UNIVERSITY OF THESSALY
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Recent developments in water electrolysis for hydrogen production

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ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΙΑΣ

ΤΜΗΜΑ ΜΗΧΑΝΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ

Πρόσφατες εξελίξεις στην ηλεκτρόλυση του νερού για παραγωγή υδρογόνου

Από

ΜΙΧΑΗΛ ΤΣΑΝΑΚΤΣΗΣ

Επιβλέπων:

Καθ. Δρ. Π. Τσιακάρας

Υποβλήθηκε σε μερική εκπλήρωση των απαιτήσεων για την απόκτηση διπλώματος

Μηχανολόγου Μηχανικού στο Πανεπιστήμιο Θεσσαλίας

Βόλος,2025

Με πλήρη επίγνωση των συνεπειών του νόμου περί πνευματικών δικαιωμάτων, δηλώνω υπεύθυνα ότι η παρούσα εργασία με τίτλο «**Πρόσφατες εξελίξεις στην ηλεκτρόλυση του νερού για παραγωγή υδρογόνου**», αποτελεί προϊόν αυστηρά προσωπικής εργασίας και όλες οι πηγές που έχω χρησιμοποιήσει έχουν δηλωθεί κατάλληλα στις βιβλιογραφικές παραπομπές και αναφορές. Τα σημεία όπου έχω χρησιμοποιήσει ιδέες, κείμενο ή/και πηγές άλλων συγγραφέων, αναφέρονται ευδιάκριτα στο κείμενο με την κατάλληλη παραπομπή και η σχετική αναφορά περιλαμβάνεται στο τμήμα των βιβλιογραφικών αναφορών με πλήρη περιγραφή.

Σημειώνεται ότι οποιοδήποτε εφαρμογή τεχνητής νοημοσύνης χρησιμοποιήθηκε αποκλειστικά και μόνο για την επιμέλεια και τη γλωσσική βελτίωση του κειμένου και **όχι για την παραγωγή ή συγγραφή του περιεχομένου της διπλωματικής**.

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RECENT DEVELOPMENTS IN WATER ELECTROLYSIS FOR HYDROGEN PRODUCTION

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Abstract

Hydrogen is a carbon-free alternative energy source for use in future energy frameworks with the advantages of environment-friendliness and high energy density. Among the numerous hydrogen production techniques, sustainable and high purity of hydrogen can be achieved by water electrolysis. Therefore, developing electrocatalysts for water electrolysis is an emerging field with great importance to the scientific community. On the one hand, precious metals are typically used to study the two-half cell reactions, i.e., hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). However, precious metals (i.e., Pt, Au, Ru, Ag, etc.) as electrocatalysts are expensive and with low availability, which inhibits their practical application. Non-precious metal-based electrocatalysts on the other hand are abundant with low-cost and eco-friendliness and exhibit high electrical conductivity and electrocatalytic performance equivalent to those for noble metals. Thus, these electrocatalysts can replace precious materials in the water electrolysis process. However, considerable research effort must be devoted to the development of these cost effective and efficient non-precious electrocatalysts. In this thesis, we provide key fundamental knowledge of water electrolysis, progress, and challenges of the development of most-studied electrocatalysts in the most desirable electrolytic solutions: alkaline water electrolysis (AWE), solid-oxide electrolysis (SOE), and proton exchange membrane electrolysis (PEME). Lastly, we discuss remaining grand challenges, prospects, and future work with key recommendations that must be done prior to the full commercialization of water electrolysis systems.

Key words: water electrolysis, electrocatalysts, hydrogen production, AWE, SOE, PEME

ΠΡΟΣΦΑΤΕΣ ΕΞΕΛΙΞΕΙΣ ΣΤΗΝ ΗΛΕΚΤΡΟΛΥΣΗ ΤΟΥ ΝΕΡΟΥ ΓΙΑ ΠΑΡΑΓΩΓΗ ΥΔΡΟΓΟΝΟΥ

ΜΙΧΑΗΛ ΤΣΑΝΑΚΤΣΗΣ

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Περίληψη

Το υδρογόνο είναι μια εναλλακτική πηγή ενέργειας χωρίς άνθρακα για χρήση σε μελλοντικά ενεργειακά πλαίσια με τα πλεονεκτήματα της φιλικότητας προς το περιβάλλον και της υψηλής ενεργειακής πυκνότητας. Μεταξύ των πολυάριθμων τεχνικών παραγωγής υδρογόνου, η βιώσιμη και υψηλή καθαρότητα του υδρογόνου μπορεί να επιτευχθεί με ηλεκτρόλυση νερού. Ως εκ τούτου, η ανάπτυξη ηλεκτροκαταλυτών για ηλεκτρόλυση νερού είναι ένα αναδυόμενο πεδίο με μεγάλη σημασία για την επιστημονική κοινότητα. Από τη μία πλευρά, τα πολύτιμα μέταλλα χρησιμοποιούνται συνήθως για τη μελέτη των αντιδράσεων των δύο μισών κελιών, δηλαδή, αντίδραση εξέλιξης υδρογόνου (HER) και αντίδραση εξέλιξης οξυγόνου (OER). Ωστόσο, τα πολύτιμα μέταλλα (δηλαδή, Pt, Au, Ru, Ag, κ.λπ.) ως ηλεκτροκαταλύτες είναι ακριβά και με χαμηλή διαθεσιμότητα, γεγονός που εμποδίζει την πρακτική εφαρμογή τους. Από την άλλη πλευρά, οι ηλεκτροκαταλύτες με βάση μη πολύτιμα μέταλλα είναι άφθονοι με χαμηλό κόστος και φιλικότητα προς το περιβάλλον και παρουσιάζουν υψηλή ηλεκτρική αγωγιμότητα και ηλεκτροκαταλυτική απόδοση ισοδύναμη με εκείνα των ευγενών μετάλλων. Έτσι, αυτοί οι ηλεκτροκαταλύτες μπορούν να αντικαταστήσουν πολύτιμα υλικά στη διαδικασία ηλεκτρόλυσης νερού. Ωστόσο, πρέπει να καταβληθεί σημαντική ερευνητική προσπάθεια για την ανάπτυξη αυτών των οικονομικών και αποδοτικών μη πολύτιμων ηλεκτροκαταλυτών. Σε αυτή τη διατριβή, παρέχουμε βασικές θεμελιώδεις γνώσεις για την ηλεκτρόλυση νερού, την πρόοδο και τις προκλήσεις της ανάπτυξης των πιο μελετημένων ηλεκτροκαταλυτών στις πιο επιθυμητές ηλεκτρολυτικές λύσεις: ηλεκτρόλυση αλκαλικού νερού (AWE), ηλεκτρόλυση στερεού οξειδίου (SOE) και ανταλλαγή πρωτονίων ηλεκτρόλυση μεμβράνης (PEME). Τέλος, συζητάμε τις υπόλοιπες μεγάλες προκλήσεις, την προοπτική και το μελλοντικό έργο με βασικές συστάσεις που πρέπει να γίνουν πριν από την πλήρη εμπορευματοποίηση των συστημάτων ηλεκτρόλυσης νερού.

Λέξεις-κλειδιά: ηλεκτρολύση νερού, ηλεκτροκαταλύτες, παραγωγή υδρογόνου, AWE, SOE, PEME

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Chapter 1 Introduction

1.1 Energy Demand

In modern societies, energy demand is a multidimensional and ongoing phenomenon. While it's being referred to as energy demand the correct term to use is exergy demand. Energy is a fundamental characteristic of objects and systems that cannot be created or destroyed, only transferred between systems and transformed into different forms. Exergy on the other hand accounts for both the amount and the quality of energy and, unlike energy, can be lost during conversion processes, such as when electricity is turned into low-temperature heat (high exergy form into low exergy form) [1].

In the global market nowadays, energy needs are in constant thrive. Non-renewable energy sources, mostly fossil fuels (coal, petroleum, gas, oil) are at a production peak. Global oil reserves were only 500 Bb (Billion barrels) in 1970 yet due to new explorations, after two decades the world had 900 Bb despite consumption of 600 Bb. Oil and gas reserves increase rates were 0.11 Mb and 7.4 trillion cubic meter (TCM with 1 TCM ≈ 6.29 trillion barrels) per year in 2010 as shown in **Figure 1** [2].

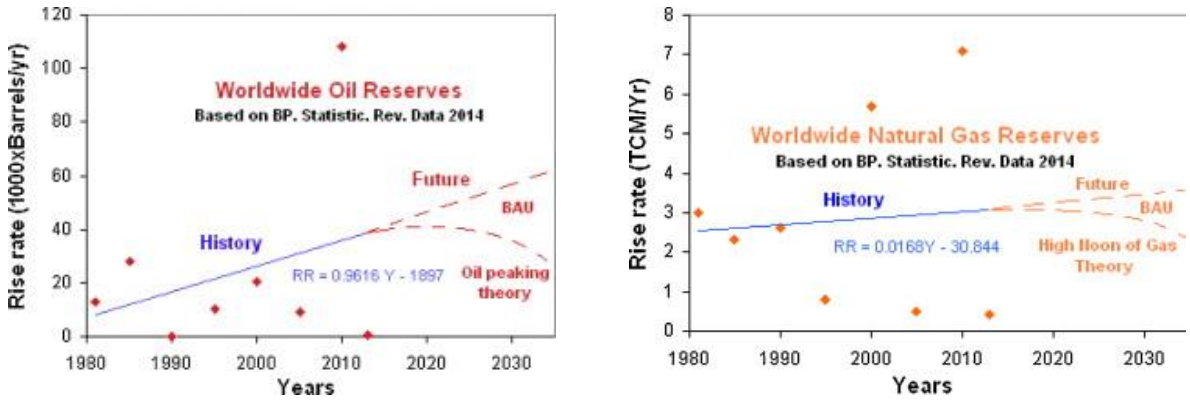

Figure 1: Annual oil and gas reserves increase rates from 1980 to 2030[2].

1.2 Hydrogen Production Benefits

Hydrogen is a clean energy source with high energy density, offering a carbon-free alternative for future energy systems while being environmentally friendly. Given its properties, hydrogen can be a good fuel because:

- Its use for energy purposes does not cause greenhouse gas emissions (water is the only by-product of the process).
- It can be used to produce other gases, as well as liquid fuels.
- Existing infrastructure (gas transport and gas storage) can be repurposed for hydrogen.
- It has a higher energy density than batteries so it can be used for long-distance and heavy-goods transport [3].

Also, hydrogen has a higher energy per unit of mass but a lower energy per unit volume than any other fuel. By weight, hydrogen “carries” three times the energy of our most common fuels. For example, 1 kg of hydrogen has approximately the same amount of energy as 1 U.S. gallon of gasoline (approximately 3 kg) [4].

Since the Industrial Revolution, humanity has been facing critical challenges surrounding the 3Es—Energy, Environment, and Economy—and has been striving to solve the energy equation in a way that is both environmentally friendly and cost-effective. Due to growing environmental concerns, particularly related to global climate change, there is now a stronger focus on zero- or near-zero-carbon solutions.

Among the potential solutions, hydrogen stands out as the only clear pathway toward zero-carbon emissions, and it is widely expected to play a pivotal role in enabling a carbon-free economy. However, producing hydrogen is not without cost or effort—it requires specific methods to split water into hydrogen and oxygen. These methods can be broadly categorized into electrolysis, thermochemical cycles, photonic processes, and others.

Each method carries its own technical and economic challenges, making the development of efficient, affordable, and scalable hydrogen production technologies crucial to realizing hydrogen’s potential as a sustainable energy carrier.

Chapter 2 Electrochemical Devices

2.1 Introduction

Electrochemical devices describe a system in which energy of one form (i.e. chemical energy) can be converted to energy of another form (i.e. electrical energy) through the process of reduction-oxidation (herein referred to as a redox reaction). The electrostatic phenomena usually relate to the movement of electrons and ions between the electrodes in an electrolyte solution. Some examples are the existence of batteries, supercapacitors, fuel cells etc.

2.2 Batteries

Batteries produce electrical energy out of chemical energy. They include four major elements namely the cathode (positive terminal), the anode (negative terminal), separator which separates the two electrodes and an electrolyte which allows the flow of ions between two electrodes. The energy required in batteries is stored in the form of chemical compounds and when discharging it; the chemical reaction takes place to release energy that can be used in a battery in the form of electric current at a given voltage. Batteris are electrochemical devices made by placing two chain reactions in an outer electrical circuit. One of the reduction reactions in the material Anode and one oxidation in the Cathode material. Those two reactions are shown below [5]:

$$Anode\ reduction:\ S(N)red \rightarrow S(N)ox + ne^{-} \quad (2.1)$$

$$Cathode\ oxidation: S(P)ox + ne^{-} \rightarrow S(P)red \quad (2.2)$$

The market has two types of batteries namely primary and secondary batteries. Primary batteries are disposable since they can only experience the conversion process of one time. They are fast disposed and have to be recycled after using them. On the contrary, secondary batteries, which are mostly referred to as rechargeable batteries, are designed with more than a single cycle of charge-discharge activities and have the ability to repeat conversion of chemical energy into power as electricity [5].

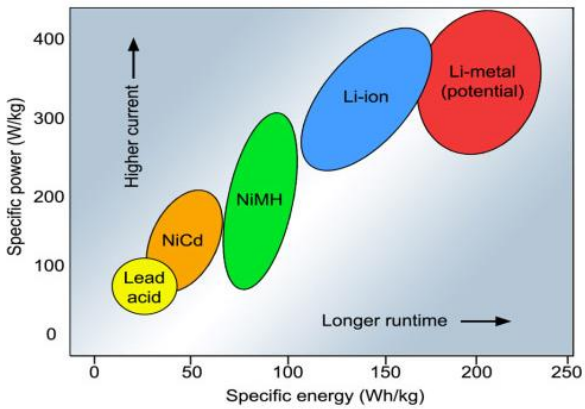

Figure 2: Comparison of battery technologies in terms of specific energy (Wh/kg) and specific power (W/kg) [6].

It is worth noting that battery performance has evolved much slower than advancements in electronics. Many materials in modern batteries are reaching their limitations. This statement is clarified in the graphs below (**Figure 2, Figure 3**) [6]:

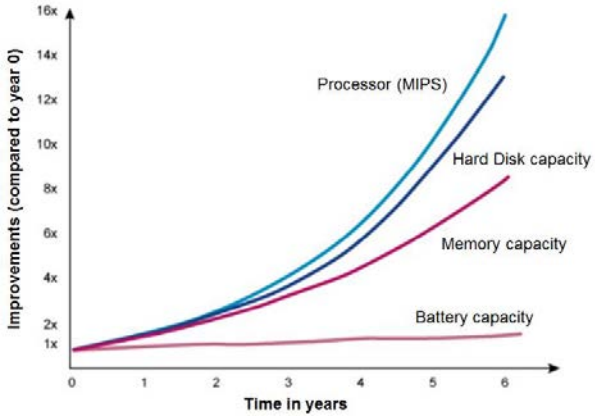

Figure 3: Improvements in battery and computing technologies [6].

2.2.1 Types of batteries

Batteries are of two main types; the primary and secondary ones. Primary batteries are low capacity because they can only pass through the energy conversion process once. Thereby; they leak easily and have to be recycled. On the contrary, there are secondary batteries which are simply batteries which are rechargeable and are disposed to convert chemical energy to electricity, several times so that they can serve the same purpose [5].

Types of the main battery of its category are:

Primary Batteries

- Alkaline Batteries
- Lithium Batteries

Secondary Batteries

- Lead acid (Lead Acid, Sealed Lead Acid, SLA)
- Nickel cadmium (Ni-Cd)
- Nickel Metal Hydride batteries (NiMH)
- Li-Ion batteries Lithium-ion

2.2.1.1 Alkaline Batteries

Primary battery an alkaline battery is a zinc/manganese dioxide (Zn/MnO2)-chemistry, potassium hydroxide (KOH)-electrolyte primary battery. It is a battery that consists of a negative zinc electrode and a positive manganese dioxide electrode. The most viable option in supplying electric and electronic devices with the portable power is alkaline manganese-zinc batteries. Their voltage is about 1.5V and they provide a high-performance discharge, a long operate even in heavy loads and low temperatures, good shelf life, leak resistance and good price [7], [8]. The average composition of alkaline battery material is represented in tabular form in table 1.

Table 1. Materials Used on Average in Composition of Alkaline Batteries [8]

Material	Percentage of battery weight (%)
Manganese Electrolytic	32-38
Graphite	3-5
Zinc	11-16
Steel	19-23
Potassium hydroxide (KOH)	5-9
Barium sulfate ($BaSO_4$)	<5
Water, paper, plastic, other	Balance

2.2.1.2 Lithium Batteries

Lithium batteries known as Lithium metal batteries are non-rechargeable with 1.5 to 3.7V depending on battery chemistry. They possess carbon cathode and metallic lithium anode. There are different types of lithium battery such as the lithium carbon fluoride (Li-CFx), lithium manganese dioxide (Li-MnO_2), lithium iron disulfide (Li-FeS_2), lithium thionyl chloride (Li-$SOCl_2$), and lithium sulfur dioxide (Li-SO_2). These batteries are light, sturdy, have a high cell voltage (3-4 V), high energy content, low self-discharge, a wide operating temperature range, enhanced antileakage abilities along with long shelf and usage lives [9].

2.2.1.3 Lead acid batteries (SLA)

The early rechargeable battery to be developed was the lead acid battery. The concept was first voiced back in 1860 by a French Physicist called Gaston Plante. It is important to find out the fundamental elements of an SLA battery. A lead dioxide paste covers the positive plate. The negative plate is formed of a sponge lead. The separator contains an insulating substance even as it enables the process of conduction among the plates. Lastly, it is constructed of an electrolyte that is water and sulphuric acid. The battery is made up of a number of cells connected in series to produce the necessary voltage because each cell will deliver 2.1 volts of EMF. The advantages of an SLA battery are mentioned below [10]:

- Maintenance Free
- Lower Cost Than Li-ion Options
- Long Service Life
- Built Tough

Discharging in lead-acid batteries causes a strain in every discharge and repetitive charge-discharge cycles degrade the capacity slowly. This loss is negligible in well maintained batteries but the level of performance declines tremendously as the capacity falls to below 50% [5]. Table 2 shows the composition of materials of the typical lead acid battery.

Table 2. Materials used in composition of a Pb-A battery[8]

Material	Percentage of battery weight (%)
Lead	25
Lead oxides	35
Polypropylene	10
Sulfuric acid (H_2SO_4)	10
Water	16
Glass	2
Other (e.g., antimony)	1

2.2.1.4 Nickel Cadmium Batteries (Ni-Cd)

A nickel-cadmium (Ni Cd) battery is alkaline battery having nickel oxyhydroxide (NiOH) as positive electrode, and a porous cadmium (Cd) as negative. Nickel cadmium battery Nickel-cadmium, or NiCd batteries consist of a negative cadmium electrode and a sintered positive nickel electrode dipped into an aqueous potassium hydroxide solution. During the last several years, these batteries have been identified as balanced in their performances in the parameters of specific energy, specific power, cycle life, and reliability. Nonetheless, the recovery of Ni-Cd battery is very important and comprehensive due to the toxicity and hazardous effects of cadmium on the environment. Use of these has been eliminated due to their negative effects on the environment.

Ni-Cd batteries have a high rate of the charge and discharge and may withstand about 2,000 deep discharge operate. They actually have a very low internal resistance, usually in the low ranges 0.4 m, 1 m and 4 m direct current (DC) resistance values at a 100 Ah charge value to high, mid and low charge rates respectively. Fall in temperature or loss of charge in battery will cause an increase in inner resistance. Their lifespan based on the operating conditions and the design of the battery can be between 8 years to reach 25 years [11],[12]. Table 3 presents common material composition of NiCd battery.

