ or Cl⁻, different nanostructures appeared, showing the role of halides in controlling morphology. The synthesis method was effective in producing uniform, well-defined nanocubes with improved catalytic properties.

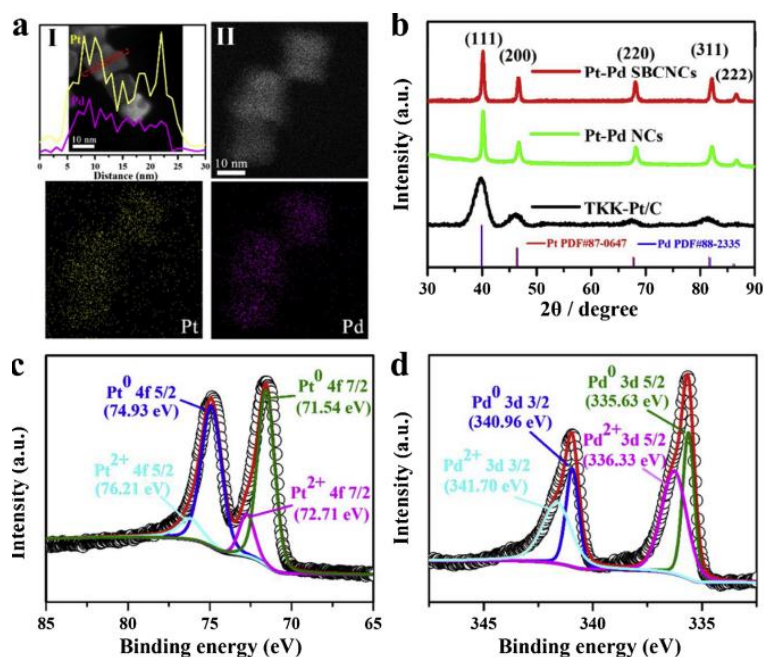


Figure 58. a_I) EDS line scan profiles of a single Pt-Pd SBCNC and a_{II}) HAADF-STEM image and corresponding elemental mapping, b) XRD patterns of commercial TKKPt/C, Pt-Pd NC and Pt-Pd SBCNC, at a scan rate of 10°min⁻¹, c) , d) XPS pattern for the Pt 4f region.

The electro-catalytic properties of the Pt-Pd SBCNCs were tested in the oxygen reduction reaction (ORR), comparing them to Pt-Pd NCs and commercial Pt/C catalysts. **Figure 59 (a)** shows the cyclic voltammograms (CVs) of the Pt-Pd SBCNCs, of the Pt-Pd NCs and of the commercial Pt/C catalyst. These were recorded in a 0.1 M HClO₄ solution. The electrochemically active surface areas (ECSAs) for Pt-Pd SBCNCs/C, Pt-Pd NCs/C, and Pt/C were 45.2, 37.4, and 52.7 m²/g_{Pt}, respectively. The ORR polarization curves **on Figure 59 (b)** showed the Pt-Pd SBCNCs/C catalyst significantly higher mass and specific activities, 6.2 and 7.7 times better than commercial Pt/C, with values of 0.87 A/mg Pt and 1.93 mA/cm². The enhanced performance was attributed to the Pt-rich surface and the synergistic effect between Pt and Pd. In durability tests (ADT), Pt-Pd SBCNCs/C maintained excellent stability, showing only a slight decrease in mass activity (0.47 A/mg Pt) and specific activity (1.12 mA/cm²) after 15,000 cycles as illustrated in **Figure 59 (c)**. The catalyst structure remained largely intact, with high-index facets still visible, as confirmed by XPS analysis. In this experiment a simple and cost-effective Pt-Pd SBCNCs catalysts were synthesized in a one-pot method. Pt-Pd SBCNCs demonstrate superior catalytic activity and long-term durability, thanks to the high-index facets exposed on the Pt-rich surface and the synergistic interaction between Pt and Pd. These catalysts with enhanced electrochemical oxygen reduction performance, offering a practical solution for improving the efficiency and longevity of PEMFCs [81].

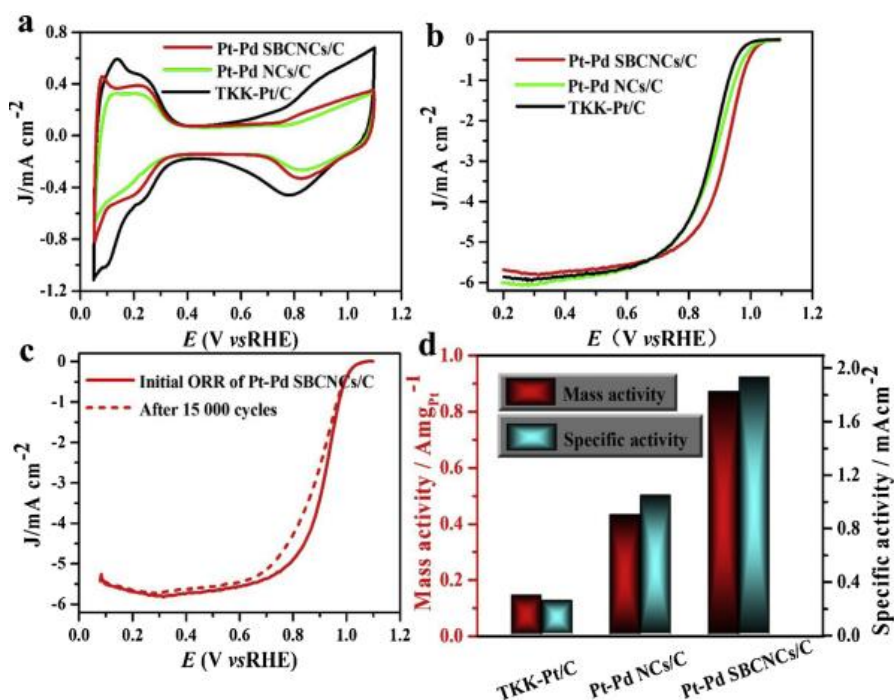


Figure 59. (a) Cyclic voltammograms of commercial TKK-Pt/C, Pt-Pd NCs/C and Pt-Pd SBCNCs/C recorded at room temperature in an N₂-purged 0.1 M HClO₄ solution with a sweep rate of 50 mV/s, (b) Corresponding ORR polarization curves recorded in an O₂-saturated 0.1 HClO₄ solution with a sweep rate of 50 mV s⁻¹, (c) ORR polarization curves of the Pt-Pd SBCNCs/C catalyst before and after 15,000 potential cycles, (d) Histogram of specific and mass activities at 0.9 V versus RHE for three catalysts.