Table 3. Materials used in Nickel Cadmium Batteries [13]

Material	Percentage of battery weight (%)
Active Nickel	10-25
Active Cadmium	10-19
Cobalt	0-2
Alkaline Electrolyte	14-27
Plastics	3-6
Steel	25-45

2.2.1.5 Nickel Cadmium Hydride Batteries (NiMH)

Power tools and hybrid automobile applications use nickel-metal hydride (Ni MH) batteries. Ni-MH batteries technology has equally been given priority by major manufacturers of cars. These batteries consist of nickel hydroxyl oxide cathode, metal hydride ion anode, potassium hydroxide

(KOH) electrolyte and separator. The Ni-MH batteries have quite a number of attributes such as higher energy density, higher specific energy compared to lead-acid (Pb-A) and nickel cadmium (Ni-Cd) batteries, good temperature and rate performance, good charge retention, long cycle life, long shelf life in addition to fast charge capability. They, however, cost more than Pb-A batteries, they are not as specific in energy and power, and they perform poorly in the low temperatures [8]. Table 4 indicates the material structure of Ni-MH batteries.

Table 4. Materials used in Nickel Metal Hydride Batteries [14]

Material	Percentage of battery weight (%)
Iron-Fe	15-30
Nickel-Ni	30-45
Rare Earth – Mn / Al	7-15
Cobalt	1-5
Plastics	2,5-3,5
Other (Alcalis-H_20-$0H^-$)	13-35

2.2.1.6 Lithium Ion Batteries (Li-Ion)

Lithium battery has a high storage rate of 83 percent and is ideal choice of energy source in sustainable transport. Li-ion batteries are also well-suited to small-scale electronics and in renewable energy as well as in micros-grid systems. Special properties are easy to design sealed, maintenance-free cells, high cycle life, wide operating temperature range, fast charging, high charge and discharge efficiency, high energy density, and construction flexibility. Table 5 states the composition of the materials used in Li-ion batteries as used in HEV and PHEV as well as in BEV.

Table 5. Materials used in making Li-ion batteries of HEV, PHEV and BEV [8].

Material	Percentage of mass (%)		
	HEV	PHEV	BEV
Lithium manganese oxide (LiMn2O4)	27	27	33
Graphite/Carbon	12	12	15
Binder	2.1	2.0	2.5
Copper	13	15	11
Wrought aluminum	24	22	19
Lithium hexafluorophosphate (LiPF6)	1.5	1.6	1.8
Ethylene carbonate (EC)	4.4	4.7	5.3
Dimethyl carbonate (DMC)	4.4	4.7	5.3
Polypropylene	2.0	2.2	1.7
Polyethylene	0.26	0.4	0.29
Polyethylene terephthalate	2.2	1.6	1.2
Steel	2.8	1.8	1.4
Thermal insulation	0.43	0.33	0.34
Glycol	2.3	1.2	1.0
Electronic parts	1.5	0.9	1.1
Total battery mass (lb)	41	196	463

Design flexibility refers to the electrolyte salts used whereby lithium hexafluorophosphate ($LiPF_6$) is the traditional option. $LiPF_6$ batteries however are limited in thermal instability, moisture sensitivity and toxicity of by-products produced by degradation. The efforts are underway to come up with alternative salts in order to address these shortcomings. The use of solid-state determines arouses the high performance of Li-ion battery by providing greater thermal and chemical stability, but high prices provide a problem. They are being improved in terms of their commercial viability. Li-ion batteries have some disadvantages besides these advantages in that they are an expensive system to purchase, they are very unstable during both charge and discharge periods, they require charging regularly, and have poor cycle life [8].

2.3 Supercapacitors

2.3.1 General Information

A supercapacitor is a special form of capacitor used when very high amounts of energy have to be stored (as compared to regular capacitors). Supercapacitors lie between traditional capacitors and batteries in energy stores capacity, having more storage capacity than capacitors, but less than batteries. The characteristics of supercapacitors are that they charge quickly and able to deliver power instantly that makes them appropriate in hybrid automobiles, energy harness applications, and smartphones [15]. The energy in a capacitor is held in the form of a static charge rather than by a chemical reaction.

The capacitor is charged after application of a voltage difference across the positive and negative plates. There are three major categories of capacitors and the most basic type is the electrostatic capacitor that has a dry separator. This is a low capacitance capacitor of a long tradition and it is preferably used as filter and radio frequency tuning. Its based capacitance is normally a few pico-farad (pF) to somehow microfarad (lF). The electrolytic capacitor provides much larger than the electrostatic capacitor capacitance, in microfarads (10 to the 6 th power of equations namely 10 6 = 1,000,000 pico-farads (10 to the 12 th power). Such capacitors use wet separator and they are normally used to filter, buffer and couple signals.

Electrolytic capacitors, like batteries, are composed of a positive and negative terminal and these must be properly oriented to be used. The third one is the supercapacitor that is rated up to thousands of times higher than the electrolytic capacitors, as its capacitance values are expressed in farads (F). Supercapacitors are targeted at applications which need frequent charge/discharge with a lot of electrical power contained within a small volume of power storage [16]. Based on **Figure 4**, there are three primary kinds of capacitors as indicated below.

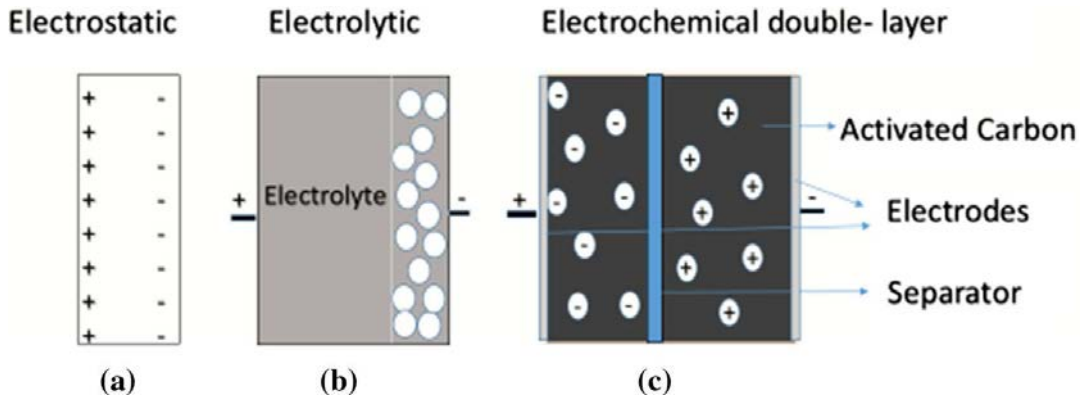

Figure 2: Types of capacitors: (a) dry capacitor, (b) electrolytic capacitor, (c) supercapacitor [17].

Supercapacitors are electrical devices that store energy in an electrical field by accumulating the charge, mainly by creating a double-layer type of capacitor at the electrodes-electrolyte interface. No chemical reactions or combustion occurs in this storage mechanism, only quick and reversible reactions on the electrode surface (Faradaic reactions or charge transfer reactions), acting to add their own capacitance to the total.

Following weights, charging method, the power they produce, the time it takes to charge them back up, lifetime, the chemical reaction and temperature sensitivity of capacitors, batteries and supercapacitors have been compared as below [17][18]. A comparative table between batteries, capacitors, and supercapacitors is a detailed table in **table 6**.

Table 6. Comparison between batteries, capacitors and supercapacitors

Parameters	Batteries	Capacitors	Supercapacitors
Weight	Large weight (10g to >10kg)	Lower weight (1-100g)	Lower weight (1-2g)
Charge method	Current and voltage	Voltage across terminals	Voltage across terminals
Power delivered	Constant voltage	Rapid Discharge	Rapid Discharge
Charge/discharge time	Large	Less	Very Less
Lifetime	150-1500 cycles	>100 k cycles	>100 k cycles
Chemical reaction	Chemicals are required	No chemicals required	No chemicals required
Temperature sensitive	More temperature sensitive	Excellent temperature performance	Excellent temperature performance

2.3.2 Fundamental of Supercapacitors

A simplified SC construction has aluminum current collection and electrodes whereas dielectric materials are eliminated. The working principle of the SC is premised on the storing of the energy through dispersion of the ions around the surface of the two electrodes. The two interfaces form zone charge known as electrical double layer (EDL).

Structurally, the SC consists of two electrodes, a membrane separator, and electrolyte as shown in **Figure 5** [19].

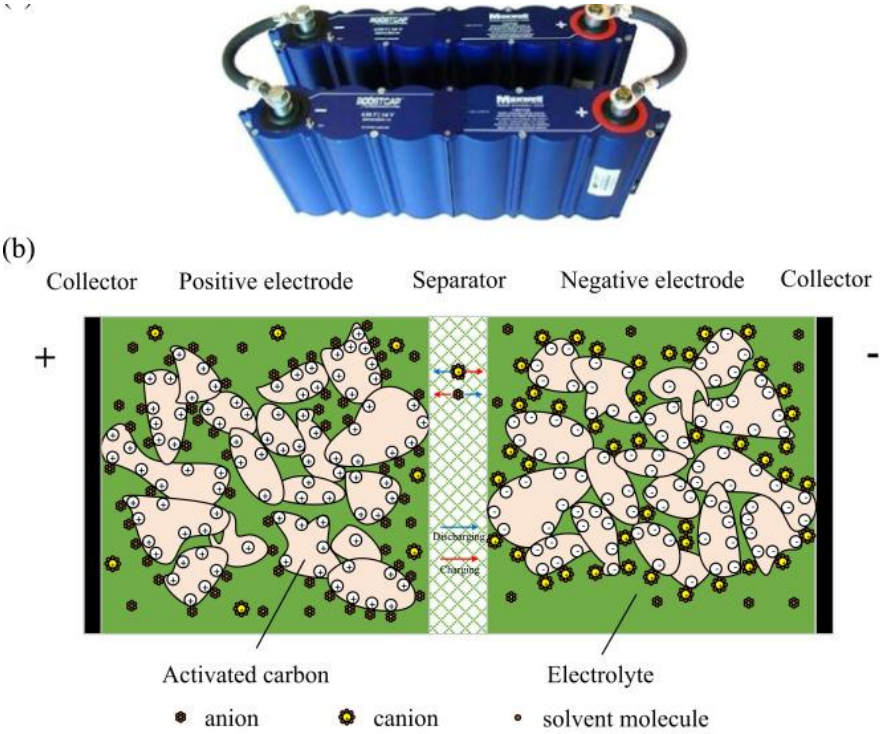

Figure 3: (a) Photograph of a supercapacitor module manufactured by Maxwell; (b) schematic representation of the internal structure of a supercapacitor [19].

At this stage, it is important to present the advantages and drawbacks of supercapacitors in comparison to other energy storage devices. This comparison is illustrated in **Figure 6** [20].

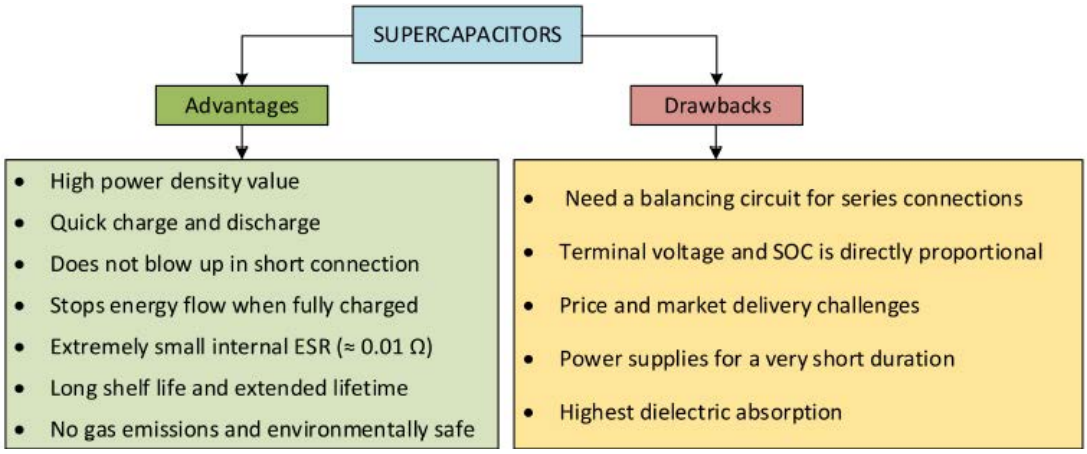

Figure 4: Advantages and drawbacks of supercapacitors in energy storage applications [20].

The classification of supercapacitors is based on their energy storage mechanism, which includes three main categories: electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors, as illustrated in **Figure 7** [21].

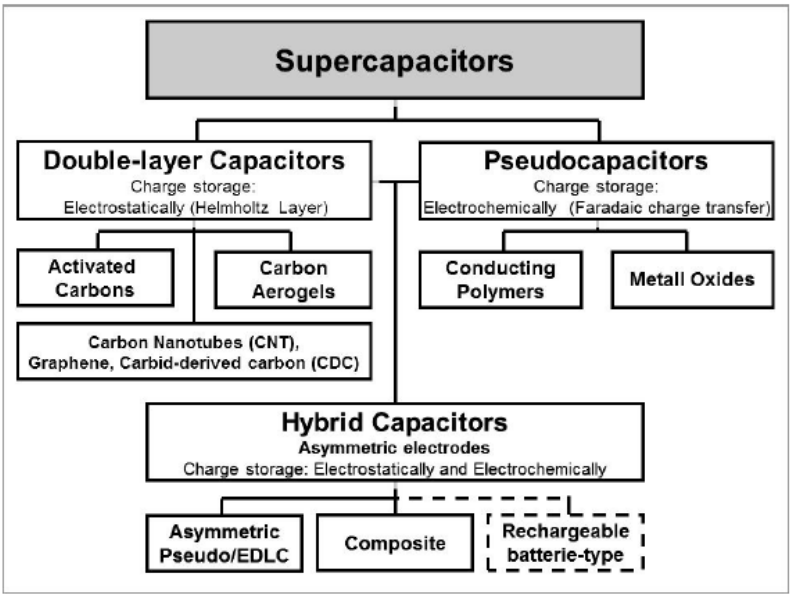

Figure 5: The Classification of Supercapacitors [21].

2.3.2.1 Electrochemical double layer Capacitors (EDLCs)

Electrostatic means of storing energy in electrochemical double-layer capacitors (EDLCs) is used. EDLCs do not use a dielectric as compared to the conventional capacitors. Rather, they are two electrodes and an electrolyte. The capacitance of a conventional capacitor is given by:

$$C = \frac{\varepsilon o \varepsilon r A}{d} \quad (2.3)$$

Where C= capacitance, εo= the permittivity of the free space, εr= the relative permittivity of the dielectric medium, A= the area of the electrodes and d=distance between the two electrodes in **Figure 7**. Experimentally, capacitance can also be determined using:

$$C = \frac{T}{R} \quad (2.4)$$

For where R is the resistance and T is the discharge time. Capacitance as represented by Eq (2.3) is proportional to the surface area of the electrodes and is inversely proportional to the separation of the electrodes. This means that materials with large surface areas give high capacitance [20].

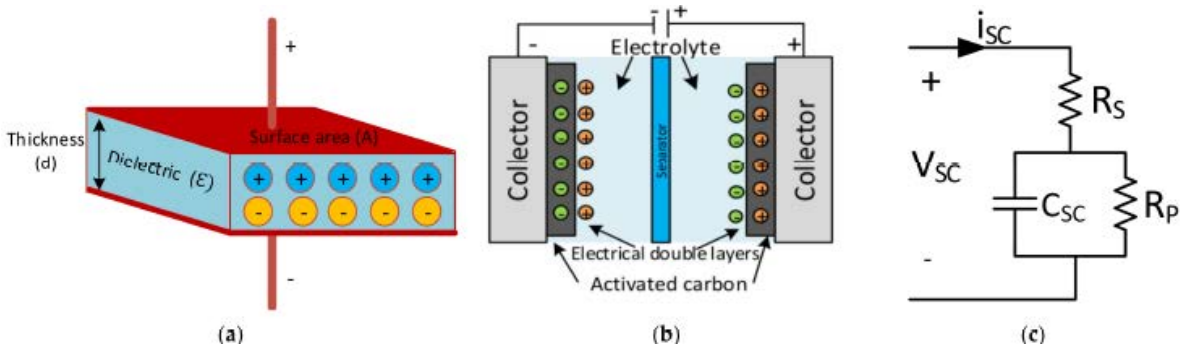

Figure 6: a) Structure of electrostatic capacitor b) Structure of SC c) Equivalent circuit model of SC [20].

The ions contained in the electrolyte solution are diffused in the membrane or layer, through the pores of the electrode with opposite charge. The electrode, however, imparts formation of a recombination of positive and negative charges as indicated in **Figure 8, Figure 9**.

As a result, the charge generates on the two electrodes. The two-layer system has the advantage of resulting in a high surface area and narrow gap between the electrodes which allows directly connecting the electric double-layer capacitors (EDLC) to have a much higher energy density than conventional analogs.

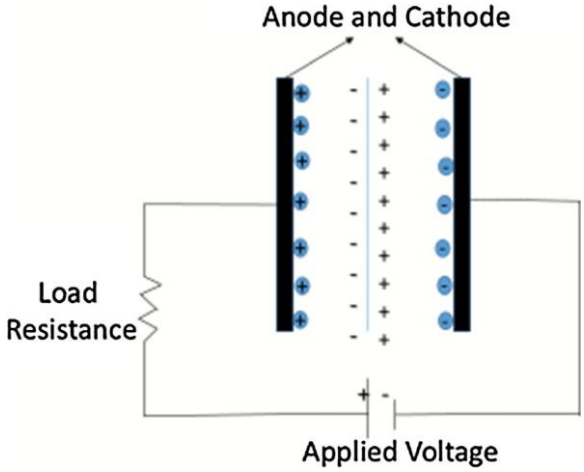

Figure 7: Schematic diagram of an electric double-layer capacitor, indicating charge separation between anode and cathode under applied voltage [17].

The selection of electrode materials plays a crucial role in achieving high capacitance. Activated carbon is widely used due to its high surface area, which facilitates charge storage in EDLCs. Charging and discharging is performed when adsorption of ions and de-adsorption of ions on the electrode surface takes place. The porosity of the material is another important capacitance enhancing factor as the entire surface-to-volume ratio is significant. The pore size should be ideal such that it is about two times of the ion diameter so that ion cannot adsorb on the walls of pore effectively. The specific capacitance, however, is not directly proportional to the surface area (specific) and more surface area will not necessarily increase the capacitance only. When in operation, the application of a voltage leads to the attraction of ions toward the surface of the electrode where an electric double layer is created storing charge. On the contrary, during discharge, ions are ejected off a surface, and released energies occur. The ions spread out within the electrolyte wherein pores are present in the electrode structure barring recombination of oppositely charged species. The effect of this mechanism is to both increase the effective surface area and decrease distance between electrodes enabling EDLCs to reach much higher energy densities than conventional capacitors. Electrolyte is a very important component of EDLC. Aqueous

and organic electrolytes are the ones usually used and the choice would depend on their compatibility with the current collectors and electrode materials [17].

2.3.2.2 Pseudocapacitors

In 1962 the term pseudocapacitance was coined to describe the reversible capacitance of the electrochemical ion adsorption on the electrode surface. The first hypothesis held mostly on the adsorption of ions upon the electrode surface, which is now known as adsorption capacitance, which takes place because of the monolayer of adsorbed ions upon the surface of the electrode (e.g., a platinum surface with a Hydrogen monolayer). Afterwards, when novel materials, e.g. hydrous RuO_2 -based compounds were developed, an extra type of pseudocapacitance called redox pseudocapacitance was introduced, which can be explained by the Faradaic processes in acidic media (e.g. H_2SO_4). Intercalation pseudocapacitance is another type caused by solid-solution electrochemical intercalation as seen in such materials as T-Nb_2O_5. These pseudocapacitive processes store charge by surface adsorption, surface redox reactions, and intercalation, with charge storing properties that are linearly (or approximately linearly) dependent on potential, as expected by thermodynamic concepts of pseudocapacitance. One should note that some materials, e.g., RuO_2 do not present a characteristic Faradaic signature in their electrochemical response. Since pseudocapacitive charge storage occurs through both Faradaic and capacitive processes, a brief review was given. **Figure 10** illustrates graphically these three kinds of pseudocapacitive processes [22].

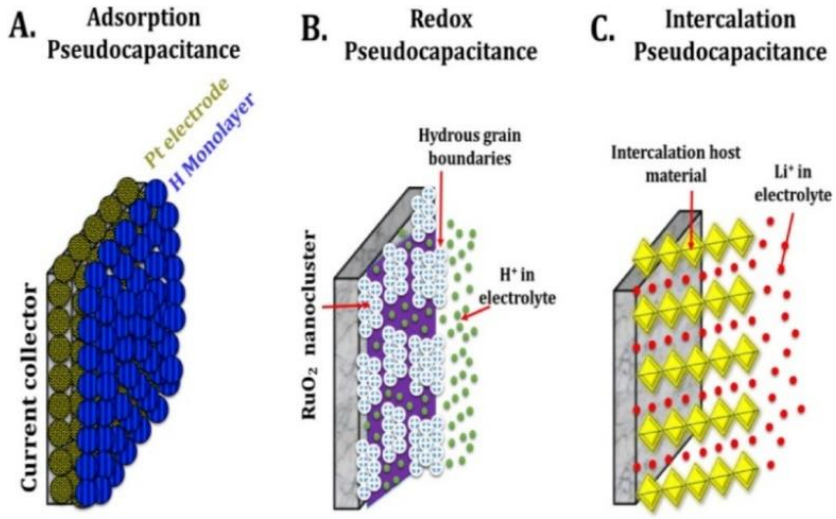

Figure 8: The three types of pseudocapacitive mechanisms: (a) Adsorption pseudocapacitance, (b) Redox pseudocapacitance, and (c) Intercalation pseudocapacitance [22].

2.3.2.3 Hybrid Capacitors

Hybrid supercapacitor is a unique type of asymmetric supercapacitor, in which an anode using the lithium/sodium ion battery technology and a capacitor like cathode is used in organic electrolytes. Combined with more than one energy storage mechanism, a hybrid supercapacitor allows taking advantage of the unique benefits of different mechanisms without their shortcomings. These are long

cycles life, low maintenance, high power density, quick charge, and more operational safety. The three-fold classification of hybrid supercapacitors is made in terms of the electrode configuration into composite, asymmetric and battery-type hybrid supercapacitors.

Composites of hybrid supercapacitor incorporate the characteristics of carbon and metal oxides in the same electrode demonstrating synergetic phenomenon in aspects of specific capacitance, cycling stability, and electrical conductivity. In such layout, carbon provided charge transport, whilst metal oxide can add to charge storage due to redox reactions, improving the specific capacitance and energy density. The nature of the carbon material, microporous, mesoporous or macroporous, used determines the degree of adsorption of ions on the carbon surface and hence the total conductivity of the composite. Nevertheless, the main drawback of the composite hybrid supercapacitors lies in the possible imbalance between redox reaction sites and the electrical conductivity.

The asymmetric hybrid supercapacitors have two unequal electrodes and are of two types. In the first one an activated carbon (AC)-based one of two symmetric supercapacitor electrodes is substituted by a battery-type electrode. The battery-type electrode can be made out of, for example lead dioxide (PbO_2), nickel oxyhydroxide (NiO (OH)), lithiated graphite ($Li_{11}C_6$), lithium titanate ($Li_4Ti_5O_{12}$) , transition metal oxides, electroactive polymers or lithium manganese oxide ($LiMn_2O_4$). In the second, one electrode is a carbon based material, works in capacitive mode, and is usually the negative electrode (cathode), the other is metal or metal oxide or conducting polymer and works by Faradaic charge storage and is usually the positive electrode (anode) [23].

2.3.3 Future Prospects

Supercapacitors are the indispensable energy storage and they are being used in areas such as hybrid cars, military, telecommunication equipments, uninterrupted power systems, cellular phones, lasers and solar energy storage. They have multiple benefits; such as great power density, and fast charging/ discharging. Nonetheless, there are two serious disadvantages as to cost and energy density that have to be overcome without sacrificing their long cycle life and outstanding rate capability.

With supercapacitors closing the gap of energy densities with the use of battery power, it can be expected that the automotive sector will embrace the use of supercapacitors as an alternative source of energy storage as an alternative to chemical batteries. Supercapacitors are currently used as the electrical analog of flywheels as elements of an energy storage system. They are mostly applicable in the energy storage and rapid charging. They are supposed to drive the medical devices e.g. pacemakers and knee implants with a continuous source of energy over prolonged cycles. They are also available in fast charging which makes them applicable in robotics and unmanned aerial vehicle. Supercapacitor-based

engine starter, charging station, or inclusion into renewable energy systems are other prospective applications.

An increase in the operating voltages can also work towards improving the efficiency of operation. The higher electromotive force of the cell cells permits specific-voltage systems to be reduced in numbers of cells in series (compared to low-voltages systems) and consequently, the requirements of external voltage-regulating circuits are minimized. Supercapacitors performance strongly depends on the material used as electrodes. Hence, there are rigorous studies conducted towards the development of efficient and cost-efficient energy storage methods. There is one potential solution, which exploits the use of waste carbon derived, as is the case with coal combustion, in the manufacture of the electrodes. Nonetheless, more work will be necessary to maximize storage methods and equipment compatibility before such materials can be brought to the marketplace in large amounts [17], [20].

2.4 Fuel Cells

2.4.1 Introduction

A fuel cell, an electrochemical cell, converts the chemical energy of a fuel (typically hydrogen) and an oxidant (typically oxygen) to electricity via a pair of redox reactions. Most fuel cells differ with most batteries in the fact that a fuel cell needs continuous input of fuel and oxygen (normally air) to maintain the chemical reaction process, in a battery the chemical energy is typically contained in material already in the battery. Fuel cells have the ability to generate electricity indefinitely with provision of fuel and oxygen [24,95].

2.4.2 Historical Background

In 1801, British chemist Humphry Davy (17781829) carried out electrolysis researches with the voltaic pile, and managed to break down some common compounds and identify some novel metals, such as sodium, potassium, and other alkali metals. His contribution formed the scientific basis of fuel cells that would be theorized in 1838 by German-Swiss chemist Christian Friedrich Schonbein.

Fuel cells that operate on an electrochemical reaction between hydrogen and oxygen were invented by Welsh chemical physicist William Robert Grove who in 1839 developed the earliest gas voltaic battery that could deliver an electric current. Later on, a British chemist, Ludwig Mond and Charles Langer presented coal as fuel to fuel cells and came up with the term cell fuel. This performance attained a current density of 20 A/m^2 at 0.73 V.

British engineer, Francis Bacon, improved the fuel cell concept in 1932 by Langer and Mond, and in 1958 its first alkaline fuel cell (AFC) was made. This was again used in the Apollo space craft. In 1959

Bacon achieved a demonstration of a 5 kW fuel cell about which he subsequently demonstrated a 15 kW fuel cell that was mounted on an agricultural tractor driven by Harry Ihrig.

In the late fifties NASA had started using fuel cells in space. The earliest Polymer Electrolyte Membrane Fuel Cell (PEMFC) was developed by Willard Thomas Grubb and Leonard Niedrach and was installed in NASA Gemini space program. Also, Apollo missions used the 1.5 kW AFC that gave astronauts electrical power and drinking water. Subsequently, the 12 kW AFC was incorporated unto the space shuttle program. The development of fuel cell as an application by electric cars has been increased since the 1990s and has continued increasing up to date when it was commercialized in 2007 [25,96].

2.4.3 Structure and principle of cell operation

A fuel cell is a combination of two electrodes, anode (positively charged) cathode (negatively charged) and an electrolyte. Its working principle is based on the oxidation of the fuel at the anode and the reduction of oxygen at the cathode, as depicted in **Figure 11** [26].

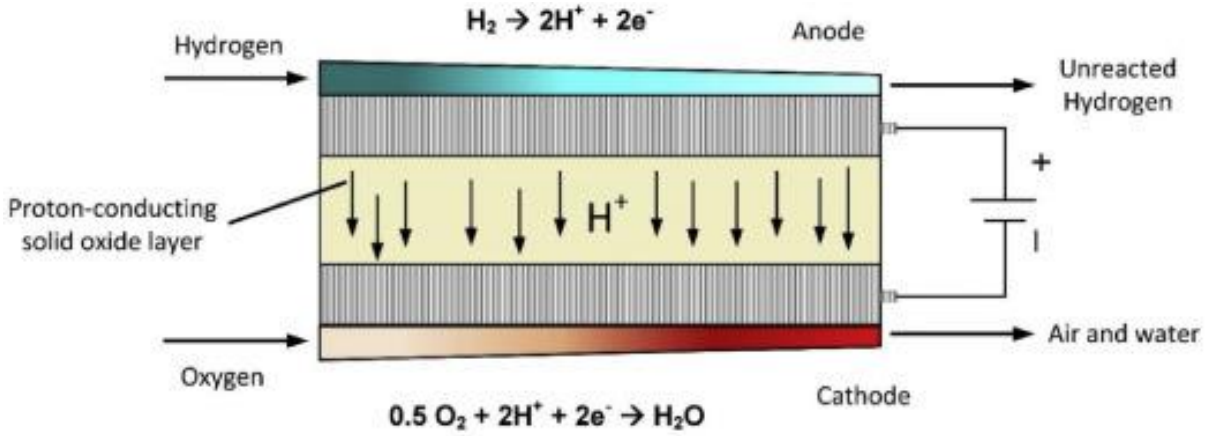

Figure 9: Schematic representation of a proton-conducting fuel cell showing the flow of hydrogen and oxygen, the separation of charges, and the electrochemical reactions at the electrodes [26].

Alkaline fuel cells qualified to be the earliest to be developed. They operate in the opposite direction to water electrolysis with hydrogen oxidized to produce water delivering electrical energy in the process.

Anode (Hydrogen electrode) $2H_2 \rightleftharpoons 4H^+ + 4e^-$ (2.5)

$4H^+ + 4OH^- \rightleftharpoons 4H_2O$ (2.6)

Cathode (Oxygen electrode) $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ (2.7)

Overall reaction: $2H_2 + O_2 \rightleftharpoons 2H_2O$ (2.8)

An oxygen molecule is attracted to the cathode surface and there it accepts four electrons and reacts with two water molecules, found in the electrolyte, to produce four hydroxyl ions. In the meantime, the anode is bonded by two molecules of hydrogen, which are oxidized and turned into hydrogen ions, which in turn, react with hydroxyl ions and form water and releasing four electrons [27,28,97].

2.4.4 Components of a fuel cell

Fuel cells are divided into a number of parts. Two electrodes (anode and cathode), the electrolyte, the gas diffusion layers and the bipolar plates and the last two will have to be there in both anode and cathode material. The role of its part is shown below (**Figure 12**) [29]:

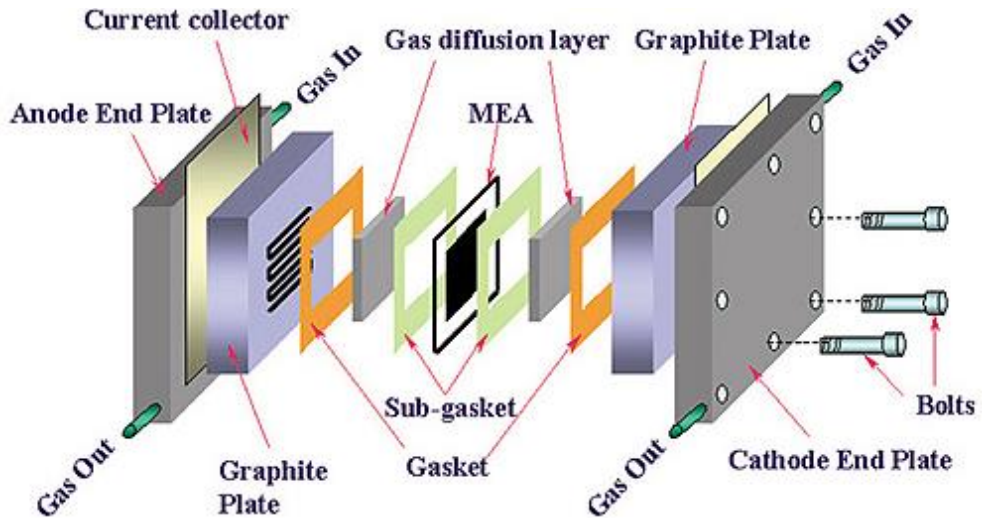

Figure 10: Typical Fuel cell exploded view with all the major components such as electrodes, membrane electrode assembly (MEA), gas diffusion layers, graphite plates, and bipolar end plates[29].

Electrolyte

The electrolyte plays a very important role in the formation of electrochemical cells to separate the cathode and the anode to avoid oxidation and reduction reaction in the same side. And it should also be impermeable to both reactants and electrons to avoid the unwanted transportation that would entail debilitating the integrity of the system. Nevertheless, to work effectively, the electrolyte should induce selective transport of sets of definite ionic entities and fit their transfer rendering them to go through and preserve the entire system stable.

Electrodes

Redox reactions take place in electrodes. They are usually made out of a porous medium, in the vast majority of cases graphite, in order to make them as porous as possible to increase surface area to volume ratio. To reduce activation energy of the reactions as well as to increase reaction kinetics, catalytic nanoparticles, i.e. catalysts, e.g. platinum or other metallic elements are deposited on the surface of carbon. Electrodes are however very sensitive to defects, which could be present in the reactants, as these impurities could cause electrode poisoning, thus, impair performance.

Gas Diffusion Layer (GDL)

Gas diffusion layers (GDLs) allow the extraction of byproducts of the electrochemical reaction and uniform delivery of fuel and oxidant to the electrodes. They are usually made of carbon paper or Teflon coated objects that make them more hydrophobic thus reducing water management problems and hence comprising the best performance of cells.

Bipolar plates

They separate fuel cell units, of a fuel call stack, between them. Particularly, to generate more electrical output power, fuel cell units are wired; the units are parallel or in series providing, respectively, a parallel and series fuel cell stack, along with that fashion. Besides, they direct electrons into an internal circuit. Bipolar plates are constructed of graphite, which gives them high electrical conductivity and avoids such phenomena as corrosion The first three components constitute Membrane Electrode Assembly (MEA) placed between the two plates: the collector and the separator plates. The collector plate holds the electrical collection and conduction path in stimulated electrical flow and the separator plate provides the isolation between neighboring fuel cells in one stack. In an array of fuel cells, the anode of a fuel cell is electrically coupled to the cathode of an adjacent fuel cell, in order to transfer charge efficiently. **Figure 13** displays the components of a Fuel Cell [29, 98, 99].

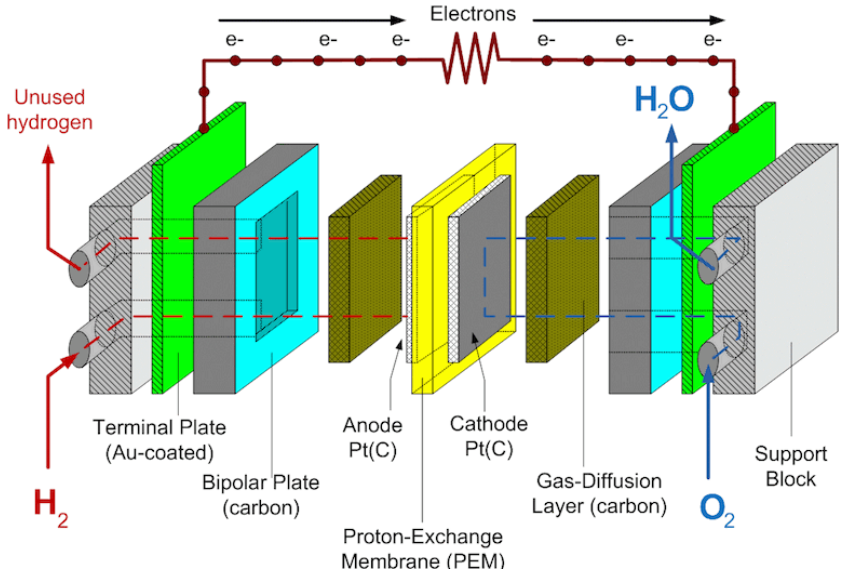

Figure 11: Components of the Fuel Cell [29]

2.4.5 Types of fuel cells

There are key factors on which fuel cells will be characterized: the type of electrolyte utilized. This division will dictate the type of elect-chemical reactions involved in the cell, type of catalysts needed, the temperature at which the cell functions, the fuel needed and others. These proprieties,

in their turn, influence the purposes, to which these cells are best applied. A number of fuel cells exist at the development stage with different advantages, shortcomings and prospective uses [32].

1. Proton-Exchange Membrane Fuel Cells (PEMFC).
2. Alkaline Fuel Cells (AFC)
3. Solid Oxide Fuel Cells (SOFC)
4. Carbonate melt Fuel Cells (MCFC)
5. Direct Methanol Fuel Cells (DMFC)
6. Phosphate Acid Fuel Cells (PAFC)

2.4.5.1 Proton-Exchange Membrane Fuel Cells (PEMFC)

A PEMFC is an electrochemical energy converter, which feeds the flow of hydrogen and oxygen via a membrane electrode assembly (MEA) to transform into water and generates electricity. Proton Exchange Membrane Fuel Cells (PEMFCs) have been found to have great potential especially in being an efficient Proton Exchange Membrane Fuel Cells (PEMFCs) are known to convert hydrogen and oxygen into electricity and some water by means of a membrane electrode assembly (MEA). PEMFCs are well known due to their high power density, low temperatures of operation and environmental purity, which makes them promising candidates as clean energy systems. At the center of their operation is solid polymer electrolyte membrane, usually a material based on perfluorosulfonic acids that allows selective transportation of protons whilst preventing electrons. The electrochemical reactions between oxygen reduction and hydrogen oxidation at the electrodes are assisted by the platinum catalysts hence resulting in high efficiency and fast start-up of the PEMFCs. **Figure 14** presents the major parts of a PEMFC [33,101].

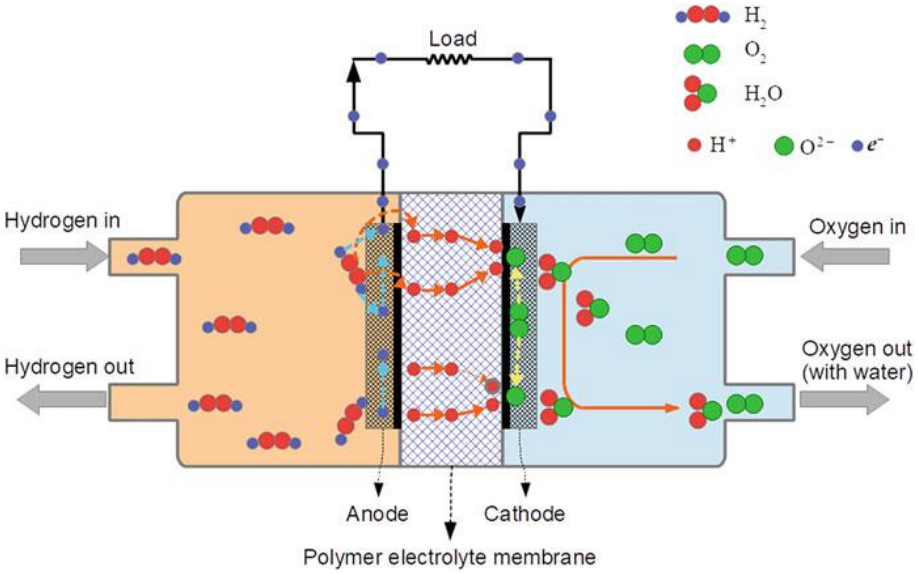

Figure 12: Schematic illustration of a PEMFC, indicating its main components and operating principle [33].

Nevertheless, large-scale commercialization is limited by several challenges notwithstanding these benefits. Due to platinum, which is very rare and expensive, the cost of the

system is very high. Also, degradation of catalysts, especially in the cathode, is an issue. The poor electrochemical environment leads to carbon corrosion of the carbon-supported Pt nanoparticles and to Pt dissolution. Themes to enhance catalyst stability are the chemical treatment on carbon carriers, structural integrity and creation of catalysts possessing uniform and less Pt loading [24], [34]. The prevention of such degradation is one of the most important issues when it comes to extending the life and preserving the funnel of the fuel cells.