4.6 DEFC Catalysts

In a direct ethanol fuel cell (DEFC) the component which has the biggest effect in the system performance is the membrane electrode assembly (MEA). The MEA consists of the electrolyte, electrode support, and electrode catalyst. The presence of catalyst is essential as it provides a surface for ethanol electro-oxidation to take place at lower activation energy and at a higher rate. Catalysts are mandatory for both anode (for ethanol oxidation reaction, EOR) and cathode (for the oxygen reduction reaction, ORR) electrodes. If one of these reactions is slowed down, overall cell performance declines significantly. Since the reactions on electrodes are different, a different design is required to ensure optimal performance.

4.6.1 Anode Catalysts

Catalyst plays a key role in how efficiently ethanol is oxidized. However, its performance is often limited by challenges like catalyst poisoning and the difficulty of breaking ethanol's C-C bonds. The most widely studied anode catalysts are platinum (Pt) and palladium (Pd).

4.6.1.1 Platinum (Pt) Catalysts

Monometallic Pt is widely used in fuel cells and is known for its strong ethanol oxidation properties, particularly in acidic conditions. Ghumnan et al. found that while Pt can fully oxidize ethanol to CO₂ in H₂SO₄ solution, it does so in small amounts. However, Pt alone is easily contaminated, reducing efficiency. Alloying Pt with metals like Ru improves tolerance to contaminants (e.g., CO_{ads}) at low temperatures and current densities. At 80°C, Pt performs slightly better than other catalysts but still achieves less than 20% CO₂ conversion. Zignani et al. noted that higher temperatures increase contamination, making the catalyst degrade faster. To maintain steady ethanol oxidation, bimetallic Pt-based catalysts at lower temperatures offer a more effective solution. Research by Beyhan et al. found that PtSn/C is the most effective bimetallic catalyst for ethanol oxidation in acidic conditions. While other combinations like Pt-Ni, Pt-Ru, and Pt-Co showed good results, Pt-Sn had the highest performance, as indicated by its early peak in cyclic voltammetry (CV) tests (**Figure 60 a**). This shows that tin (Sn) integrates more easily with the Pt surface, enhancing its effectiveness. While other co-catalysts help improve hydrogen adsorption on Pt, Sn proves to be the most effective, significantly boosting adsorption and overall reaction efficiency. **Figure 60 b**) presents the CV curves of PtSn-based catalysts. Essentially, Sn acts as a hydrogen attractor, aiding Pt in the electro-oxidation of ethanol, as evidenced by its highest recorded peak of approximately 900 mA mg⁻¹.

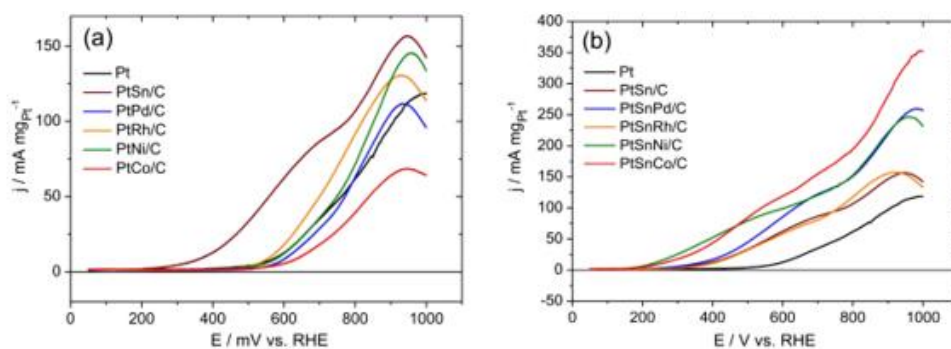


Figure 60. Linear sweep voltammograms for electrooxidation of 1 M ethanol in 0.1 M HClO₄ on the (a) Pt-based catalysts, (b) PtSn-based catalysts. Scan rate: 1 mV/s.

Zhou et al. further confirmed that PtSn/C outperformed PtPd/C, PtW/C, PtRu/C, and Pt/C in CV experiments, proving its high compatibility as an excellent bimetallic catalyst for ethanol oxidation in low-pH environments (**Figure 61**). However, in methanol oxidation, PtRu performed better due to Ru's ability to dissociate water more effectively. In contrast, Sn helps prevent catalyst poisoning by improving tolerance to adsorbed CO (CO_{ads}), making it particularly useful for ethanol oxidation.

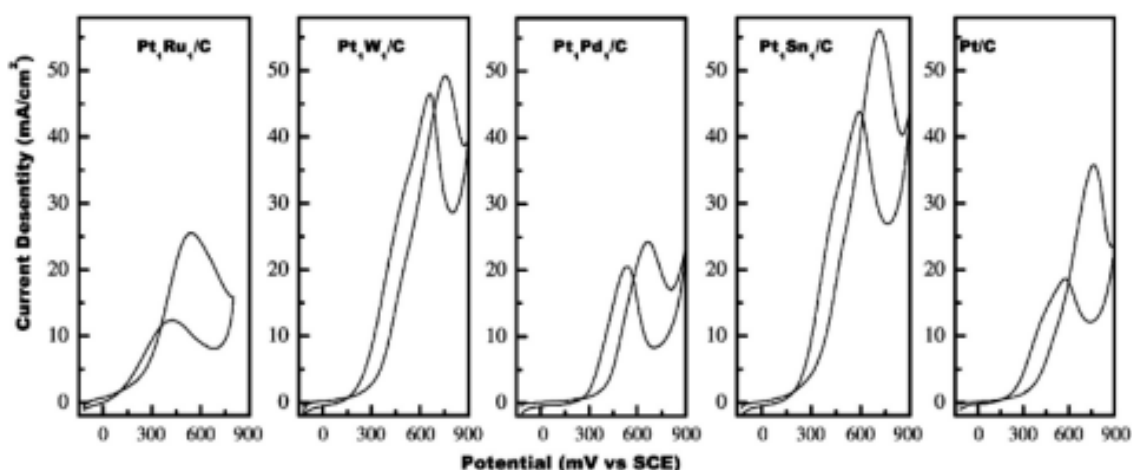


Figure 61. CV of different Pt-based catalyst; concentration of ethanol 1.0 M, concentration of H_2SO_4 0.5 M, scan rate 10 mV/s.