The design of bipolar plates can also be viewed as another area of concern since the plates act as current collectors and distributors of fluids. Conventional graphite plates are breakable and expensive with metallic ones being subject to corrosion. An acceptable solution is a polymer-carbon fiber composite, carbon black-reinforced polymer composites, and graphene-reinforced polymer. These elements require material innovation to achieve cost and durability targets that are required to deploy in the commercial area.

The objective of attaining competitive power density and system cost depends on the optimization of various, and inter-dependent, factors: the electrochemical activity of the gas diffusion electrodes, the membrane structure and catalyst layer structure and the reduction of mass transport losses. The quality of fuels is a critical factor as well because hydrogen fuel containing a trace of carbon monoxide can poison the platinum catalyst and perform much worse [35, 36]. In summary, the development of PEMFC technology lies in the efficiency of materials, integration of the system, and strong design solutions that are used to cut down on cost without compromising on the performance.

2.4.5.2 Alkaline Fuel Cells

Alkaline Fuel Cell (AFC) became the first viable method of fuel cells implementation in practice showing the existence of a possibility to use hydrogen in the generation of electricity. First designed to support space missions, AFCs provide high efficiency to convert the energy, reliability of operations as well as a design without moving parts. These fuel cells are operated using potassium hydroxide (KOH) in aqueous form as an electrolyte, which usually has an approximate concentration of 30 per cent. The general chemical equations which control the functioning of AFC are as follows [37, 102]:

Anode reaction $2H_2 + 4OH^- \rightarrow 4H_20 + 4e^-$ (2.9)

Cathode reaction $O_2 + 2H_20 + 4e^- \rightarrow 4OH^-$ (2.10)

Overall cell reaction $2H_2 + O_2 \rightarrow 2H_20$ + electric energy + heat (2.11)

This inherently produced by-product water and heat, produced in the course of the Alkaline Fuel Cell (AFC) operation, should be effectively flushed out in order to allow optimum performance. This is normally done through recirculation of the electrolyte which also functions as a coolant with unnecessary water being eliminated via evaporation. The recirculating electrolyte AFC is shown schematically in **Figure 15** [38].

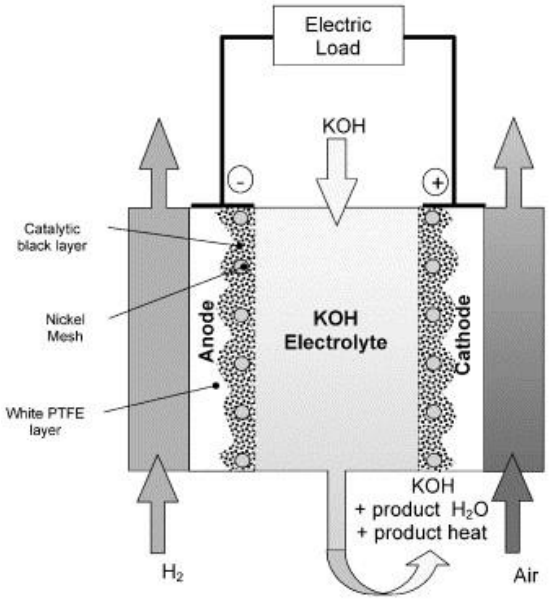

Figure 13: Schematic representation of an Alkaline Fuel Cell (AFC) illustrating its structure and operating principle [38]

AFCs operate with pure hydrogen and oxygen at temperatures of 150–200 °C. In an Alkaline Fuel Cell, hydroxyl ions (OH^-) are transported between the cathode and the anode where they combine with hydrogen and form water and give out electrons. The electrons produced at the anode serve to drive an external circuitry and then they are released into the cathode where they combine with oxygen in the presence of water to release more OH - ions. Efficiencies of up to 70% can be obtained by AFCs, and they were used in the early space missions because they do have the ability to generate potable water as a by-product.

The AFCs, however, demand extremely clean hydrogen as well as oxygen to work effectively. Carbon oxide gases (CO_x) in the reactant gases can cause undesirable chemical interactions with potassium hydroxide (KOH) resulting in solid carbonates which can cause poor performance of the cells. This inhibits production of OH 1 ions hence lowering the ionic conductivity of the solution of the electrolyte. To counter this problem, AFCs normally features a known as a scrubber system that is meant to reduce the content of CO_x in the supply of air and fuel.

The other issue in fuel cell development is the gap in the large dosage of platinum (Pt) that catalyzes the slow oxygen reduction reaction (ORR). To minimize the Pt loading, it is possible to pursue the maximization in the amount of catalytically active surface area and increase the catalytic activity, to optimize the configuration of the electrodes, or use another type of catalyst instead of platinum namely Pt-alloy.

2.4.5.3 Solid Oxide Fuel Cells (SOFC)

Solid Oxide Fuel Cells (SOFCs) are high-temperatures electrochemical devices, which allow direct conversion of chemical energy into electricity. The SOFCs, which are operated above 1000 K in temperature, are a solid electrolyte, which comprises of an oxygen ion (O^{2-}) conductor between two electrodes that act as the cathode and the anode. Able to operate within a wide variety of fuel sources due to their high operating temperature, they are also electrically efficient over conventional energy conversion systems [39,103].

SOFC Small stationary units of power 1 kW to 100 kW can attain electrical net efficiency of up to 50 percent and overall system efficiency of about 70890 percent, when including thermal power. Smaller pressurized SOFC/gas turbine (SOFC/GT) systems in the megawatt scale should achieve 70 per cent electrical net efficiency. SOFCs are also being considered in recent years in mobile application in addition to their already existing uses in stationary power production, including small-scale combined heat and power (CHP) systems to dwellings, medium-scale cogeneration systems and large-scale SOFC/GT power plants.

The expansion into the automobiles (e.g., Honda Clarity), trucks (e.g., BMW/Delphi), and military markets through development of SOFC based auxiliary power units (APUs) and the growth in lower-cost high power-density SOFC core modules done with programs such as the Solid-state Energy Conversion Alliance (SECA) has increased the application range of SOFC. Performance of SOFC materials and components have also grown under these developments.

Other important SOFC system specifications besides efficiency and power density would be long-term stability, thermal cycling performance, short start time and the capability to use a wide versatile fuel supply with high fuel utilization. An overview of the estimates of the performance targets of both stationary and moving SOFC systems is listed in Table 7. Although the targets of stationary applications would be met even at a lower operating temperature (600-800^{o}C), a deeper enhancement in cell/stack properties, especially long-term stability and thermal cycling stability, multi-fuel operation and cost reduction are still essential to the permeation of the SOFC technology in the near future. [40,104].

Table 7. Target areas for mobile and stationary SOFC-systems [40].

Application	Stationary	Mobile
Operation Temperature	700°C-1000°C	500-700°C
Power Density	>0.25 W/cm^2	>1 W/cm^2
Lifetime	>40000 h	>2000 h
Degradation rate	< 1μV/h	<10μV/h
Fuel utilization	>80%	>80%
Thermal Cycles	>100	>5000
Heating rates	>1 K/min	>100 K/min
Fuel	Natural gas, fuel oil	Gasoline, diesel
Oxidant	Air	Air
System costs	<$500/kW	<$100/kW

2.4.5.4 Molten Carbonate Fuel Cell (MCFC)

In 1960 G.H.J. Broers and J.A.A. Ketelaar announced the invention of a high-temperature fuel cell that had operated successfully over six months. Its electrolyte involved a solution of alkali metal carbonates held in disc of magnesium oxide. This cell operated at temperatures well beyond that of the carbonates melting point, and the cell used carbonate ions (CO_3^{2-}) as the principal charge carriers of the molten electrolyte. Successes in the materials used in the manufacture of the molten carbonated fuel cells (MCFCs) have been realized over the last forty years, but the basic working principle has been kept. This is portrayed schematically in **Figure 16** which also indicates one of the features that help set this kind of a fuel cell apart as compared to all the other fuel cells, i.e. that there is a net flow of CO_2 towards the anode of the cell through the electrolyte where it originated on the cathode side of the cell. Figure 16 indicates the working principle of the molten carbonate fuel cell and depicts reactions that occur at the anode and the cathode when hydrogen is used as the fuel [41][42].

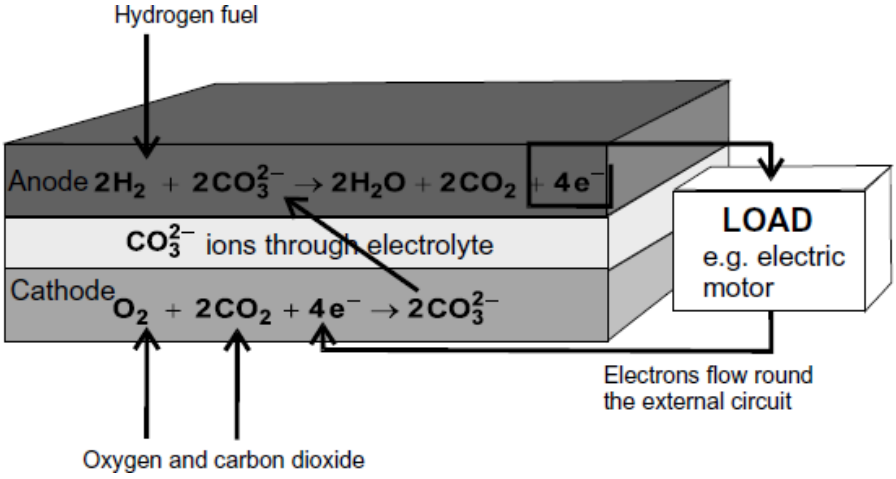

Figure 14: Operating principle of the molten carbonate fuel cell [41].

It is of great interest to compare the features of the MCFC with the features of other forms of Fuel Cells. **Figure 17** shows the polarization characteristics of representative fuel cells of different types of hydrogen oxygen, average of the characteristics of individual-cell from models of the experiment, the most widely used operating conditions of fuel cells of each type. The phenomenon that is peculiar to the voltage-current density curve in molten carbonate fuel cells (MCFCs) is its linear nature. Although linearity of polarization dependence may be often blamed to the ohmic drop present across the cell, the reason of this phenomenon in MCFCs is not fully understood. Of all the hydrogen-oxygen fuel cells screened, MCFC has the steepest polarisation curve, which means that it has the lowest current densities at high power range and high efficiency of cell over the small range of low current densities, at or below 150mA/cm^2 [43,105].

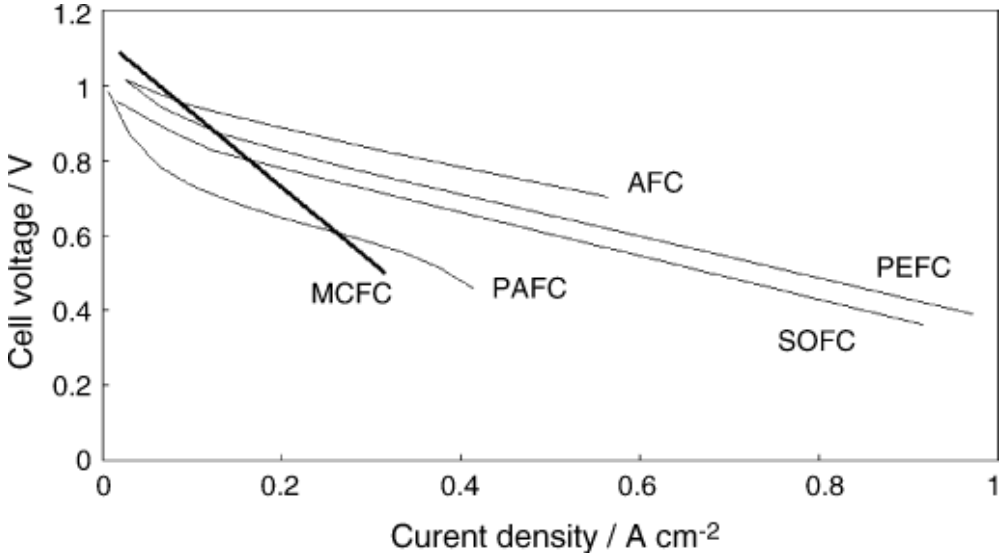

Figure 15: Polarization curves for various hydrogen–oxygen fuel cells [43].

2.4.5.5 Direct Methanol Fuel Cell (DMFC)

The direct methanol fuel cell (DMFC) allows the direct conversion of the chemical energy contained in the liquid methanol fuel to electrical energy, water and carbon dioxide being by-products. Compared to the more common hydrogen fueled polymer electrolyte membrane fuel cells (H_2 -PEMFCs), DMFCs have a number of interesting benefits and a good number of challenges. Direct methanol fuel cell is in the family of low temperature fuel cell and utilizes methanol as a fuel. The electrode is a polymer membrane electrode and bears similarities with that of a PEMFC. A key part of a direct methanol fuel cell (DMFC) is the membrane electrode assembly (also called MEA), whose anode and cathode catalyst electrodes are in direct contact with one side of the polymer electrolyte membrane (PEM) and the other, respectively.

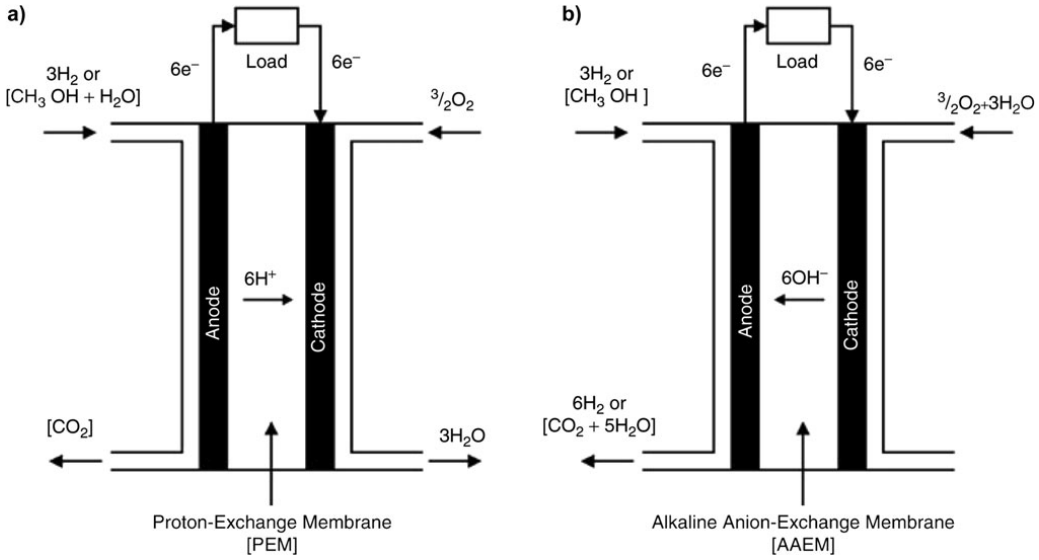

Figure 16: (a) Principles involved in the operation of acid and (b) alkaline based DMFCs [44]

DMFCs may have Proton Exchange Membrane (PEM) in an acidic or Anion Exchange Membrane (AEM) in an alkaline operation, depending upon the system design. Traditionally, anode has PtRu on carbon or un-supported PtRu black catalyst while the cathode has Pt or Pt black carbon supported catalyst. Gas diffusion layers (GDLs) are used in close contact to the catalyst layers to allow maximum reactants distribution, to improve current collection, and protection of the catalyst layers structure. This is given in **Figure 18**, a copy of the basic operating principles of both acid and alkaline based DMFCs [44,106].

The overall reaction process that occurs in an acid-based DMFC is shown below [45]:

Anode reaction $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (2.12)

Cathode reaction $\left(\frac{3}{2}\right) O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (2.13)

Overall reaction $CH_3OH + \left(\frac{3}{2}\right) O_2 \rightarrow CO_2 + 2H_2O$ (2.14)

2.4.5.6 Phosphoric Acid Fuel Cell (PAFC)

Most common fuel cell and the best documented is the phosphoric acid fuel cell (PAFC). Over 500 PAFC power plants have been set up in over 20 countries around the globe since the 1970s. Each time a new product was to be released, the number of sold units increased and the power rating per unit too. The schematic diagram of the working position of a phosphoric acid fuel cell (PAFC) is in **Figure 19**. Hydrogen or hydrogen rich gas mixture is fed at the anode and chemical reaction at the anode is as given below:

$$H_2 \rightarrow 2H^+ + 2e^- \quad (2.15)$$

The most effective electrolyte consists of phosphoric acid (H_3PO_4) serving as the proton conductor which allows the movement of protons between the anode and the cathode. At the same time

electrons flow in an outside circuit creating an electric current. At the cathode, the protons in the electrolyte plus the oxygen in the air that is introduced and the (free) electrons coming back through the outside circuit combine to form oxygen molecules [46].

$$\left(\frac{1}{2}\right) O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2.16)$$

The overall reaction is:

$$H_2 + (\frac{1}{2})O_2 \rightarrow H_2O \quad (2.17)$$

A schematic representation of the PAFC operating configuration is depicted in **Figure 19**

In phosphoric acid fuel cells (PAFCs) the electrolyte used is phosphoric acid (H_3PO_4) because it offers good thermal, chemical and electrochemical stability. Moreover, H_3PO_4 is very tolerant to carbon dioxide (CO_2) that is normally found in blends of reformate gas. early versions of PAFC systems diluted the acid so as to prevent corrosion of the materials, but in the present-day systems pure H_3PO_4 is used. Because there may be some liquid loss as it runs it will need either regular re-charging of the electrolyte or there has to be an excess supply added before it is used. An effective way of addressing this challenge is through incorporation of an electrolyte reservoir plate (ERP) as this will provide enough supply of electrolyte so that the cell can last more than 40,000 hours [47].

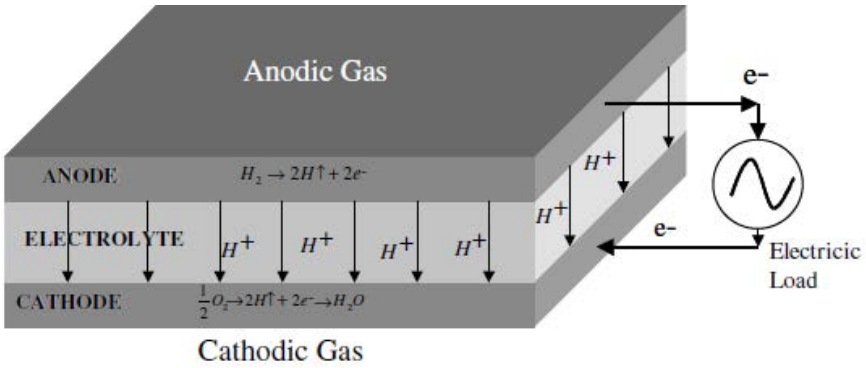

Figure 17: Schematic representation of a phosphoric acid fuel cell [47].

2.5 Electrolyzers

Electrolyzers are electrochemical apparatus which consume electricity to separate water into oxygen and hydrogen where the individual hydrogen output is significant and oxygen a by-product. Compared to other methods of hydrogen production, the production of high-purity hydrogen with an electrolyzer is commercially accessible and requires neither carbon-bearing raw materials nor the emission of carbon dioxide. However, they have not been widely adopted despite their development more than a hundred years ago. This is mainly because, compared to the other methods of hydrogen production, it is more affordable and also because no one, especially in the

industry and among the masses, seems to know the extent to which the electrolyzer is environmental friendly in the production of hydrogen gas [107].