Research by Ribadeneira et al. found that PtRuNi was the most effective trimetallic catalyst for ethanol oxidation, as it displays a higher electrocatalytic activity, outperforming PtSnNi. In bimetallic catalysts phases, the synergistic effect between Pt and the co-catalyst is less pronounced, as each element plays a distinct role, Sn improves poison tolerance, while Ru enhances water dissociation. However, in trimetallic systems, the interaction between all three elements creates a more complex yet highly effective catalyst structure, leading to better EOR performance. Ribadeneira also stated that Nickel (Ni) is a valuable secondary co-catalyst, further enhancing EOR efficiency when added to PtRu. This was supported by Wang et al., who observed significant performance improvements with Ni addition in PtRu catalysts. Tayal et al. found that rhenium (Re) added to PtSn resulted in a lower onset potential and higher voltage peak at low current densities. While Sn alone helps reduce poisoning by minimizing Pt-CO formation, it only slightly improves water dissociation. The addition of Ru enhances both water and CH_3CO dissociation, much like Ni in other trimetallic systems, making it another promising co-catalyst for ethanol oxidation. Zhao et al. explained the synergetic effect of the trimetallic catalysts, when they found that adding a second co-catalyst enhances ethanol oxidation (EOR) by weakening the Pt-CO bond during adsorption and desorption. Co-catalysts like Sn and Ru, are more electropositive than Pt and create electron cloud repulsion, which reduces the bond strength between Pt and CO_{ads} . This making adsorption, desorption, and oxidation reactions faster, set more active sites available and increasing EOR efficiency. Additionally, this bond enfeebling enhances Pt's poison tolerance. Bimetallic catalysts also have a good Pt poison-tolerance, but it is much pronounced more in trimetallic systems. Tayal et al. supported this, demonstrating that trimetallic catalysts had the highest voltage and

activation peaks in cyclic voltammetry (CV) compared to mono- and bimetallic catalysts as illustrated in **Figure 62 a)**. They also exhibited lower polarization rates, as seen in **Figure 62 b)**, where trimetallic catalysts maintained the highest voltage and activation peaks over time. Another key advantage of trimetallic catalysts is greater stability. The presence of co-catalysts disrupts Pt particle arrangement, slowing down catalyst agglomeration. This improves long-term stability and reduces oxide formation, further enhancing DEFC performance.

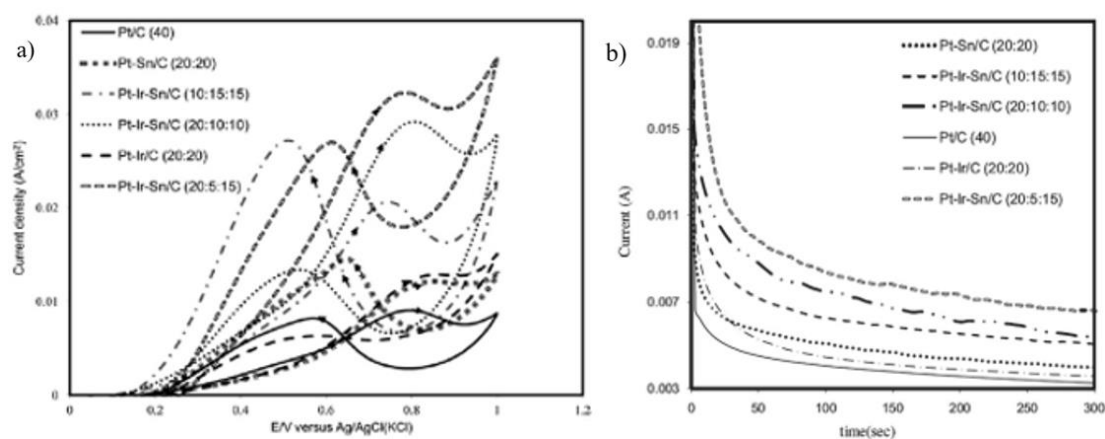


Figure 62. a) CV of different Pt-based catalyst, concentration of H_2SO_4 0.5 M, concentration of ethanol 1.0 M, temperature 25 °C, scan rate 20 mV/s . b) Chronoamperometry test of different Pt-based catalyst under same condition at 25 °C.

In most cases Trimetallic catalysts show better performance than the other two types of catalysts. They have though a certain drawback, which is that excessive co-catalyst concentrations can block active surface sites, similar to CO poisoning, reducing the electrochemically active surface area (ECSA) and hindering ethanol oxidation (EOR). To prevent this, careful optimization of catalyst ratios is needed to achieve the best performance. One more disadvantage is that trimetallic catalysts are difficult to operate at high potentials and temperatures. At elevated levels, Pt forms oxides, which reduce the available catalytic surface for ethanol oxidation. This degradation also affects co-catalysts, leading to electrode dissolution into the solution. To maintain stability and efficiency, operating conditions must remain within the catalyst's optimal range .

4.6.1.2 Palladium catalysts

The high cost of platinum (Pt) catalysts and their lower reactivity with ethanol compared to its success in methanol fuel cells have led researchers to explore palladium (Pd) as a promising alternative. Pd, belonging to the same group as Pt, is more electropositive and performs significantly better in alkaline media than Pt. While it is less effective in acidic environments,

it excels when the pH is above 8, making it a strong candidate for alkaline direct ethanol fuel cells (DEFCs). Another advantage is that Pd is more affordable than Pt, reducing cost. Like Pt-based catalysts, Pd provides a surface for ethanol adsorption, forming Pd-CO intermediates, before the CO_{ads} is desorbed and oxidized to CO₂. Because the research of Pd is still new, most studies are focused on bi-metallic catalysts and only a few concentrate on trimetallic catalysts.

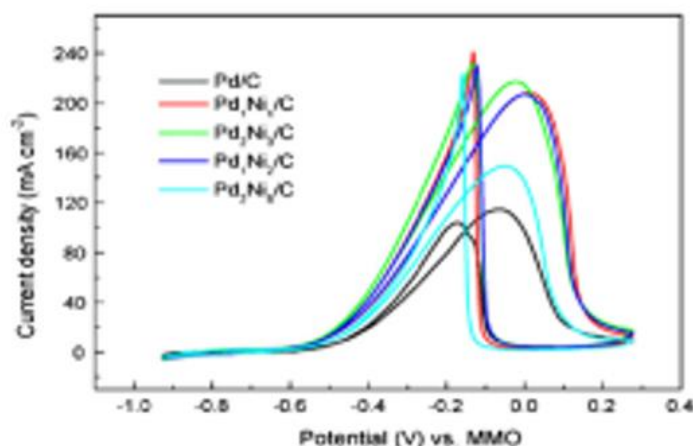


Figure 63. CV curves of several Pd-based catalysts at scan rate 50 mV/s. The highest peak was found to be Pd₁Ni₁. As the ratio of Ni increases, the CV maximum peaks decrease.

Just like with platinum, adding a co-catalyst to palladium (Pd) helps improve its performance in DEFCs. Zhang et al. found that the active sites on Pd surface are vulnerable to CO poisoning due to strong Pd-CO binding, like Pt. A co-catalyst helps weaken this bond, speeding up the adsorption/desorption process and improving ethanol oxidation. Li and Zhao noted that in alkaline media, Pd allows a wider range of material selection for co-catalysts. This wider range of selection can reduce costs by replacing expensive metals like Ru with cheaper alternatives like Ni. Li's study on PdNi showed that Ni enhances ethanol oxidation (EOR) by both weakening CO binding and attracting oxygen species (OH⁻) needed for ethanol oxidation. Since alkaline conditions naturally have high OH⁻ concentrations, EOR is higher than in acidic media, even without water-splitting co-catalysts like Ru. However, like Pt-based catalysts, adding too much co-catalyst can reduce the active surface area for ethanol adsorption and oxidation and lower the ethanol oxidation rate per area. Therefore, optimizing the PdNi ratio is essential for achieving the best performance. **Figure 63** shows that the peaks of CV curves are higher when the ratio of Ni is bigger. Some other metals (e.g Ag, Ru, Sn) have good catalytic reactivity when paired with Pd. These co-catalysts have their own characteristics, but all aim to increase Pd poison tolerance, as well as to facilitate the ethanol oxidation.

Su et al. found that adding nickel (Ni) to palladium (Pd) creates adsorption sites for OH^- ions, helping the oxidation of CO_{ads} to CO_2 . Additionally, introducing gold (Au) to the Pd lattice disrupts Pd- CO_{ads} bonding, enhancing resistance to poisoning and, hence increasing the performance. However, studies by Geraldine et al. and Qin et al. showed that while PdAuNi trimetallic catalysts improve poison tolerance, they exhibit a lower peak voltage in cyclic voltammetry (CV) tests. This happens due to co-catalyst inhibition, where excess Ni and Au block active sites, reducing ethanol oxidation efficiency. This process is illustrated in **Figure 64**. Another issue is metal compatibility—while Pd pairs well with both Ni and Au, Ni and Au together tend to form an incompatible alloy, leading to self-aggregation and reduced catalytic performance. To overcome these issues, researchers suggest exploring Pd-based trimetallic catalysts with NiSn or NiRu, which have already shown strong reactivity with Pt-based systems and could enhance ethanol oxidation in Pd-based DEFCs.

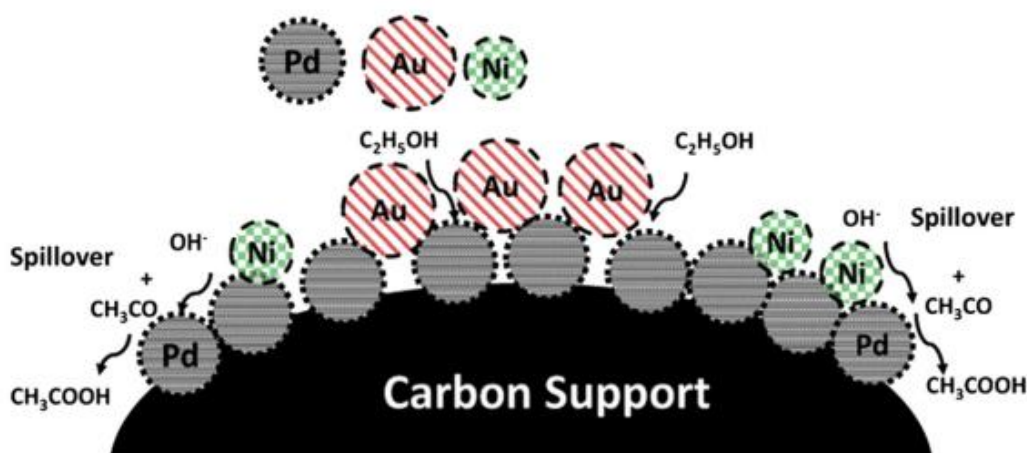


Figure 64. A schematic diagram that illustrates the blocking of Pd surface site due to high concentration of co-catalyst.

4.6.1.3 Comparison of Pd and Pt as Catalysts

Sun et al., Ma et al., and Santasalo-Aarnio conducted many studies about Pt and Pd catalysts and concluded that both have unique catalytic properties depending on the medium. Specifically, Pt performs well and has excellent ethanol oxidation in both acidic and alkaline environments, making it a versatile option. In contrast, Pd is almost inactive in acidic conditions but demonstrates significantly higher catalytic activity than Pt in alkaline media. Another study by Zhang et al. found that Pd achieved nearly four times the peak current of Pt in cyclic voltammetry (CV) tests under identical alkaline conditions, proving its superior ethanol oxidation reaction (EOR) performance in high-pH environments. This, combined with its lower cost, makes Pd a strong candidate to replace Pt in alkaline DEFCs.

Santasalo-Aarnio et al. further compared the oxidation of three fuels (methanol, ethanol, and iso-propanol) using both catalysts. Their findings confirmed that Pt is better for methanol oxidation, while Pd outperforms Pt in ethanol oxidation in alkaline conditions. However, both catalysts showed low efficiency for iso-propanol, likely due to its more complex oxidation pathway. As seen in **Figure 65** the highest peak for Pd in the CV test of ethanol is three times higher than the peak of Pt.

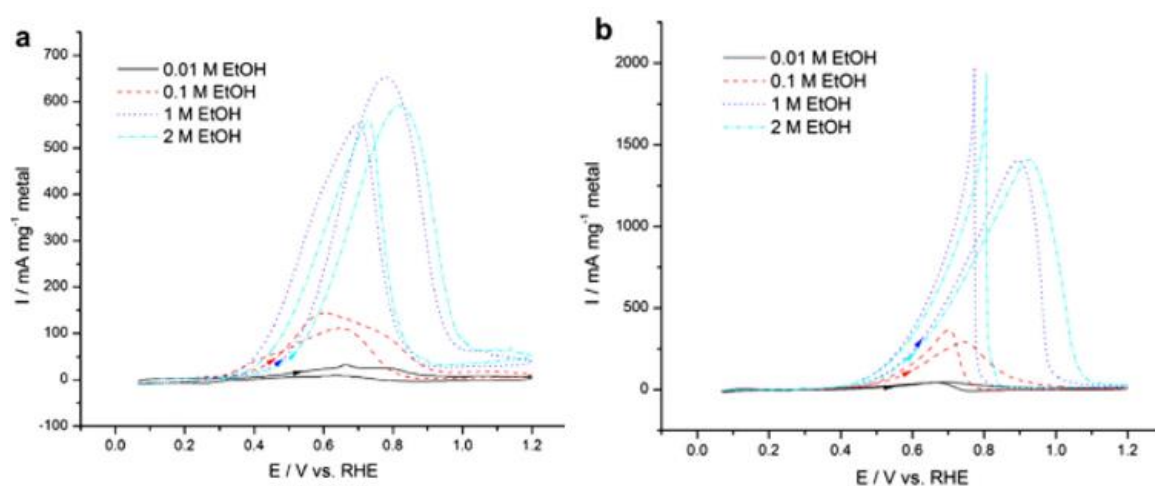


Figure 65. The CVs of electrodes in a 1 M NaOH + ethanol solution, a) Pt/C, and b) Pd/C. Scanning rate: 10 mV/s.

Pt and Pd belong to the same metal group, hence it is natural to have similar characteristics, reaction mechanisms, and co-catalyst interactions. This allows researchers to apply knowledge from Pt-based catalysts when developing Pd-based systems, making Pd a promising alternative for next-generation fuel cells.