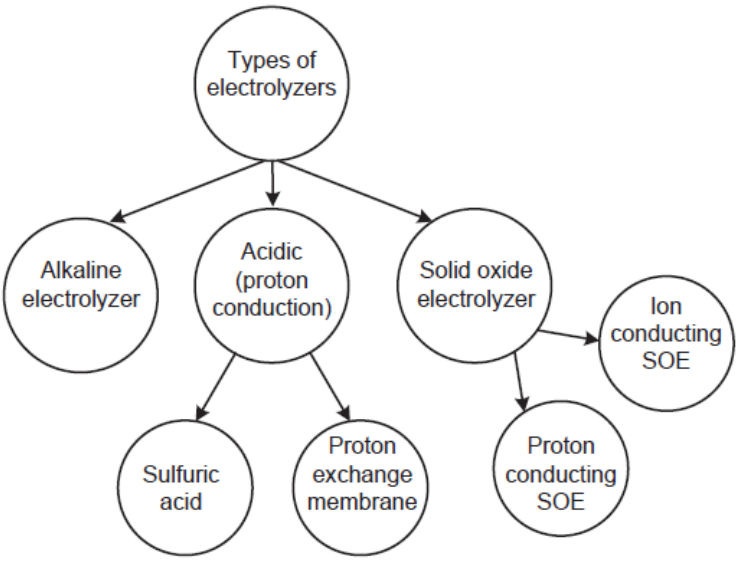

Figure 18:Classification of water electrolyzers based on the electrolyte type [90].

The different types of electrolyzers have been classified based on various attributes such as the type or composition of the electrolyte used in it, the phase of electrolyte used and the temperature as well as the pressure at which they are operated. Nevertheless, the most popular classification of electrolyzers can be made following the type of electrolyte, but it can also defer according to the operating temperature. Based on the type of electrolyte used, there are three major groups of electrolyzers namely alkaline electrolyzers, proton exchange membrane electrolyzers and solid oxide electrolyzers. This classification (including its sub-categories) is shown in figure 20. Operation temperature-wise, electrolyzers fall into low-temperature electrolyzers typically below 80 ^{o}C and high-temperature electrolyzers above 500 ^{o}C degrees. Also, the situation in terms of the state of the electrolyte is also taken into consideration as there are two basic categories in respect to which electrolytes can exist in a liquid form: acidic, alkaline solutions, or in a solid form: ceramic materials like yttria-stabilized zirconia [90].

2.5.1 Selection Criteria of Electrolyzers

The choice of suitable electrolyzer for making hydrogen is a complex interdependent factor that involves technical performance, economies, environmental nature and also regulatory positioning. The first is the requirement in defining the hydrogen end-use requirements, such as the purity, rates of production, and the ability to respond to the loads. In some industrial processes such as ammonia production or steelmaking, the quality of the hydrogen matters, as it must be high

purity, but in others, such as energy storage or mobility, flexibility and dynamic operation might be the need.

Temperature and pressure are the other operating parameters that determine electrolyzer performance. Alkaline and PEM electrolyzers are low temperature and are suitable to distributed systems or smaller systems. Conversely, high-temperature solid oxide electrolyser (SOE) works best by taking place at high temperatures and are helpful in scenarios where there is nearby waste heat which offers an elevated level of efficiency. Nevertheless, the SOEs require material specifications and greater maintenance of thermal loads. The durability and the lifecycle reliability of systems require matching of electrolyzer specifications to the operation environment.

One of the largest factors in the selection of electrolyzers is cost. Included in capital costs is not only the electrolyzer stack itself, but also auxiliary systems whereas operating costs are mainly determined by electricity consumption and maintenance. The economic sustainability, especially when it comes to incorporating intermittent renewable sources, closely relates to efficiency and flexibility to the variable power inputs. The life cycle cost analysis serves to give in depth understanding of long-term viability, including service lives and component swap. In addition, the region-specific policies and fiscal support can redistribute cost, which impacts technology adoption practice.

The environmental factors are gaining more prominence, particularly, as the production of hydrogen is becoming aligned with the decarbonization. Low-emission electrolysis of renewable electricity generates the so-called green hydrogen whereas the use of fossil-based grids might undermine the environmental advantage despite a high system efficiency. Also, the usage of water and possible wastes water difficulties should be evaluated, especially in the area of water deficiency. Sustainability alignment requires a full analysis of direct and indirect emissions.

Deployment decisions are further determined by compatibility of the type of electrolyzer and available local energy resources. Low-temperature systems might be most advantageous in locations where low-cost electricity is available, but in locations with access to industrial heat, high-temperature works can use such heat to provide added efficiency. Both the ability to run at fluctuating electricity prices and the flexibility of electrolyzers in modern energy systems is somewhat improved. There is also the technological maturity. Alkaline systems have been known and widely accessible but PEM units, though more recent, have their advantages which include compactness and ease of start-up. SOEs are still under development and render potential efficiency under a high-temperature environment.

Vendor reliability, supplies of parts and the definition of maintenance procedures is important, particularly on time sensitive or technically limited projects. Lastly, policy climate such as carbon prices, renewable requirements, as well as subsidy systems has a profound influence on the technology choice. Favorable regulation can cause investment to skew in favour of particular types of electrolyzers which highlight the need to ensure that policy sceneries be aligned with technical ones. The mutual interaction of such criteria requires a comprehensive analysis to make sure that the choice of technology satisfies the both current short-term objectives of operations and more strategic objectives pertaining to cost-efficiency, resiliency and sustainability [90,91,108].

2.5.2 Alkaline Electrolyzers

Hydrogen can be produced by alkaline water electrolysis, which is the most developed method and commercially applied decades of time in industry. It works with concentrated solution of Potassium hydroxide (20-30wt%) as an electrolyte and has a good compromise between conductivity and material compatibility particularly with steel (especially stainless steel) components. The standard operating conditions of 70-100 ^{o}C and up to 30 bars offer efficient kinetics with the minimum risk of material degradation.

Electrolyzer stack is a combination of several cells along with diaphragms which permit the movement of ions without mixing up of gases. There are two stack configurations, namely, monopolar and bipolar. Monopolar, less compact, is easier to use with large systems, whereas they are more robust. Bipolar stacks are more efficient and compact on the grounds of fewer current paths, but entails issues of parasitic currents and local corrosion, more rigorous engineering is necessitated, therefore.

Developments Policies of alkaline electrolyzer design have concentrated on enhanced efficiency and diminished internal resistance. The zero-gap arrangements reduce the distance between the electrodes and diaphragm, reducing ohmic losses. To increase the ionic conductivity, the materials used in the construction of the diaphragm are low-resistivity high-performance. To increase the performance of the electrolyte further, some systems use a higher temperature up to 160 ^{o}C but this demand a higher material durability to endure more thermal and chemical loads.

Innovation of catalysts has also played a decisive role. Conventional nickel-based electrodes have been enhanced in terms of mixed-metal oxides and developed surfaces. There is enhanced oxygen evolution by the use of Cobalt oxide anodes and hydrogen production by the use of Raney nickel cathodes, thereby increasing cell voltage efficiency and reducing energy usage.

The current commercial-scale alkaline electrolyzers reach the efficiency of 43-69% (HHV basis) depending on design and operational conditions. Capital costs of 600 to 2600/kW are quoted, and average of 1100/kW. The costs will however go down to an estimated range of 400-900euros/kW due to the projected technological advancements and economies of scale. These systems are suitable in centralized production of hydrogen and are scalable and have lower initiation cost.

Alkaline systems have also long life and are of great service due to a lot of industrial experiences and maintenance procedures. The popular saturation and availability of vendors and their technological maturity make the deployment less risky, especially in large-scale application. Nevertheless, major shortcomings are seen. Alkaline electrolyzers run at lower current densities compared to proton exchange membrane (PEM) electrolysers and this leads to greater cell area and system footprint requirements. Also, the corrosive character of the electrolyte implies the need to select the material carefully, as well as increased maintenance requirements in the rough environment. The other challenge is operational flexibility. Alkaline systems have poor cold-start times, and little dynamic response which does not make them suitable to rapid swing electricity supply. They can work at 20 to 150 percent of rated output, but this might faster the degradation of components and reduce system life. This limits their flexibility in high variability renewable-integrated energy systems.

To overcome these problems research aims at more durable diaphragm, better catalyst coating, and better integration of the system. Special materials should be able to withstand elevated temperatures and interactions with chemicals, whereas smart thermal and electrical control solutions improve sensitivity and efficiency. These trends will help to make alkaline performance more comparable to more maneuverable systems such as PEM electrolyzers, making them more versatile. Although alternative methods have been developing, the alkaline electrolyzers are still at the core of hydrogen production, particularly, in scenarios that require robust, large scale- and cost-efficient mechanisms. Their relevance will be maintained as they continue to innovate their materials and design as there is an increase in global demand in low-carbon hydrogen [91,109].

2.5.3 Proton Exchange Membrane Electrolyzers

Proton exchange membrane (PEM) electrolyzers are a very efficient and compact technology of hydrogen production, which involves the separation of hydrogen and oxygen in the water by the use of redox reactions across a solid polymer membrane. The water is oxidized at the anode to yield oxygen, electrons and protons. The protons enter the external circuit by passing

through the membrane and the electrons through it to be recombined to form hydrogen at the cathode. Such architecture allows the spatial separation of the gases which can enhance system safety, and electrochemical efficiency. It is around the membrane electrode assembly (MEA), which takes central position in PEM systems, a perfluorosulfonic acid membrane, sandwiched between catalyst and gas diffusion layers and supported by bipolar plates that control current and fluid movement.

Noble catalysts of like platinum in the evolution of hydrogen and either iridium or ruthenium oxide in the evolution of oxygen enable the hydrogen to have noble ion kinetics and low overpotentials in the acidic cell. The materials, however, constitute a big part of the capital costs. The mitigation of this is made by preparing nanostructured catalysts and minimization of noble metal loadings. In contrast to alkaline electrolyzers, PEM systems have the potential to permit high current densities and consequently small footprints and rapid production of hydrogen per unit area. The solid polymer membrane also removes the caustic electrolytes requirement making the membrane design simpler to allow greater safety, corrosion resistance and environmental compatibility.

PEM electrolyzers are especially suitable to be coupled with fluctuating sources of renewable energy since they respond fast to changes of power. Their capacity to respond promptly, as well as rapidly to start or stop, qualifies them with grid-balancing applications. The use of high pressure in operation increases the integration also given the fact that there is minimal or no compression of the gas after undergoing electrolysis. Although these benefits exist, PEM systems cost and lifespan is still a great area of concern. The membrane may also chemically erode with time, particularly under conditions of extreme oxidative load causing a loss of efficiencies and an increased amount of maintenance. Also, crossover of the gases, especially at high pressures, is problematic in terms of purity and safety and means that downstream purification and membrane engineering is required.

Enhancement of membrane and electrode technology has seen elevation of performance and durability. Direct deposition assembly is carried out to create catalyst-coated membranes primarily optimized in terms of ion transport and structural integrity. Graded porosity and ionomer distribution are some innovative inventions that enhance catalytic activity, and mechanical stability. On the same note, gas diffusion layers (GDLs) are designed to ensure that reactants and products flows are controlled efficiently. Carbon GDLs are flexible and provide high conductivity on the cathode and on the anode, titanium-based materials resist the oxidative

degradation. The architecture and material of the layers have a vital influence on the cost, duration and performance of systems.

Bipolar plates are to aid in effective flow of fluid across the MEA and uniformity in the current distribution. They are normally titanium or stainless steel coated plates providing a compromise between electrical conductivity, structural integrity, and corrosion resistance. Nonetheless, the price factor and the intricacy of fabrication makes entering titanium expensive. The search is on to develop cost-effective ways of coating and enhancing manufacturing processes in order to keep the benefits of titanium without going to an expanse. PEM electrolyzers have gained popularity in more advanced hydrogen systems, particularly those integrating renewable energy or limited in space, due to their high efficiency, small size and their rapid dynamic response, despite the current need to optimize costs and materials [93,111].

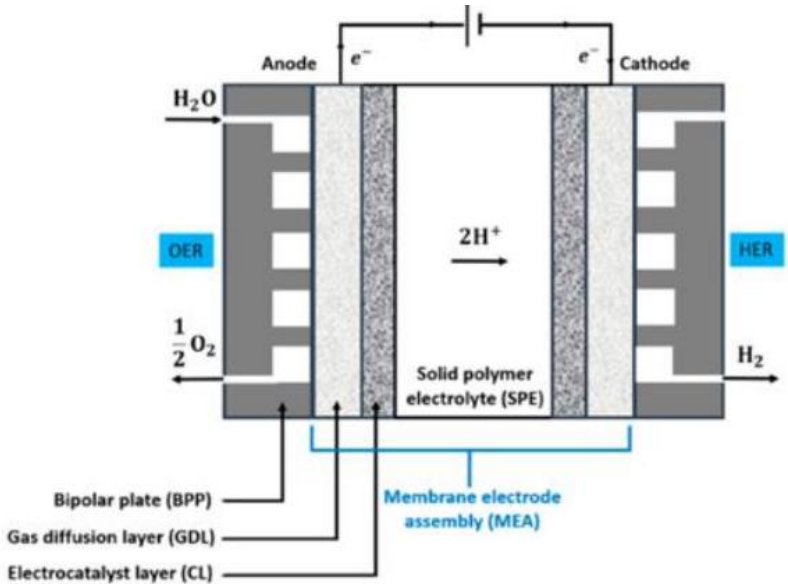

Figure 19: Schematic of the PEM electrolyzer showing its main components [93].

2.5.4 Solid-Oxide Electrolyzers

Solid oxide electrolyzers (SOEs) are type of high-temperature electrochemical cell which can be used to convert steam into hydrogen and oxygen with operating temperatures of 700-1000 ^oC. Such conditions lead to the reduction of electricity energy need by using thermal energy resulting in high thermodynamic efficiency. And central to the SOE is dense electrolyte material which is commonly composed of yttria-stabilized zirconia (YSZ) that makes the movement of oxygen ions possible but electron movement impossible, as shown in **Figure 22**. Doping zirconia with Yttria makes its high-temperature phase more stable and ionic conductivity is increased without going through the damaging phase transitions during heating. The steam is passed through the porous cathode which is reduced at

the triple-phase boundaries to give hydrogen gas and oxygen ions. The latter then diffuse into the electrolyte, and are oxidized at the anode to produce molecular oxygen as a reaction by product.

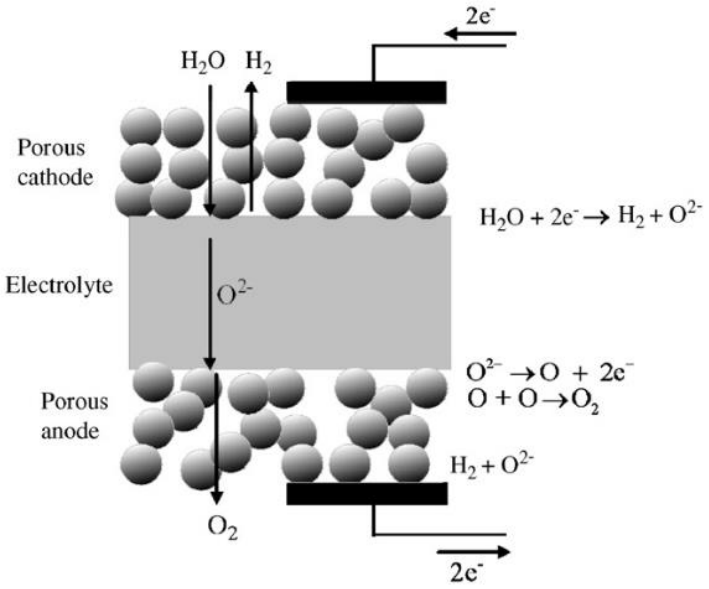

Figure 20: Schematics of SOEC hydrogen production [94].

The cathode is usually a nickel-based cermet that combines the electronic conductivity of nickel with YSZ that has ion conducting characteristics. The structure increases the active site of reaction and enhances electrochemical activity at very low oxygen contents. In the anode part, where the oxidative conditions are ensured mixed oxides such as lanthanum strontium manganate is good because of the chemical stability and the electrical conductivity. Compared with noble metals, which are effective but too expensive and volatile because it is difficult to handle the materials at high temperatures, these perovskite materials are able to sustain harsher chemical and thermal conditions that exist during the operation of SOE. The inspired difference is one of the greatest strengths of an SOE such that they can fit industrial environments which, by product others use, can provide excess heat as, in the case of steel manufacturers or chemical factories, to employ hybrid methods of energy provision. Also, under high temperatures overpotentials are minimized which is an energy save. The SOEs also form steam/ CO_2 co-electrolysis, which produces syngas for synthetic fuel formation, thereby uniquely allowing multiple decarbonization pathways.

The carbon intensity of hydrogen and syngas can be reduced, and the productions of both can be made more sustainable by integration with renewable non-fossil heat sources, such as concentrated solar thermal power. But SOEs experience significant challenges. The high temperatures place mechanical stress as a result of the differentiation in thermal expansion and impositions strong chemical stability to all cell compounds. Both the electrolyte and electrodes can be degraded after long term operation in the reactive atmosphere, leading to lowering the system

durability and raising maintenance expenses. Investigations are being directed at the improvement of the materials by the use of dopants and new ceramic composites which are stable at lower temperatures, and more refined electrode microstructures are being directed towards increase in longevity and catalytic activities.

Economically, the SOEs have huge capital expenses because of the demand of specialized materials and exact manufacturing and these are built with better productivity than the SOEs and also the high efficiency of using the waste heat of SOE provides benefits in terms of cost of operation. They will be deployed based on tradeoffs among performance of materials used, durability of the system and cost-effectiveness. With industries demanding low emission solutions, the SOEs are well placed to provide a critical role in the hydrogen economy when thermal integration and high efficiency production of hydrogen or syngas is required [94,112].

Chapter 3 Hydrogen Production

3.1 Background

The main reason why the hydrogen technology evolved is climate change and depletion of fossil fuel. Both natural gas and coal require conventional energy sources to come up with hydrogen, but it can be generated through nuclear power, as well as via biomass, solar and wind energy alongside alternative sources of energy. The persisting use of fossil fuels has caused introduction of the greenhouse gas (GHG) into the atmosphere, which is a major threat to the global environment occasioned by climate change. Also, increased energy demand across the globe has been contributing to the rising costs of conventional fuel as the fossil fuel resources are getting depleted and economies that are dependent on importation are becoming relatively more susceptible. Future energy resources have to be both renewable and carbon-free so they could deal with the problem of climate change in the long term and help cut down on the amount of oil imports. Hydrogen is not easily available in nature like fossil fuel. It can however be generated using most of the primary sources of energy and can be utilized as a fuel when burned directly in an internal combustion engine or in a fuel cell, the resulting emission being water. Since it is the only fuel that is non-carbon emitting and the one that has the greatest energy content of all the known fuels, hydrogen is commonly referred to as a clean energy source as compared to fossil fuels. The other major asset of this is that hydrogen can be transported safely to the domestic users through many traditional means in case the proper storage technologies are gained. In stationary fuel cells it can be stored either as compressed gas, cryogenic liquid or solid hydride [48].

- It is possible to get hydrogen using renewable methods and lessen the reliance upon fossil fuels as well as abridging the ecological interaction of energy generation.
- Hydrogen can be possibly simpler to store than electricity, thus enabling the production of excess energy to be stored as hydrogen and dispensable when demand arises, hence increasing energy efficiency.
- Hydrogen can be injected either into the natural gas network that is currently in place, or it can be transformed into methane (CH_4), which is a process of carting out CO_2 into a chemical procedure to methanate it, in this way corresponding with the idea of power-to-gas storage.

Hydrogen is potentially made out of a range of energy sources, through an assortment of process technologies. These energy resource alternatives are fossil, nuclear as well as renewables. The most important industrial process (75 percent of world production) used to produce hydrogen is in large-scale steam reforming of natural gas because the associated costs are rather low

(approximately 1 $ / kg of hydrogen). Nevertheless, a possible clean-energy economy future depends upon the development of clean, sustainable, and inexpensive processes of production of hydrogen provided that the identification resources-based ones currently available are increasingly impeded by law. There are three categories of Hydrogen production technologies [49].

- thermal processes
- electrolytic processes
- photolytic processes.