4.6.1.4: Other Catalysts for Ethanol Oxidation in DEFCs

1. Gold (Au) : Au presents similar behavior to Pd. It is inert in acidic environments but relatively active in alkaline media. However, in alkaline environments ethanol oxidation on Au is slow compared to the conventional Pt, with a high onset potential ($> 0.7\text{V}$). Even with Ru as a co-catalyst, reaction rates did not improve due to slow adsorption/desorption on the Au surface.

2. Tungsten Carbide (WC): WC as an anode material, shows that it binds well with carbon nanofibers. WC demonstrated comparable ethanol oxidation performance to Pd, although slightly lower. When added as a co-catalyst to Pd, WC significantly improved EOR because electrochemically active surface area (ECSA) is getting larger with this addition. The ECSA of WC is quite high, thus increasing oxygen adsorption.

3. Iridium (Ir): This catalyst shares many properties with Pt but suffers from catalyst poisoning over time, like Pt. However, when combined with Sn as a co-catalyst, IrSn demonstrated excellent ethanol oxidation performance, comparable to PtSn. This makes Ir a strong candidate for replacing Pt in fuel cells.

4. Cadmium-doped cobalt (Cd-Co): During a study by Barakat et al. it was found that Cd was very efficient in the adsorption/desorption and oxidation of the CO_{ads} species. On the other side Co alone had low catalytic activity. However, when combined with Cd, Co enhanced Cd's reactivity, similar to how Ru and Ni improve other catalysts through a synergistic effect that weakens intermediate bond energy. On cyclic voltammetry (CV) tests, Cd-Co outperformed Pt, showing a lower onset potential and a higher peak current. Due to its low cost compared to Pt and Pd, Cd-co catalyst showed great potential as a cost-effective catalyst. This makes Cd-Co one of the most promising alternatives for commercial DEFC applications, though more research is needed.

4.6.2 Cathode catalysts

The other component that influences the performance of DEFCs is the cathode. A good anode electrode combined with a sluggish cathode that decreases the oxygen reduction reaction rate (ORR) degrades the FC performance. So, it is required the development of a good catalyst for ORR. Currently, platinum (Pt) is the most commonly used cathode material in both alkaline and acidic DEFCs due to its stability and strong oxygen reduction capabilities. Research on DEFC cathode development is limited, however studies using Pt have shown promising performance so far.

4.6.2.1 Pt-based catalysts

To enhance the oxygen reduction reaction (ORR) performance of Pt/C cathodes, researchers have suggested adding co-catalysts as Pt/C alone has shown a moderate ORR performance. This strategy is similar to this used for improving anode ethanol oxidation reaction (EOR) performance. Lopes et al. found that adding Pd to Pt significantly boosts ORR performance. This improvement occurs because Pd disrupts the Pt-Pt configuration, making it easier for oxygen to interact with the catalyst. Essentially, the addition of Pd reduces Pt's affinity for OH_{ads} and CO_{ads} species while increasing its attraction to O₂. This change in interaction enhances the catalyst's overall ORR efficiency. His research also stated that Co can improve ORR, though it doesn't boost ethanol tolerance in the same way Pd does, as Pt/C and PtCo/C

have identical EOR activity. However, Co's addition still helps improve oxygen reduction on the Pt surface. The addition of Pd not only improves the Pt catalyst's tolerance to ethanol (EOR activity) but also enhances its ORR performance. This suggests that catalysts with greater tolerance to EOR can achieve better overall ORR efficiency. Beyhan et al.'s confirmed this statement and showed that adding co-catalysts like Sn and Ni can similarly reduce OH and CO adsorption, helping O₂ species to adsorb more easily. Interestingly, PtSn/C exhibited the highest ORR performance, even surpassing trimetallic catalysts like PtSnNi/C, which might occur cause of the overlap of active sites in the trimetallic configuration. Consequently adding co-catalysts like Pd, Co, Sn, and Ni can significantly enhance ORR performance, but the optimal ratio of base catalyst to co-catalyst needs careful optimization to minimize site overlap and maximize effectiveness.

4.6.2.2 Pd-based catalysts

The PdAu alloys as cathode catalysts have a comparable performance with Pt cathodes. During a study from Xu et al. it appeared that the oxygen reduction rate (ORR) reached up to maximum of 50 mA cm² at the sweep rate of 50 mV/s in alkaline medium of KOH. Xu stated that the reason for this great performance of PdAu was due to its low ethanol oxidation rate, but the most possible reason is the presence of Au as a co-catalyst. Although Au shows a bad performance in oxidizing, shows an opposite reaction towards reduction performance.

Other Catalysts

Zhiani et al. presented HypermecTM K14, a non-noble catalyst, as an alternative to Pt/C for the cathode. Made using a painting method with PTFE, K14 has a better ORR performance than Pt/C, especially in alkaline media. The transition metals in K14 were found to be more reactive for ORR compared to Pt. Moreover, K14 is highly resistant to ethanol oxidation. During testing, Pt/C suffered significant performance loss due to ethanol crossover, while K14 showed near-zero ethanol-crossover current density, selective properties for oxygen reduction reaction and high tolerance to any ethanol oxidation reaction. This minimization of crossover effect makes K14 a very promising material for catalyst in DEFC cathodes [132].

4.7 PSM-PSCM electro-catalysts for SOFCs

The pursuit of a sustainable, clean, and cost-effective energy supply has sparked significant interest in fuel cells for the direct conversion of chemical fuels into electricity. Among various fuel cell types, solid oxide fuel cells (SOFCs) stand out as the cleanest and most efficient, offering

exceptional fuel flexibility. They can directly utilize a diverse range of fuels, including hydrogen, hydrocarbons, coal gas, and bio-derived fuels. A serious problem the SOFC technologies face is their high operating temperature that requires the use of expensive materials. Improving cathode activity is crucial for lowering the operating temperature of SOFCs since the resistance to the oxygen reduction reaction (ORR) is the main cause of energy loss, especially at lower temperatures. A decent SOFC cathode material characterized by fast oxygen exchange kinetics and high mixed ionic-electronic conductivity. We can address some cathode materials as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBC). While some cathode materials exhibit high ORR activity at low temperatures, their application in SOFCs is limited due to challenges with long-term stability and compatibility with the electrolyte or other cell components. Consequently, cathode materials are based on LSM ($> 800^\circ\text{C}$) and LSCF ($< 800^\circ\text{C}$). LSM cathodes face performance limits due to low oxygen ion conductivity at low temperatures, reducing active ORR sites. In contrast, LSCF cathodes may have low ORR surface activity and poor long-term durability, linked to changes in surface chemistry, structure, and morphology during operation.

A solution infiltration process has been developed to enhance LSCF cathodes by coating their surface with electro-catalytically active and stable materials. This method leverages the LSCF backbone's excellent ambipolar conductivity for efficient oxygen ion and electron transport while modifying the surface to boost catalytic activity and durability. Studies have shown that coatings of SSC, LCC, and SDC reduce polarization resistance, while a thin-film LSM coating enhances ORR activity and stability. While surface modification has demonstrated its potential, further optimization can enhance performance even more.