The heat energy is used in different sources which include natural gas coal or biomass to release hydrogen content in their molecules during thermal processes. We can also convert feedstocks to hydrogen using thermochemical processes; this is done by heating materials containing elements of hydrogen using chemical reactions fueled by the heat, these processes include:

- Reforming of natural gas
- Gasification of coal
- Gasification of biomass
- Reforming of renewable liquid fuels (derived liquid reforming)
- High-temperature water splitting (thermochemical production through heat-driven water splitting reactions)

Figure 23 indicates the share of energy provision in the world. Fossil fuels have an enormous division of 81.2% in energy provision all over the world preceded by 13.8 percent share of renewable sources of energy (9.3 percent of biofuels, 2.0 percent of wind/solar etc. and 2.5 percent of hydro) and 4.8 percent nuclear energy.

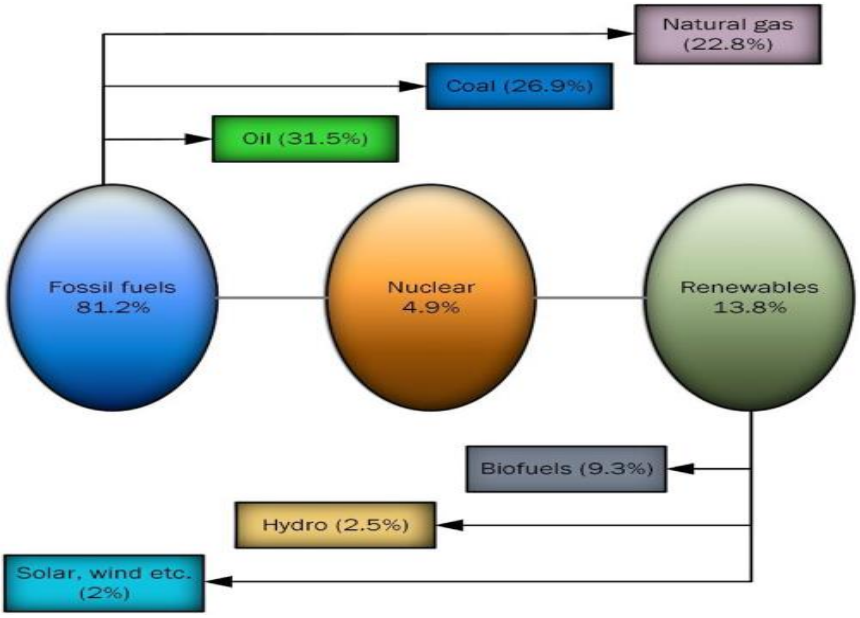

Figure 21: Share of global energy supply [50].

The hydrogen fuel is becoming an issue of world attention due to several reasons and some of them are listed below:

- There are numerous sources of energy which can be used to generate hydrogen.
- It is among the cleanest fuels because the only byproduct of their consumption in fuel cells or combustion activities is water.
- Hydrogen can fulfil many kinds of energy requirements and can be employed in fuel cell vehicles, domestic use, energy storage and in combined heat and power (CHP).
- It has a vital part to play in decarbonizing shipping, where off-grid resources such as offshore wind may be deployed to generate clean shipping fuels such as hydrogen and ammonia.
- Hydrogen may act as an energy carrier as well as a multi-purpose storage.
- Unlike other carbon-based fuels e.g. methanol, dimethyl ether or synthetic methane (CH_4).
- Hydrogen does not provide any CO_2 emissions at the point of use which would be consistent with Direct Air Capture (DAC) and Carbon Capture and Storage (CCS) initiatives [50,113].

3.2 Production from Fossil Fuels

Most fossil fuels can be converted to hydrogen by different methods all of which have their complexities. In this chapter, we talk about production of hydrogen using natural gas and coal. These processes produce carbon dioxide as byproduct, which should be captured in order to guarantee cleaner production of hydrogen. The viability of hydrogen produced using fossil fuel relies upon the size of its plant and the way it is utilized as a centralized or a distributed settlement.

3.2.1 Production from Hydrocarbons

The majority of the industrial hydrogen is produced through the next hydrocarbon-based oxidative-type industries: steam reforming of the light hydrocarbons (such as natural gas and naphtha), partial oxidation (POx) of the heavy oil fraction, and autothermal reforming (ATR) is a combination of steam reforming and POx. The generic chemical equation that explains the oxidative conversion of hydrocarbons into hydrogen is the following one:

$$C_nH_m + [O_x] \rightarrow xH_2 + yCO + zCO_2 \quad (3.1)$$

Where C_nH_m is a hydrocarbon ($n \geq 1, m \geq n$) and O_x is an oxidant such as O_2,H_2O,CO_2

It also finds use on the relatively high operating temperatures of the oxidative conversion processes because the production of hydrogen via the reaction of methane and other saturated hydrocarbons that comprise the hydrocarbon feedstock operate relatively inert to the reaction.

The presence of carbon dioxide is also released as a by-product in such processes and should be trapped to make sure that the production of hydrogen would be clean [51,114].

3.2.1.1 Steam Methane Reforming (SMR)

The steam methane reforming (SMR) is the main technology to produce hydrogen in the industrial field, and it has been being used over the past decades. Being one of the old and considerably productive processes, SMR runs close to the process limits. It accounts also with almost all of the hydrogen (in mixture with carbon monoxide) used in the chemical industry and supplementary hydrogen transferred to the refineries

In 1930 the steam methane reforming (SMR) was first used at an industrial scale. The raw materials of this process are methane, naphtha and No. 2 fuel oil. SMR is a catalytic process with multiple steps with severe reaction conditions. It entails a reaction between natural gas of other light hydrocarbons and steam to fulfill a mixture of hydrogen, carbon monoxide, carbon dioxide, and water in three reactions. The initial reforming process (Equation (3.2) and (3.3)) in a conventional SMR process (as illustrated in a schematic flowsheet of the process (**Figure 24**), catalytically produces hydrogen and carbon monoxide (by the endothermic reaction), by a reforming of methane with steam in the reformer combustion-based furnace.

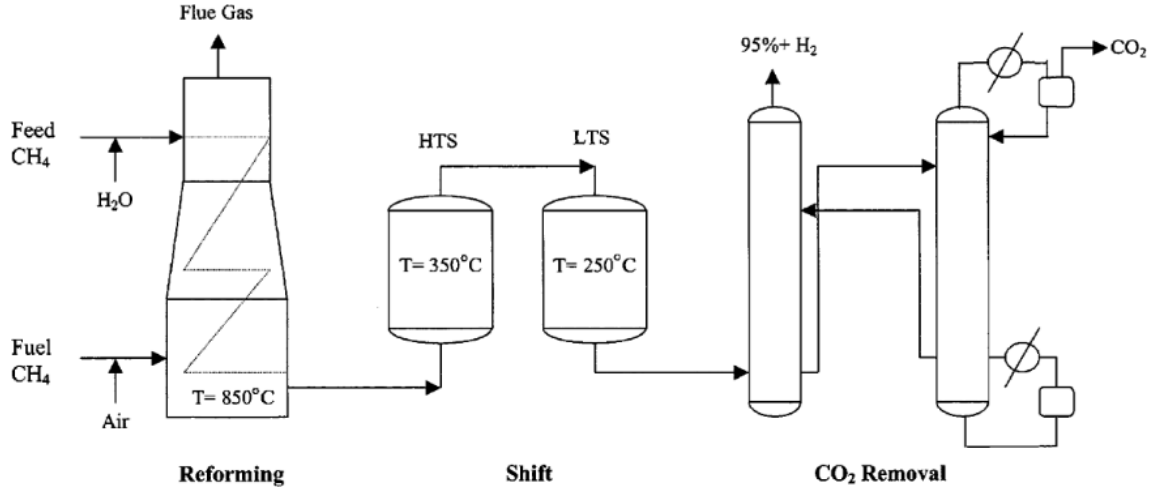

Figure 22: Flowsheet for a conventional SMR process[48].

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^{o}_{298}=206.2 \text{ kJ/mol} \tag{3.2}$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H^{o}_{298}=165 \text{ kJ/mol} \tag{3.3}$$

The temperature in which such reactions are commonly performed is 800 1000°C and the pressure is 14 20 atm and over nickel-based catalyst. Reforming reaction is very endothermic, and

it requires a lot of heat which is paid by supplying additional natural gas to the furnace. The reformer effluent gas is approximately 76 mol% H_2, 13 mol% CH_4, 12 mol% CO and 10 mol% CO_2 (dry-basis).

Then the reformer products are fed to a WGS reactor where the following reaction (Equation (3.4)) occurs:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^{o}_{298} = -41.2 \text{ kJ/mol} \tag{3.4}$$

Reaction expressed by Equation (3.4) is moderately exothermic and is therefore favored by low temperatures.

To obtain the desired purified H_2 product and avoid the deposition of coking on the surface of the catalyst the parameters of reforming reaction are chosen at high temperatures, pressures which can reach 3.5MPa and steam-carbon ratios to 3.5. Following the reformer, the gas mixture will be subjected to a heat recovery process after which it is fed into a WGS reactor in which the CO reacts with steam to form more H_2 and then, the mixture is fed into a CO_2-removal and methanation or a pressure swing adsorption (PSA) leaving H_2 purer of almost 100%. CO_2 capture and storage (CCS) can very efficaciously cut down the CO_2 emissions, perhaps by capturing them and storing them in geological traps or in the ocean. On **Figure 25** a Flow diagram of the steam methane reforming process is presented [48,115].

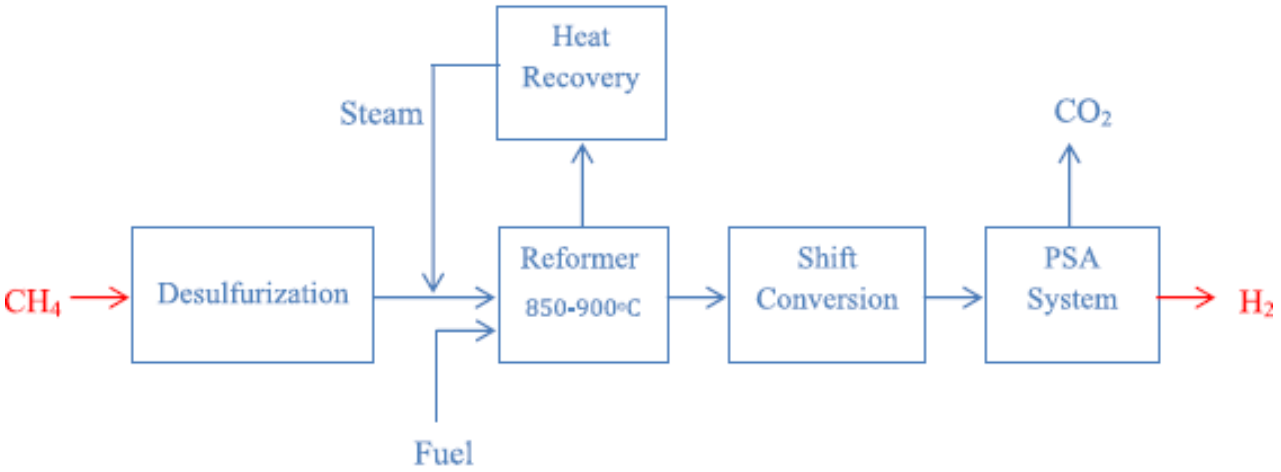

Figure 23: Flow diagram of the steam methane reforming process [52].

Thus, on the assumption of an effective high temperature (beyond 750°C) to provide a significant conversion of reforming CH_4, the resulting gas is associated to a 8-10% dry basis CO concentration. In order to lower the CO content at the outlet of the SMR reactor, the generated syngas is typically directed to WGS reactor where the temperature is limited to the minimum of 300 400 °C to allow WGS reaction to prevail [52,116].

3.2.1.2 Partial Oxidation (POX)

Partial oxidation (POX) process implies that steam, oxygen, and hydrocarbons can be converted into hydrogen and carbon oxides. Feedstocks used are methane to naphtha and the temperature in the catalytic process involves around 950^{o}C. Conversely, the non-catalytic route that is carried out at elevated temperatures (1150-1315^{o}C) is able to process a broader spectrum of hydrocarbons that include methane, heavy oil and coal.

Sulfur should be removed prior to the reaction and the O_2 is pure enough to oxidize the hydrocarbon feedstock to a limited extent. The resulting syngas is then further processed which is the same product gas as steam reforming (SR) process. Nevertheless, POX plants are very capital-intensive because of the cost of producing the oxygen needed and extra desulfurization measures.

On the catalytic POX process heat is liberated by controlled combustion and the catalytic process has a thermal efficiency of 60-75 percent in the case of methane as the feedstock. The chemical expressions of catalytic and non-catalytic reforming are given in Equation (3.5) and (3.6) whereas water-gas shift (WGS) and methanation processes are portrayed in Equation (7) and (8).

$$C_nH_m + \left(\frac{1}{2}\right)nO_2 \rightarrow nCO + \left(\frac{1}{2}\right)mH_2 \quad \text{(3.5) (catalytic)}$$

$$C_nH_m + nH_2O \rightarrow nCO + (n + \left(\frac{1}{2}\right)m)H_2 \quad \text{(3.6) (non-catalytic)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(3.7) (WGS reactor)}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \text{(3.8) (Methanator)}$$

The most viable technology that can be adopted in the production of hydrogen using heavier feedstocks which include heavy oil residues and coal is partial oxidation (POX). Owing to their lower hydrogen to carbon ratio instances of these feedstocks than methane, a substantial amount of hydrogen generated is steam. For representation of residual fuel oils, n=1 and m=1.3 can be applied in Equation (3.6). The common syngas mixture will be about 46 % H_2, 46 % CO, 6% CO_2, 1 % CH_4 and 1 % N_2 at 880 psi (6 MPa).

The syngas is purified after being converted through shift. The typical cost breakdown of the production of hydrogen by POX of residual fuel oil include: 34.8 per cent feedstock, 47.9 per cent capital investment and the rest, 17.3 per cent, is operation and maintenance (O&M) [48,117].

POX is exothermic and practically a lot of steam is added along with the methane to control the generation of any carbon. In this aspect the design of the burner that causes a very strict mixing process of oxygen and natural gas is decisive. Due to the availability of excess steam, it also has a high temperature non-catalytic methane to steam reforming, which takes place [53].

In comparison with the other reforming technologies the exothermic thermal POX process possesses a number of beneficial features. No use of outside heat source and more feed, like water as in the case of steam reforming. Furthermore, it is catalyst free and consequently catalyst deactivation issues are not on the cards. It has an excellent dynamic response, its system design is very simple and it could be used in virtually all hydrocarbons. The disadvantages, however, are that it has a relatively low yield of hydrogen and it usually forms soot [54].

3.2.1.3 Autothermal Reforming (ATR)

In Autothermal reforming (ATR) method, the exothermic partial oxidation is used to supply the heat whereas endothermic steam reforming to raise the volume of hydrogen production. In simple terms, the injection of steam and oxygen/air, into the reformer leads to the parallel progress of the reactions of reforming and oxidation forming the reaction written in Equation (3.9)

$$C_nH_m + \left(\frac{1}{2}\right)nH_2O + \left(\frac{1}{4}\right)nO_2 \rightarrow nCO + (\left(\frac{1}{2}\right)n + \left(\frac{1}{2}\right)m)H_2 \quad (3.9)$$

Using methane (by putting n=1, m=4 in Equation (3.9)), the thermal efficiency will be 60-75 percent, whereas the optimum operating value has been found to be approximately 700 °C inlet temperature and the ratios S/C=1.5 and O 2 /C=0.45 at which the highest yield of hydrogen is approximately 2.8. The costs of investment are approximated to be 15-25 percent and 50 percent off the SMR and the coal gasification respectively.

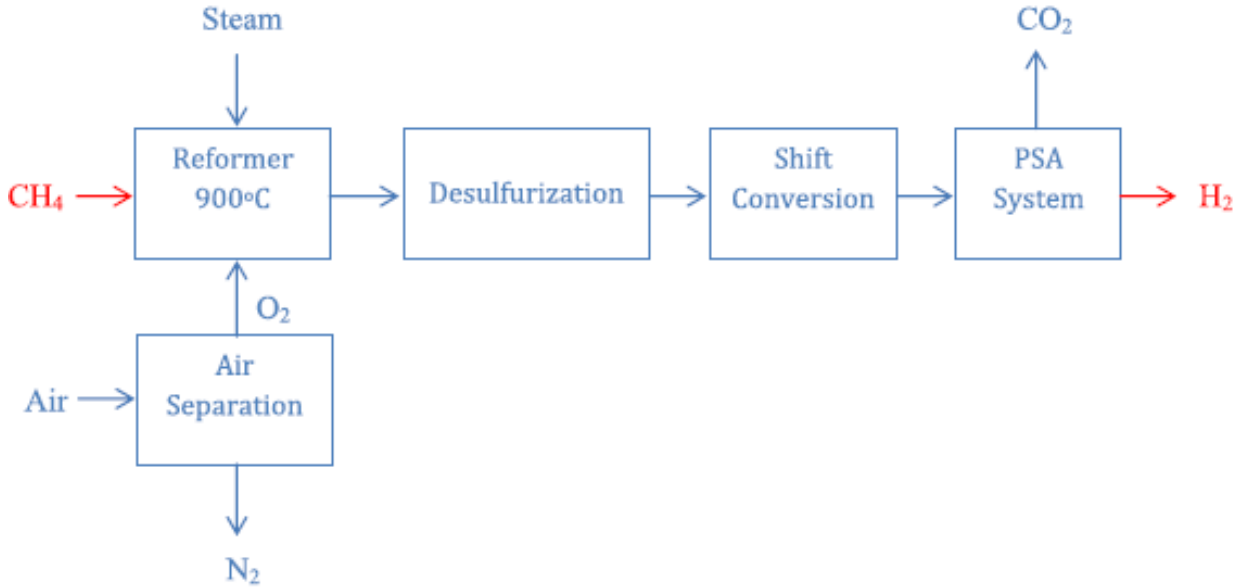

Figure 24: Flow diagram of the autothermal reforming of methane process

Each process has certain advantages and disadvantages, which are summed up in **Table 8**.

Table 8. Technology comparison of natural gas-based hydrogen production [54].

Technology	Pros	Cons
SMR	High efficiency Emissions Costs for large units	Complex system Sensitive to natural gas qualities
POX or ATR	Smaller size Costs for small units Simple system	Lower efficiency H_2 Purification Emissions and flaring

3.2.2 Production from Coal

Hydrogen is under wide research to use it as source of energy transfer to cut carbon production as a result of providing power and transportation. It may be manufactured using hydrocarbons, water and by-products of some industries. The method of production is dictated on how you can get the local resource and how much it is going to cost you. The most common fossil fuel in the earth with a recoverable reserve of an estimated 216 years is coal which has the longest capacity of over 500 years at the present rate of consumption. Owing to the enormous volume of greenhouse gas emissions by existing stationary electrical generation, alternative methods are under consideration to ensure reduced imparting on the environment by the use of coal. A good technology lies in the gasification production of hydrogen which has been becoming popular over the past years. Gasification has more potential of sequestrating CO_2 and minimizes other pollutants, like NOx and SOx, when compared to conventional electricity generation. Coal, of all the fossil fuels, has the lowest hydrogen to carbon ratio, and therefore, produces more CO_2 per the mole of H_2 generated. Nevertheless, gasification provides the opportunity to generate high-pure hydrogen or highly effective electricity with fewer emissions. This is done by the separation and capture of CO_2 which occurs in high concentrations in the product stream. During the gasification process, coal that is crushed or pulverized; either in dry or as a slurry is combined with an oxidant, most common is the mixture of air, oxygen, and steam. This mixture is then fed into the gasifier where it becomes volatile between the following temperatures; 1000-1500 degrees Celsius. The resulting hydrocarbons interact, by reacting, to produce carbon monoxide and hydrogen (syngas) as defined by Equation (3.10) [55,118].

$$CH_xO_y + (1-y)H_2O \rightarrow \left(\frac{x}{2} + 1 - y\right)H_2 + CO \tag{3.10}$$

Coal gasification is a primary reaction in industrial hydrogen production. Equation 3.11.

$$C_nH_m(coal) + nH_2O \rightarrow nCO + (n + \frac{m}{2})H_2 \tag{3.11}$$

The combination of the products of the CO and H_2 mixture is composed of synthesis gas. The water gas shift reaction is then used to convert CO into H_2 and CO_2. But the process of gasification in coal is endothermic. Gasification will need a temperature in the region of about 1273 K, or more,

to give the required reaction rate. On the contrary, water-gas shift reaction is exothermic and it is more efficient at lower temperatures in conversion of CO. Somewhat conventionally, a gasification step in a reactor at temperature higher than 1273 K is followed by a step of introducing synthesis gas to another reactor (which is usually, but not necessarily, below 673 K) where conversion of CO occurs.

Also, in the standard process, after conversion of CO, CO_2 needs to be denatured. The thermodynamic analysis implies that CO can be transformed to H_2 at a quite high temperature in case CO_2 can be removed in the process of water-gas shift reaction. This means that the 3 major steps in traditional hydrogen manufacturing which include, coal gasification, the water-gas shift, CO 2 separation may just end up taking place under the same operating conditions. Provided it is possible, this might allow combining all three steps in a single reactor and making the process more efficient and less demanding. [56,119].

3.2.2.1 Issues associated with solid fuels

Most solid fuels are also carbon-based, which means that the production of hydrogen using these sources of fuels will create CO_2 which is the main greenhouse gas that has been causing the increase in the temperature of the lower atmosphere. Renewable sources of energy are one of the ways of preventing CO_2 emissions. Nevertheless, base-load renewables hydro, biomass and geothermal, have little chance of generating even the existing electricity need, and are not completely climate-neutral when installed at base-load.

The other option is coal gasification with carbon capture and sequestration (CCS) but the existing CO_2 separation processes have high energy and cost penalties. In Germany, an engineer has had constructed and is using a power plant that incorporates full CO_2-capture and storage to prove that coal-fired power generation without CO_2 is possible. CO_2 capture Research on CO_2 capture to gasification is investigating new methods such as wet scrubbing by physical sorption, chemical sorption of solid sorbents, and membrane-based separation.

Other becoming options that are limited with solid fuels- washing, drying, ash handlings and solid pollutants control, are already very familiar and well controlled in existing systems of energy with solid fuels [57,120,121].

3.2.3 Capture and Storage of CO_2

The concept of capturing CO_2 in industrial process streams is more than 80 years old. But there are no directives or economic incentives to store the captured CO_2 and it is therefore

deposited most of it back into the atmosphere. Modern captures of CO_2 involve cleaning up natural gas and making hydrogen-rich synthesis gas to make ammonia, alcohols and synthetic liquid fuels. In these applications, CO_2 capture techniques utilized are fairly the same as in pre-combustion capture.

Other industrial activities like cement and steel manufacturing plants, fermentation of food and beverage industry, emits CO_2, though they do not generally include capture systems in their processes. These sources of CO_2 may be captured by regular techniques, such as post-combustion capture, oxy-fuel combustion capture and pre-combustion capture.

3.2.3.1 Post-combustion capture

Post-combustion capture is the capture of CO_2 emitted in the air through the combustion of fossil fuel and biomass. Rather than being emitted in the atmosphere, flue gas goes through a machine that separates the majority of CO_2. The captured CO_2 is subsequently packed into a special reservoir and the rest of the flue gas is released.

CO_2 separation is usually done using chemical sorbent process, although other methods are being studied, but still at in-early-development status. Besides use in industries, post-combustion capture is especially applicable in the case of power plants that are presently constructed. This is the current installed capacity of 2,261 GW cells in oil, coal, and natural gas power plants, 155 GW in supercritical pulverized coal-fired plants and 339 GW in natural gas combination cycle (NGCC) plants, both being the high-efficiency power plant technology where the CO_2 carbon capture is the most feasible.

3.2.3.2 Oxy-fuel combustion capture

In oxy-fuel combustion, the oxygen used in combustion is almost pure rather than air and hence the main flue gasses produced are CO_2 and H_2O. Because the combustion of fuel with pure oxygen produces very high temperatures in the flames, a recycling of CO_2 and (or) H_2O rich flue gas is used to control the combustion temperature, by cooling it in the combustor.

Liquid oxygen to supply this process is mostly produced by low-temperature (cryogenic) air separation, but new methods including membranes and those involving fine chemical looping cycles are also being developed. The systems that can be used in the power plant based on oxy-fuel combustion capture are identical to those of post-combustion capture.

3.2.3.3 Pre-combustion capture

Pre-combustion capture of fuel reacted with oxygen, air or steam to generate a so-called synthesis gas (syngas), which consists mainly of carbon monoxide and hydrogen. The carbon monoxide is next catalytically reacted with water in a so-called water-gas shift process to make CO 2 and more hydrogen. The CO_2 is then isolated, most often through physical or chemical absorption, and the fuel is left fuel-rich in hydrogen, which can be used in boilers, furnaces, gas turbines, engines and fuel cells.

Such systems are regarded as being strategic. Nevertheless, the application of current power plants does not exceed 4 GW oil- and coal-based integrated gasification combined cycle (IGCC) plants, i.e. 0.1% of the total installed capacity world-wide (3719 GW).

In **Figure 27** an overview of CO_2 capture processes and systems is being shown [58,122]:

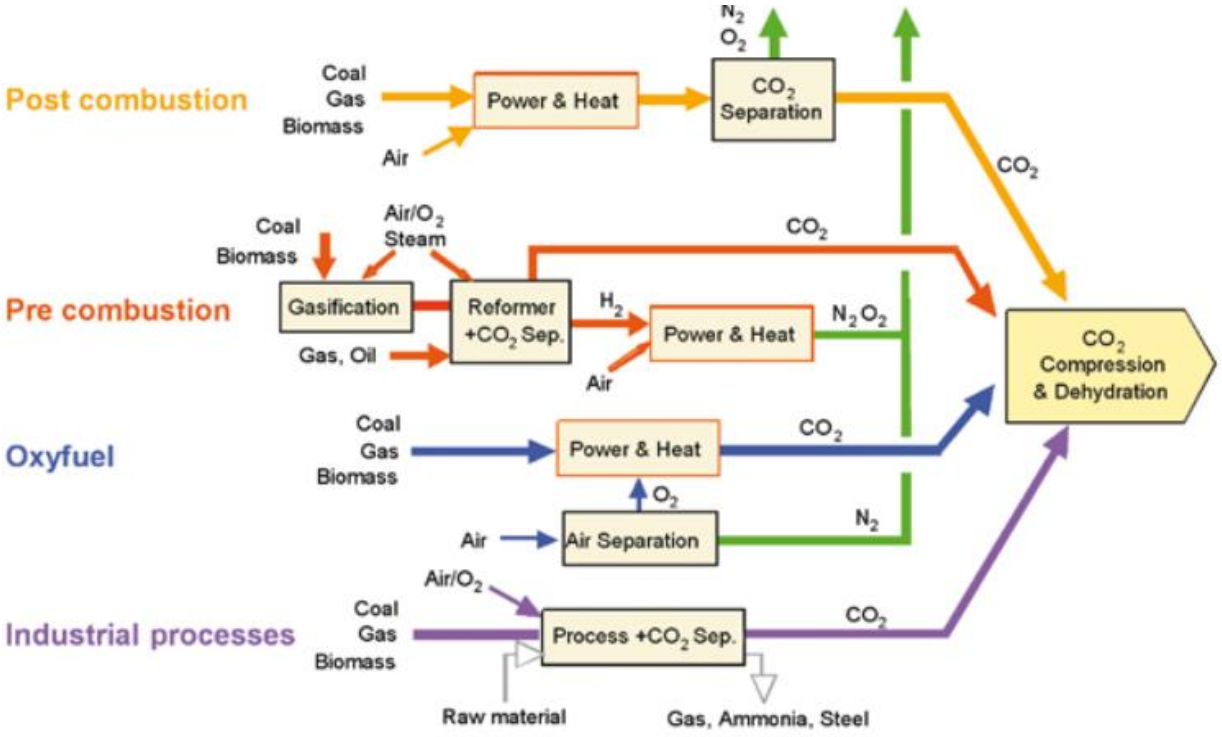

Figure 25: CO_2 capture systems [58]

3.3 Production from Renewable Sources

3.3.1 Hydrogen Production from Nuclear Energy

The world is becoming energy hungry and therefore there is a need to continually develop power generation capacity, at the same time it is important that the greenhouse gas (GHG) emissions are minimized. Additionally, to the generation of clean electricity, the high-temperature thermal energy generation is also required by using low-emission means. Therefore, the development of renewable

energy methods like wind, concentrated solar thermal, ocean, biomass, and geothermal, and others are also paid more and more attention in numerous countries across the world.

The energy source should be a stable, low emitting source of energy that will have to form a reliable base load in the future energy mix. In this regard, nuclear power has to be taken into consideration. Presently, all the operational nuclear power plants have been developed to operate continuously to provide electricity to meet the base load of electrical grids. The number of countries introducing the use of nuclear energy is raising and the trend is global especially in terms of developing the fourth generation nuclear reactors that have the ability to generate power, high-temperature heat, and hydrogen. The hybrid nature of future energy systems will rely on the combination of a variety of forms of energy and modes of conversion to ensure efficiency and with the least impact on the environment. In these hybrid systems hydrogen may be a fundamental energy carrier, favoring a complement between renewable energy resources and nuclear energy in a long term sustainable and harmless to environment.

Nuclear production of hydrogen has some important benefits:[59,123]:

- It creates yet another market-hydrogen, which can be either sold as electricity (through fuel cells) at peak when the price is higher, sold as transportation-fuel or used by industry as a chemical feedstock, whichever is better. It balances the power demand of the network.
- It enables more efficient generation of power because the generators (excluding the nuclear ones) are able to issue and maintain most of their generation close to the nominal load.
- It lessens the pollution that goes with power generation since the generators are used effectively.
- It facilitates the creation of renewable energy sources that require energy storage (like hydrogen) which can be done on a temporary basis and will ease the unbalanced energy profile that renewable sources have.
- The synthesis with high-temperature electrolysis and thermochemical cycles can make nuclear power plants more competitive in cost and secure.

Nuclear energy exists in fission reactors, which use fuel made with Uranium, and in the near future, thorium might be used. It contains nuclear reaction that generates high temperature heat that is passed through a heat transfer fluid in order to utilize it further. Conventionally, the heat is tapped to big-scale power generation. Nevertheless, some of it will also be able to be diverted towards chemical processing of hydrogen, yielded by splitting water. Further, nuclear radiation existing in the reactors and during the entire nuclear fuel cycle may be directly used in the production of hydrogen.

Five main ways of nuclear energy production of hydrogen through decomposition of water are known:

1. Radiolysis The splitting of water molecules into hydrogen and oxygen is achieved directly under the influence of nuclear radiation.
2. Electrolysis- The generation of electricity supplied by nuclear energy to break down water by electrolysis.
3. High-temperature steam electrolysis - A combined-heat and power process that combines the use of both electricity and high temperatures in the splitting of water.
4. Hybrid thermochemical water splitting -Almost the same as method (3), but now also frequency-based, like water-energy-storage system.
5. Thermochemical water splitting- Only uses the heat of high temperature in order to induce the splitting of water.

Nuclear radiation is the first conversion of the nuclear energy released either during the repairing of the reactor or the nuclear fueling cycle (Figure 28). This radiation is also converted to heat that is of high temperature. The heat as well as radiation is subsequently used in producing hydrogen using the different processes described above [60,124].

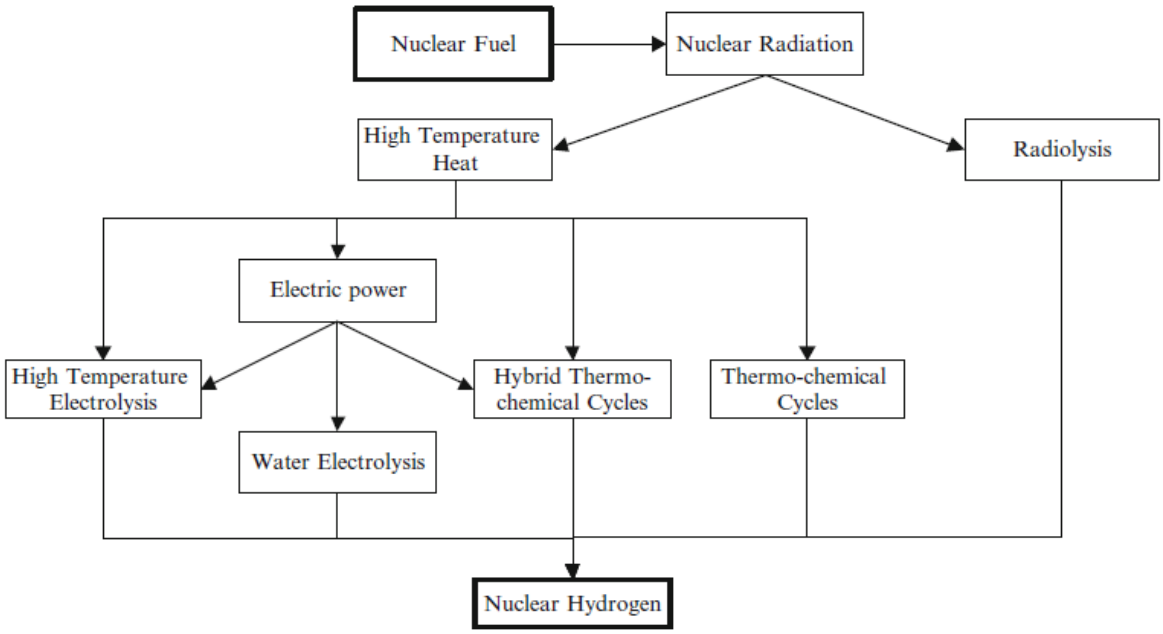

Figure 26: Nuclear water splitting pathways for hydrogen production[60]

3.3.2 Hydrogen Production from Wind Energy

As the world has increased exponentially in the use of industrial applications, there is a booming demand of energy. It is obvious that energy is a big fundamental aspect in most countries. Conversely, the sources of nonrenewable energy are diminishing and 80 percent of the world energy source is supplied by fossil fuel which was being utilized more in the past years.

Besides, there is also a variety of related energy issues such like carbon emission, global warming, environmental hazards as well as GHG (Green House Gas) emissions. Among the biggest solutions to tackling these issues is by resorting to wind energy as one among the renewable energies. Being a concept, it is a very promising method of hydrogen production not only due to the fact that both processes are renewable and nonpolluting, but also due to the fact that the wind energy conversion systems can be made even more effective by the inclusion of the energy storage medium. Wind energy is termed as the mechanical work derived by converting the kinetic energy of wind. The resultant mechanical energy can be harnessed to generate electricity through using a generator. A device that uses such conversion is known as a wind turbine generator (WTG) and a collection of them (as well as of the auxiliary equipment) is referred to as a wind farm (WF). Stand-alone wind energy system in association with electrolyzer is the most common application under current study. This installation appears on **Figure 29**.

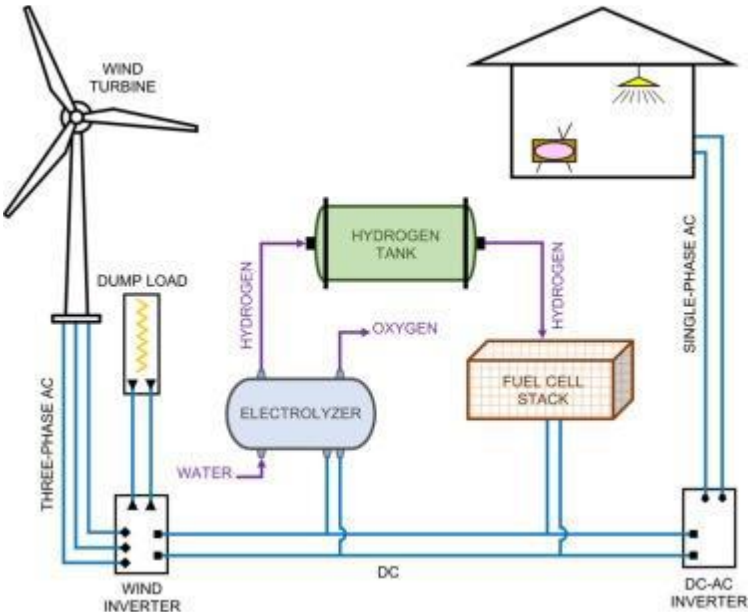

Figure 27: Design of an isolated stand-alone hybrid wind-hydrogen system for a zero-energy house [61].

Storing wind energy in form of hydrogen has a number of benefits. Hydrogen is highly suitable when it comes to seasonal energy storage without any energy reduction over the store period. Water electrolyzers are capable of taking a load on power fluctuations and therefore the issues about intermittent power generation by wind power are on the relative scale and by use of water electrolyzers the wind parks can guarantee a power output. Wind-hydrogen systems have a potential to provide high density storage facilities at low cost and predictable operating and maintenance costs. The joint work of hydrogen and wind energy systems might play a part in the development of both technologies as one is used to entertain the other due to various reasons [61,125].

3.3.3 Hydrogen Production from Biomass

Biomass can be regarded as one of the most available sources of renewable energy that are available as part of the sustained pursuit of sources of clean and renewable energy. Biomass is synthesized in the course of the photosynthesis that changes carbon dioxide and atmospheric into organic matters. Coming to this, it has been found to be carbon neutral during its lifecycle.

Biomass has been used historically as an energy source that dates many centuries ago. In the contemporary world, it represents around 12 percent of the global energy supply, although this percentage can be much higher in most of the developing world between the range of 40 to 50 percent. The recent studies made regarding biomass are under the spotlight since it can be utilized in transforming waste to energy. In other words, approximately 1.08 x 1010 GJ of energy can be derived every year with the 150 gigatons of plant-based biomass produced worldwide. Nonetheless, there is a significant problem stimulated by the inefficiency of conventional ways of using biomass. Biomass is, in most cases, burnt in the open air in cooking, heating, etc. in China with a very low thermic efficiency of 10%-30%. The best solution would be to turn biomass into gaseous and liquid fuels, electricity or, more specifically, hydrogen and utilize its energy to the full.

There are numerous biomass resources which may be converted into energy. They may be grouped into four general categories:

i. Energy crops: herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops.
ii. Agricultural residues and wastes: crop wastes and animal wastes.
iii. Forestry waste and residues: mill wood waste, logging residue, trees and shrub residue.
iv. Industrial and municipal waste: municipal solid waste (MSW), sewage sludge and industry wastes.

These available processes of biomass energy production can be classified into two broad categories and they include: thermochemical and biological processes [126,127].

3.3.3.1 Thermochemical processes

Pyrolysis is a high temperature degradation of matter, where the biomass is heated to between 6500K-8000K at a pressure of 0.10.5MPa and in absence of oxygen. Under this procedure biomass is converted to three main products namely: liquid bio-oil, solid charcoal and gaseous compounds. Pyrolysis can be categorized into two broad categories that are slow pyrolysis and fast pyrolysis. Charcoal produced by slow pyrolysis is mainly used and, thus, not generally speculated in the

production of hydrogen. Conversely, fast pyrolysis is an operation of high heat whereby biomass is rapidly heated without presence of oxygen. This causes generation of vapors which are then condensed into a dark brown mobile bio-liquid. Fast pyrolysis products are all in the three states (gas, liquid and solid) thus making this a simple extraction method in biofuel and hydrogen production [62].

i. Derived gaseous products are H_2, CH_4, CO, CO_2 and other gases depending on the organic nature of the biomass to be pyrolyzed.
ii. Tar and oils that are kept in liquid form even at room temperature such as acetone, acetic acid etc.
iii. The char and nearly pure carbon along with other inert materials constitute solid products.