To improve LSCF cathodes we introduce two high-performance electro-catalysts: $\text{Pr}_{0.75}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (PSM) and $\text{PrSrCoMnO}_{6-\delta}$ (PSCM). A study evaluated their impact on interfacial polarization resistance (R_p), long-term stability, and cathodic activation behavior under typical SOFC conditions. As derivatives of doped lanthanide manganites, PSM and PSCM share a perovskite crystal structure with LSCF, facilitating the formation of a stable, conformal coating that helps prevent SrO surface segregation and improves durability. Praseodymium (Pr) was selected for its superior oxygen exchange properties, while the inclusion of manganese ensures long-term stability. Additionally, cobalt substitution in the B-site enhances catalytic activity without sacrificing structural robustness.

4.7.1 Experimental procedure

To determine the phase composition of the catalysts applied to an LSCF cathode, PSCM and PSM powders were synthesized using the same solution as the coating process. X-ray diffraction (XRD) analysis (**Figure 66 a**) revealed that PSM forms a simple perovskite phase, while PSCM develops a complex perovskite structure after calcination at 900°C for 1 hour. A proposed structural model for PSCM (**Figure 66 b**) suggests that Mn and Co ions (B-site) are randomly arranged inside BO_6 octahedrons, while Pr and Sr ions (A-site) sit within layers surrounded by tilted BO_6 octahedrons. To assess their chemical compatibility with LSCF, mixtures of PSM, PSCM, and LSCF powders were prepared, dried, and annealed at 900°C for 500 hours in air, simulating real synthesis conditions. The XRD patterns showed no signs of secondary phases in either case, indicating that both PSM and PSCM exhibit excellent phase stability when combined with LSCF under the tested conditions.

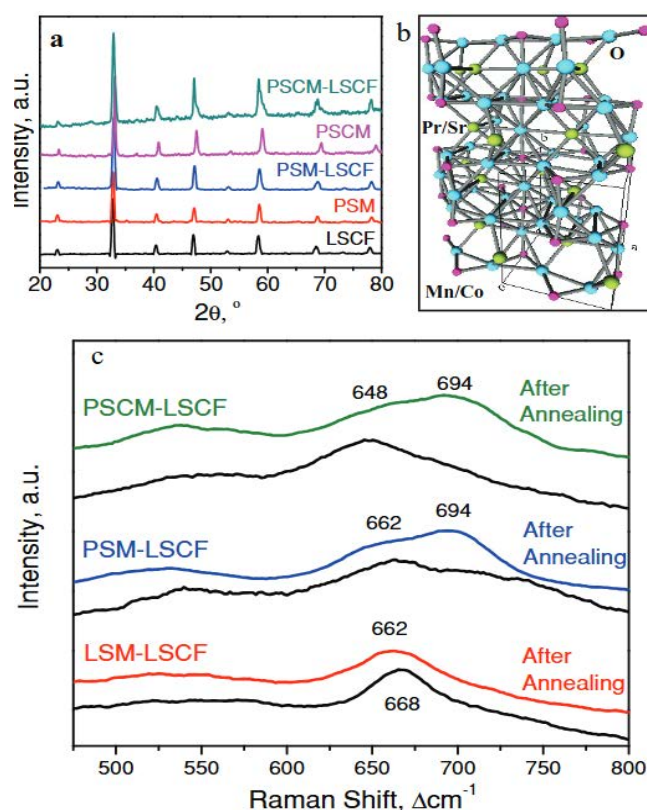


Figure 66. XRD analysis of the catalysts as well as catalyst-LSCF mixtures: (a) XRD patterns of LSCF, PSM, PSCM and the mixtures of them; (b) Proposed crystal structure of PSCM based on Rietveld refinement (The green, pink and blue atoms represent Pr/Sr cation, Mn/Co cation and O anion respectively; Cell distance is shown as doubled along a and b axis.). (c) Raman spectra collected in air from LSM-LSCF, PSM-LSCF, and PSCM-LSCF samples before and after annealing in air at 1000 °C for 100 hours.

To examine potential chemical interdiffusion between PSM/PSCM catalysts and the LSCF substrate, powder mixtures were annealed at 1000°C for 100 hours and analyzed using Raman spectroscopy. According to the Raman spectra (**Figure 66 c**) wide peaks observed between 600 and 750 cm^{-1} , corresponding to B-site ion and oxygen vibrations in the bulk material. In the LSM-LSCF spectrum, the peak remained symmetric after annealing but slightly shifted from 668 to 662 cm^{-1} , likely due to Mn, Co, and Fe ion exchange. Similar interdiffusion was previously observed in LSM-coated LSCF, forming an LSMCF interphase. For PSM-LSCF and PSCM-LSCF, the initial spectra had a slightly more prominent left-side peak, but after annealing, the right shoulder at 694 cm^{-1} became more distinct, indicating greater lattice distortion due to A-site ion exchange. This suggests interdiffusion between Pr, La, and Sr ions, likely leading to the formation of an “LPSMCF” perovskite phase. However, Raman analysis found no evidence of unwanted secondary non-perovskite phases, confirming the stability of these materials. **Figures 67 a)** and **b)** compare the surface morphologies of a blank LSCF and a PSCM-coated LSCF. The uncoated LSCF surface features smooth grains with distinct triple junctions, whereas the PSCM-coated surface exhibits a dense, continuous film, giving it a rougher texture and differing from typical particle-coated cathode structures. Additionally, noticeable contrast between grains suggests variations in PSCM film orientation, likely influenced by the underlying LSCF grain structure. When applied to a porous LSCF cathode via solution infiltration, the coatings appear similar in morphology (**Figures 67 c and d**).

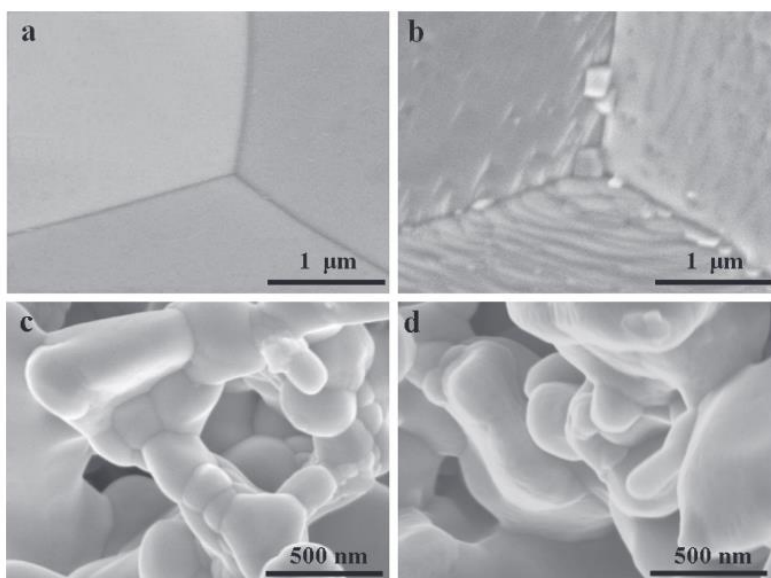


Figure 67. Surface morphology of blank and catalyst-coated LSCF: Typical surface views (SEM images) of (a) an LSCF pellet fired at 1350 °C for 5 hours; (b) a PSCM coated LSCF pellet annealed at 900 °C for 1 hour; (c) a porous LSCF cathode fired at 1080 °C for 2 hours and (d) a PSCM-coated LSCF cathode fired at 900°C for 1 hour.

4.7.2 Conclusion from the experiment

This study demonstrates that Mn-based catalyst coatings significantly improve both the electro-catalytic activity and stability of state-of-the-art LSCF cathodes, as observed in symmetrical and anode-supported SOFCs. The solution infiltration method used for coating is not only simple and cost-effective but also practical for commercial applications. One key advantage is the ultra-thin catalyst layer (10–50 nm), which is much thinner than other cell components like the anode support (0.3–0.7 mm), electrolyte (10–20 μm), or cathode backbone (50 μm). This allows the use of expensive Pr- or Pd-based catalysts, which would otherwise be impractical as bulk cathode materials. Furthermore, Pr-containing Mn-based catalysts outperform LSM in both activity and stability. Unlike traditional infiltration processes that require multiple steps to achieve sufficient conductivity, this single-step infiltration method is more efficient, making it easier to integrate into standard SOFC fabrication [133].

4.8 Bilayer anode in high-performance direct-ethanol SOFC

Despite the potential of renewable fuels in SOFCs, they have received relatively little attention. However the direct use of SOFCs with biofuels has been proposed as the most energy efficient means to use homegrown carbon neutral fuels. Among biofuels, ethanol is the most widely produced and developed, particularly in the transportation sector. It is an economical and low-emission energy source derived from renewable biomass, offering both environmental and economic benefits. Additionally, liquid fuels like bioethanol provide easier storage, handling, and transport compared to gaseous fuels, making them attractive for SOFC applications. Due to their high operating temperatures, SOFCs can directly convert primary fuels like ethanol and natural gas into electricity. However, running SOFCs on carbon-based fuels presents challenges, particularly carbon deposition on the Ni-YSZ anode, which leads to irreversible degradation. Two primary strategies have been developed to address this issue. The first involves adding an oxidizing agent (such as water, air, or CO_2) to the fuel stream to prevent carbon buildup. However, excessive fuel dilution can lower efficiency and increase system complexity. The second approach focuses on modifying or replacing the Ni-based anode to enable stable operation without dilution. Unfortunately, alternative anode materials often suffer from low electronic conductivity or poor catalytic activity. A promising approach is to keep the Ni-YSZ anode but add a specialized catalyst to improve fuel compatibility. This method helps prevent carbon buildup while maintaining high performance and stability. Unlike completely replacing the anode, this strategy is more practical and cost-effective, making it a viable

solution for using biofuels in SOFCs. Using a bi-layer anode offers the advantage of combining the Ni-YSZ anode, which works well with hydrogen, with a suitable catalyst for alternative fuels. Modern SOFCs have evolved into multilayer devices, incorporating additional functional layers to improve performance and durability. Two well-known examples are : i) Gadolinia-doped ceria (CGO) diffusion barrier, which prevents unwanted reactions between the LSCF cathode and the YSZ electrolyte and ii) Protective oxide coatings on metallic interconnectors, which help reduce chromium poisoning. Therefore, it makes sense to apply a similar approach to the anode, enabling SOFCs to operate efficiently with alternative fuels. Unlike traditional approaches, this study separates catalytic and electrochemical reactions into two distinct layers in the anode. The catalytic layer converts most of the ethanol into H_2 and CO_2 before it reaches the Ni-YSZ anode, preventing carbon buildup. Water needed for this reaction is produced naturally by the electrochemical processes in the cermet, which in turn receives H_2 from the catalytic reforming layer. It is demonstrated that high-performance SOFCs can operate on ethanol using a catalytic layer, achieving high stability and delivering almost the same current output as hydrogen-powered SOFCs.

4.8.1 Experiment Procedure

The experiment involved fabricating anode-supported SOFCs using an 8 mol% YSZ electrolyte, Ni-YSZ anode, and $La_{0.65}Sr_{0.30}MnO_3$ -based cathode at Forschungszentrum Jülich. A gadolinia-doped ceria (CGO) catalyst containing 0.1 wt.% Ir was prepared via a solution impregnation method. The catalyst was characterized using TEM and surface area analysis to ensure its quality. A catalytic ink was created by mixing the catalyst with ethanol, terpineol, cellulose, and other compounds, then applied onto the anode using an air spray method. After deposition, the sample was heat-treated to promote catalytic layer adhesion.

The electrochemical performance was tested at 850°C using a hydrogen/argon mixture, followed by switching to dry ethanol while maintaining the same flow rates. The system was designed to allow ethanol to reform into hydrogen through the catalytic layer, which sustained both the catalytic and electrochemical reactions. Durability tests were performed over 25 days, with detailed post-test analyses including SEM and carbon deposition evaluation using energy-dispersive X-ray (EDS) spectroscopy and a Leco CS600 analyzer. Additionally, a standard electrolyte-supported fuel cell was also tested as a comparison, with a lower nickel loading and reduced susceptibility to carbon formation. The performance of both configurations was carefully measured, focusing on fuel conversion and current output stability under continuous

operation. In **Figure 68 a)**, the TEM image shows that the catalyst has some agglomeration after heat treatment, but individual particles are still visible. The gadolinia-doped ceria (CGO) particles are rectangular and about 40 nm in size. The iridium (Ir) particles are small dark dots with an average size of 4 nm and are well dispersed on the CGO surface. The catalyst remains stable, with Ir particles not merging, even after testing. In **Figure 68 b)** and **c)**, SEM images show the cross section of the interface between the anode support and the catalytic layer. The catalytic layer is about 25 μm thick, well adhered to the anode surface. The catalytic layer has higher porosity compared to the anode, and coarsening of the CGO particles occurred during heat treatment. Despite this, the layer retains a porous structure due to the added pore former (cellulose), and the porosity helps with ethanol conversion.

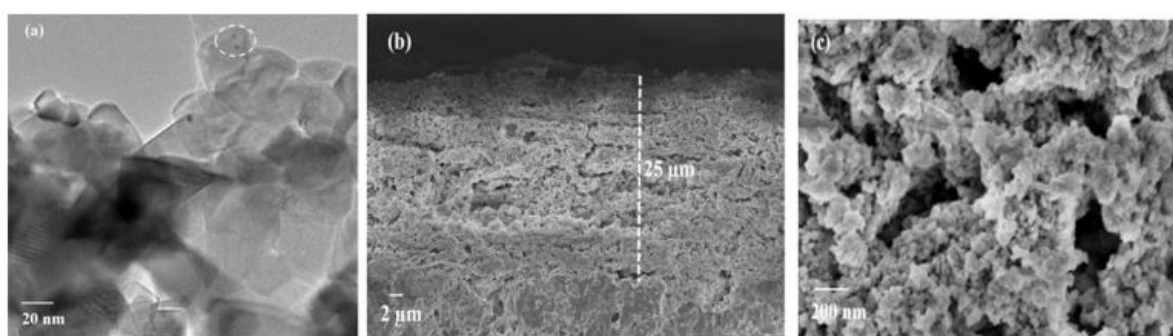


Figure 68. a) TEM image of the Ir-CGO catalyst after heat treatment at 900 °C in Ar (iridium nanoparticles are marked by the dotted circle), b) SEM image of the interface between anode support and catalytic layer c) higher magnification SEM image of the catalytic layer.

4.8.2 RESULTS

The fuel cells worked for 700 hours with dry ethanol without any carbon buildup. The Ir-CGO catalyst effectively helped break down ethanol using water naturally produced in the fuel cell. The fuel cell performed just as well with ethanol as it did with hydrogen, showing high efficiency. The results suggest that this fuel cell design is a promising way to use bioethanol, a renewable fuel, making it a clean and sustainable energy option [5].

Chapter 5

5.1 CONCLUSIONS

Energy is a key factor influencing a country's economy, infrastructure, and transportation, directly impacting quality of life. However, the global energy sector is facing a crisis due to the depletion of fossil fuel reserves and their harmful environmental effects. Despite international agreements such as the Paris Agreement and the Kyoto Protocol, most countries remain heavily reliant on fossil fuels, which are neither renewable nor environmentally friendly. The demand for energy continues to rise due to population growth and technological advancements, with the transport sector being one of the largest consumers of fossil fuels and contributors to greenhouse gas emissions. PEMFCs and SOFCs are highly efficient power sources for vehicles.

PEMFCs offer advantages such as cost-effectiveness, durability, high efficiency, quick start-up, good cold start capability, and a lightweight, compact system with low corrosion. These benefits make PEMFCs a promising candidate to replace internal combustion engines in transportation. On the other hand, SOFCs possess advantages like high efficiency, fuel flexibility, and low emissions. They operate at high temperatures with materials like YSZ for the electrolyte, nickel-YSZ composites for the anode, and lanthanum manganite for the cathode. SOFCs come in two main designs: tubular and planar. Tubular SOFCs offer simpler construction but suffer from higher resistive losses, while planar SOFCs provide higher power density and efficiency but require high-temperature seals that can cause reliability issues. Further material optimization is needed to improve performance, reduce costs, and enhance stability. Proton exchange membranes (PEMs), typically made of perfluorosulfonic acid (PFSA), need to be electrically insulating, highly conductive, and stable under mechanical, chemical, and thermal stress. Maintaining the right hydration level is crucial for performance, with Nafion being a popular choice due to its high conductivity and durability. Diffusion media, often carbon-based, facilitate gas distribution, while catalyst layers, typically platinum-based, are critical for electrochemical reactions but are susceptible to contamination by carbon monoxide (CO). Researchers are exploring alternative catalysts to improve performance and reduce costs. Bipolar plates, made from graphite or alternative materials, ensure gas flow, heat

exchange, and electrical connectivity, with metal foam being a promising innovation for improved efficiency.

PEMFCs operate at lower temperatures, offering higher efficiency (53–60%) but requiring pure hydrogen and expensive catalysts. In contrast, SOFCs function at high temperatures (600–1000°C), allowing fuel flexibility, internal reforming, and cost savings by eliminating the need for catalysts. While SOFCs have slightly lower efficiency (35–43%), they can utilize waste heat and achieve higher overall efficiency. Additionally, SOFCs provide significantly higher power output (2000 kW) compared to PEMFCs (100 kW), making them more suitable for heavy-duty applications. Fuel cells offer several advantages for automotive applications, including higher efficiency (>60%) compared to internal combustion engines (ICE), as they generate electricity directly from chemical reactions without combustion. They produce minimal pollutants, with only water and heat as by-products. Fuel cell vehicles (FCEVs) offer a wide range of power (20–250 kW) and long autonomy (over 400 km), with quick refueling times (<5 min). They operate with low noise and vibration due to the absence of moving parts. Although electric vehicles (EVs) and hybrid technologies have advanced, limitations such as range constraints and long charging times have driven the search for alternative fuels and green technologies.

Hydrogen is a highly promising fuel due to its high energy content per unit weight and zero harmful emissions. Despite its advantages, hydrogen production remains costly since it requires refining through chemical, thermal, or electrical processes such as steam reforming, electrolysis, and gasification. Although hydrogen is abundant, it must be extracted and stored efficiently for practical use. Currently, natural gas reforming is a widely used method, leveraging existing pipeline infrastructure to keep costs manageable. Storage is the main problem in hydrogen adoption. Compressed hydrogen tanks are currently the most common storage method, but their high cost and safety concerns are the main barriers to widespread adoption. Alternative storage solutions such as cryo-compressed tanks, liquid hydrogen (LH₂), and metal hydrides are being explored to improve efficiency and feasibility. Hydrogen's low energy density remains a hurdle, requiring further innovations to enable practical onboard storage for vehicles.

Hydrogen-based fuel cell vehicles (FCVs) offer a promising alternative to internal combustion engine vehicles (ICEVs) by significantly reducing greenhouse gas emissions, especially when powered by renewable sources like wind energy. However, despite their

environmental benefits, high costs remain the biggest challenge to widespread adoption. The primary cost drivers include the high production cost of hydrogen, expensive catalyst materials like platinum, and the limited availability of hydrogen refueling infrastructure. While government subsidies help lower the total cost of ownership, FCVs still face challenges related to durability, reliability, and maintenance. Unexpected repairs can disrupt daily activities, making long-term reliability a crucial factor for user acceptance. Proper management of humidity, flow rates, and temperature can extend fuel cell lifespan, but scaling up production remains difficult due to issues like uneven flow distribution. FCVs need to become commercially viable, and this cannot happen on the near future. Manufacturers must reduce production costs through technological advancements and mass production while ensuring reliability and efficiency. Without addressing these challenges, particularly those related to durability and flow distribution, improvements in catalyst materials alone will not be enough. Automakers must sell FCVs at scale to achieve profitability, and government incentives will likely continue to play a key role in supporting this transition. Ultimately, the success of fuel cell technology depends on balancing cost, efficiency, and reliability to meet consumer expectations and accelerate commercialization.

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