Most of the pyrolysis processes are made considering the production of biofuels, however, direct production of hydrogen can be carried out using fast or flash pyrolysis provided that high temperature and adequate volatile phase residence time can be obtained as follows:

$$Biomass + heat \rightarrow H_2 + CO + CH_4 + other\ products \quad (3.12)$$

Methane and other hydrocarbon vapors produced can be steam reformed for more hydrogen production:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (3.13)$$

To increase the hydrogen production, water–gas shift reaction can be applied as follows:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3.14)$$

In addition to gaseous products that are produced during pyrolysis there is also the liquid product, the pyrolysis oil which can be used to produce hydrogen. Pyrolysis oil is usually divided into two fractions according to water solubility, one is water soluble, which can be applied in hydrogen production, and one water-insoluble insoluble, which is frequently applied to adhesive manufacture.

Examination research shows that up to 90 percent hydrogen yield can be accomplished through the utilization of a nickel-based (Ni-based) catalyst. Also, the introduction of extra steam reforming and water gas shift reactions can allow a further increase of hydrogen yield.

There are a few important parameters that affect efficiency of pyrolysis in producing hydrogen namely temperature, heating rate, residence time and catalyst choice. High temperature, high heating rate and long volatile gas phase and residence time are needed to maximize the formation gaseous products, especially hydrogen. The flow of the material is presented in **Figure 30**.

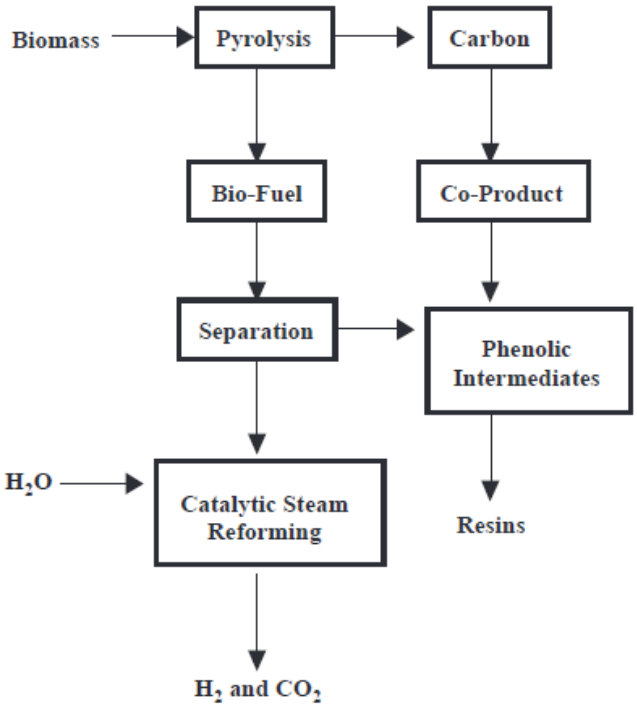

Figure 28: Biomass to hydrogen based on pyrolysis with a co-products strategy[63].

3.3.3.2 Biological Processes

Biological hydrogen production is renewable, and low-emission process that fits in the context of the global trends of sustainability and carbon neutrality. Researching really took off in the 1970s, although it was first observed in the 19th century, with researchers concentrating on microbial systems that can utilize solar energy or organic compounds to develop hydrogen. Even with the advanced scientific research, most of the procedures are still in the laboratory stage with the proceedings hindered by low production levels, and oxygen sensitivity of various pivotal enzymes as well as complexity of the activities.

Some of the biological pathways are direct biophotolysis which involves the use of photosynthetic algae like green algae to decompose water into oxygen and hydrogen through sunlight. The efficiency of this process is however restricted by the oxygen sensitive characteristic of hydrogenase enzymes. The issue is circumvented in indirect biophotolysis where photosynthesis and H_2 generation are temporally or spatially separated with CO_2 first converted to organic substrates prior to anaerobic fermentation to liberate H_2. It is promising, but it brings complexity of metabolic and process. A biological water gas shift reaction is another path that involves use of anaerobic bacteria converting CO and water into hydrogen and CO_2 which can be combined with biomass gasification. Nonetheless, it is threatened by slow microbial growth and sensitivity, which is a drawback to its scalability.

Photo-fermentation in which organisms such as purple non-sulfur species transform organic acids (such as acetate) in the presence of hydrogen under receiving light. The conversion process

has the potential to valorize waste streams but suffers constraints posed by low conversion efficiencies of light and nutrient requirements. Conversely, the dark fermentation process works based on anaerobic microorganisms like Clostridium, which use dark conditions to metabolize carbohydrates to continuously generate hydrogen and organic acids. Although it does not depend on the availability of light, it is limited both by low yields and the inhibition of byproducts. All the biological pathways include enzymes mostly hydrogenases and nitrogenases which bring about reduction in protons to hydrogen. However, oxygen sensitivity and energetic requirements seem to be a hindrance to robust open-environment function.

Performance is dependent upon environmental conditions like pH, substrate concentration, gas partial pressures and temperature. The spectral distribution and light intensity play a vital role in photo-driven schemes, whereas the intermediate accumulation and the type of substrate influence the dark fermentation. The weakness of microbial cultures, the threat of contamination, and the amount of complexity inherent in sustaining consistent environmental conditions opposes the scaling of these systems. New bio-reactor configurations such as photobioreactors and anaerobic membrane systems are aimed at a more efficient distribution of light, mass transfer and maintaining biomass, which is important to industrial applicability.

The opportunities of circular and sustainable energy could be based on integrating biological hydrogen production with waste regimes and biomass valorization. When dark fermentation is coupled to anaerobic digestion or when photo-fermentation is integrated in the wastewater treatment process, the approach will improve energy recovery and environmental performance. Although biological hydrogen production is not currently economically competitive, additional investment in microbial engineering, reactor design, and process coupling could position it as an essential building block of the next generation hydrogen economy [63].

3.3.3.3 Photobiological Production (Biophotolysis)

Bio photolysis (photobiological hydrogen production) is the use of the metabolic potential of the photosynthetic organisms, mainly green algae and cyanobacteria, to fix solar energy and water into H_2. Enzyme-catalyzed natural processes like [Fe-Fe] hydrogenase in green algae or nitrogenase in cyanobacteria make this environmentally favourable. In green algae, direct biophotolysis occurs whereby photosystem II is separated into oxygen, protons and electrons and then the resultant electrons are transported to photosystem I wherein a reaction between ferredoxin is reduced. The less ferredoxin subsequently transfers electrons to hydrogenase that reduces protons to hydrogen gas. Although the [Fe-Fe] hydrogenase is highly catalytically active, its sensitivity towards oxygen which is

also formed during the water splitting process restricts its potential users, because even very small concentration of oxygen will result in an inactivation of the enzyme.

In a bid to overcome this, methods like deprivation of sulfur have been examined to temporarily inhibit the formation of oxygen and safeguard the activity of hydrogenase. Photosynthesis and production of hydrogen are uncoupled in indirect biophotolysis in cyanobacteria. Carbohydrates are formed during the light period of plant growth. These are later fermented in the following dark phase to produce hydrogen which are catalyzed by the nitrogenase. This enzyme which contains MoFe and Fe protein subunits additionally reduces protons to hydrogen without nitrogen. However, this is an ATP intensive, oxygen sensitive reaction and special structures such as heterocysts are typically needed to ensure an anoxic environment so that the enzymes are active.

Both pathways require environmental and physiological factors to determine how efficient Hydrogen is produced. In direct biophotolysis the light intensity, quality, and duration affects the electron flow and activation of hydrogenase. In indirect processes, yield depends on the balance of (a) carbon fixation and (b) fermentation. Metabolic byproducts and intermediates can accrue to a point of halting enzyme-based activity and thus a growth condition must be controlled very carefully. In order to enhance performance efforts have been made on genetic engineering to enhance the expression of enzymes, regulation pathways and to have increased oxygen tolerance. Modification of photosynthetic light-harvesting is also being conducted to maximize conversion of sunlight to energy and its diversion of metabolic flows towards hydrogen production.

Artificial biophotolysis is a new area of growing interest; the aim is to recreate natural systems by putting light-gathering components, catalytic moieties and proton-pumping devices on artificial platforms. These artificial constructs are meant to do away with oxygen susceptibility of biological catalysts besides ensuring a more secure production of hydrogen. The approaches of synthetic biology, hybrid photoelectrochemical system, and biomimetic materials are at the center towards the scale up and cost effective artificial systems that mimics the spatial and functional assembly of natural biophotolysis.

Unfortunately, biophotolytic production of hydrogen suffers with low conversion rates as well as constraints imposed by its operation. The challenges which inhibit scaling-up include light distribution and gas - liquid mass transfer, biomass retention. The innovations of photobioreactors, such as thin-layer or internally illuminated photobioreactor, attempt to enhance the use of light and productivity. Combined with wastewater treatment or carbon capture, it provides some value by simultaneously generating power and cleaning the environment. With ongoing advances in systems

biology, metabolic engineering and reactor technology, biophotolysis has a potential to play a sustainable role within the hydrogen economy of the world.

3.3.3.4 Dark Fermentation

One of the most promising biological process in hydrogen production is the dark fermentation and this is conducted in anaerobic conditions with very broad constraints to many organic feedstocks. That it is light-independent makes it operate continuously and thus, it can be included in the waste treatment systems; it adds value to energy recovery and environmental sustainability. Dark fermentation has a greater attraction in the context of a circular economy because feedstocks can comprise agricultural wastes, food waste, and industrial effluents. The process is promoted by microorganisms like Clostridium, Enterobacter, and Thermology species which convert (in a cascade of enzyme reactions, predominantly involving hydrogenases) carbohydrates into hydrogen and organic acids.

The main start point in the metabolic pathway is the glycolysis process during which the sugars are degraded to pyruvate. In organisms such as Clostridium, the conversion of pyruvate to acetyl-CoA and reduced ferredoxin is catalyzed; the electrons of reduced ferredoxin are then given to protons by means of the activity of the hydrogenase and the formation of hydrogen gas occurs. This is coupled with synthesis of volatile fatty acid that can stabilize cellular redox though may suppress microbial growth and enzyme action when present in excess. Before effective production of hydrogen, it is important that one controls such byproducts through pH control or continuous elimination to validate the stability of microbial activity and efficiency. An important advantage of dark fermentation is the possibility of use of substrates produced by waste. These mediums usually require collaboration between different microbial communities as various species may have their roles in breaking down and fermenting complicated polymers. It is important to maintain the performance of these consortia, and thus a proper management of microbial communities exists. More so, using dark fermentation alongside other processes such as photo-fermentation or anaerobic digestion, additional energy can be recovered by using organic acids to enhance hydrogen products and contribute to cascading resource use strategies.

Research to improve on hydrogen yield has concentrated on metabolic engineering which aims at reducing the paths that lead to the removal of electrons that would produce hydrogen. Hydrogen yield can be increased by knocking out genes in solvent or acid production or insertion of more efficient hydrogenases. Concurrently, developments in the design of reactors, including packed-bed and membrane bioreactors, are intended to enhance mass transfer, product extraction and biomass

accumulation. Operational parameters such as temperature, pH and hydraulic retention time should also be optimized in order to facilitate the activity of microbes and inhibition circumstances.

Despite a great potential, dark fermentation is difficult to scale up because of low hydrogen productivity per volume of substrate and the fact that the pretreatment of the substrate and the handling of byproducts is difficult. The interdisciplinary innovation combined with improved techno-economic models which embody total lifecycle consequences is needed to address these constraints. However, the dark fermentation can provide decentralized and flexible method of production of hydrogen mainly needed by regions where there is a lot of organic waste. Further development in microbial engineering and process integration will confirm its future place in a hydrogen economy as well as in a sustainable energy system.

3.3.3.5 Photocatalytic Water Splitting

The chance of producing green hydrogen is through photocatalysis water splitting, where the water and sunlight are directly converted to hydrogen and oxygen without any emission of greenhouse gases. It is based on the photoactivation of the semiconductor materials that creates hole-electron pairs that can be utilized in the redox reaction that leads to splitting water. Paramount to efficient operation is an adequate band gap to enable visible light absorption and band edge position to allow efficient operation, and resistance to photocorrosion. Such materials such as titanium dioxide (TiO_2) have been well researched, and they tend to be restricted to ultraviolet light. Opposed to this, scientists have also tried cadmium sulfide and bismuth vanadate, and perovskite oxides but few can satisfy all the specifications of stability, redox potential and light absorption.

There are two strategies that have been devised, namely single photocatalyst system and Z-scheme dual photocatalyst system. The latter involves using a single material to do both hydrogen and oxygen evolutions and this involves a very delicately balanced electronic structure. Such Z-scheme resemble the process of natural photosynthesis in the combination of two photocatalysts, one directed at the evolution of hydrogen with the other at the evolution of oxygen with redox or solid state mediators electron pathways linking the two. This decoupling means the visible light can be used better, and the overall efficiency will be upgraded. Bismuth vanadate with tungsten trioxide as an oxygen-evolving compound in the systems has promise yet the optimization of the electron transfer and suppression of recombination and back-reactions still present difficulties.

Process of breaking the water into two: the breaking of water can be achieved through three processes that include absorption of light, separation of charges, and reaction at the surface of the photocatalyst through redox reactions. The hydrogen and the oxygen evolution are catalyzed by the

photogenerated holes and electrons in the respective catalytic sites. But charge recombination and low mobility of carrier are formidable barriers to efficiency. To overcome this cocatalysts like platinum, palladium, and ruthenium dioxide are added to enhance surface reactions and reduce activation energy hence resulting in the lower energy barrier. Transition metal oxides and sulfides are demonstrating more affordable cocatalysts as well. Their dispersion, contact with the photocatalyst and the structure of the nanoparticles play an important role in the improvement of charge transfer and reaction kinetics [128,129].

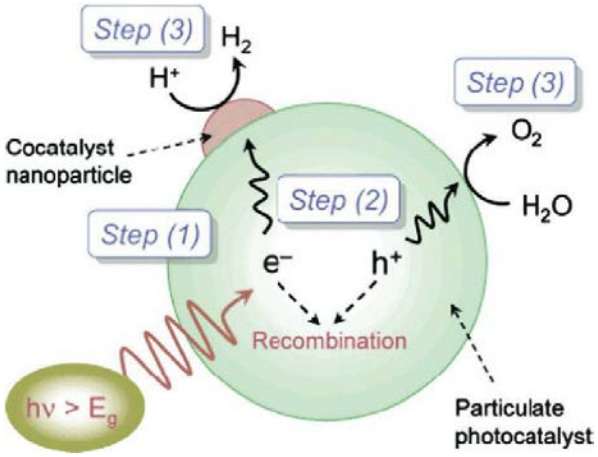

Figure 29: Processes involved in overall photocatalytic water splitting on a heterogeneous photocatalyst [129].

Material engineering holds critical function in enhancing performance of photocatalytic activity. Light absorption is optimized by elemental doping, and forming heterojunctions, and nanostructuring increases charge separation, and active surface area. As what, e.g., nitrogen-doped TiO_2 may boost light response into the visible region, and heterojunctions may realize internal electric fields to sort charge carriers. However, the best overall solar-to-hydrogen efficiencies are still below 1%, being hampered by inefficient use of visible light, rapid recombination and degradation of photocatalysts under light [130].

The design of an integrated system and the reactor engineering is necessary to bring the success of the laboratory work into real life. Mass transfer is also to be improved by making innovations, like floating photocatalyst systems and light-distributing photonic reactors, which maximize light harvesting. A combination of these systems with solar concentrators can increase efficiency even more. The potential of PWC is in its ability to provide hydrogen production, in a decentralized and low-carbon form. A sustained development of the photocatalyst materials, investigations into the reliability and stability of the systems, and scalability of reaction chambers will also be critical since its implementation requires enabling the mild decarbonized energy future [131].

Chapter 4 Future Challenges and Future Prospects

4.1 Production from Water Splitting

Hydrogen production from water splitting, as the reverse reaction of hydrogen combustion, uses water as the only feedstock and enables the close hydrogen cycle with zero carbon emission, which is thereby considered as the most green and sustainable method. Despite its potential, the high cost of water electrolysis limits its widespread adoption, currently accounting for only about 4% of global hydrogen production. Therefore, a major challenge is to develop cost-effective electrolysis methods that can gradually replace hydrogen production from fossil fuels.

One approach to achieving affordable hydrogen from water splitting is utilizing low-cost, renewable electricity sources such as solar, wind, and tidal power. However, these energy sources are intermittent, and the existing electricity grid infrastructure is not optimized to efficiently absorb their excess power.

Water electrolysis presents a promising solution by converting surplus renewable energy into chemical fuels, thereby improving the overall utilization of renewable power sources and contributing to a more sustainable energy system.

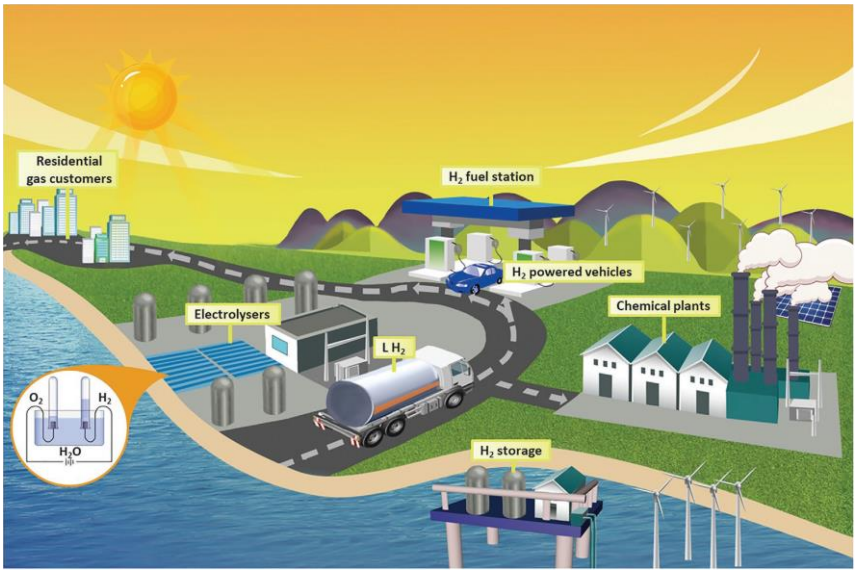

Figure 30: The blueprint of the future hydrogen economy society [64].

Clean hydrogen fuel can be produced by harvesting renewable sources (e.g., solar, wind, geothermal, and tidal energies) to split water, which can be further stored and used in ammonia production, petroleum refining, coke/iron production, fuel cell electric vehicles, and residential life as shown in **Figure 32** [64].

Water electrolysis involves passing a direct current through water to split its molecules into hydrogen and oxygen. This process takes place within an electrolytic cell, where two electrodes are immersed in an electrolyte to enhance ionic conductivity.

For optimal performance, the electrodes must be resistant to corrosion, exhibit high electrical conductivity, possess strong catalytic properties, and maintain structural integrity. The electrolyte should remain chemically stable throughout the process, ensuring it does not react with the electrodes. A crucial component of the electrolysis system is the diaphragm or separator, which prevents the recombination of hydrogen and oxygen produced at the electrodes. This separator must exhibit high ionic conductivity while also having sufficient electrical resistance to prevent short-circuiting. Additionally, it should maintain both physical and chemical stability under operating conditions.

Together, the electrodes, diaphragm, and electrolyte form the electrolytic cell, enabling the overall electrolysis reaction Eq (4.1) [65].

$$H_2O \rightarrow H_{2(g)} + (\tfrac{1}{2})O_{2(g)} \quad (4.1)$$

In a basic electrolysis cell, the following reactions take place:

In the electrolyte: $2H_2O \rightarrow 2H^+ + 2OH^-$ (4.2)

At the cathode: $2H^+ + 2e^- \rightarrow H_2$ (4.3)

At the anode: $2OH^- \rightarrow \left(\frac{1}{2}\right) O_2 + H_2O + 2e^- \; \Delta Hr = -285.6 \frac{KJ}{mol}$ (4.4)

Where ΔHr is the enthalpy of the reaction.

The anode is the electrode connected to the positive terminal of a power supply and the cathode is the one connected to the negative terminal of a power supply. This is an endothermic reaction because water is more stable than its elements, so energy must be added to split it [27].

Different electrolytes systems developed for water electrolysis include alkaline water electrolysis (AWE), proton exchange membranes (PEMs), alkaline anion exchange membranes (AEMs), and solid oxide water electrolysis (SOE). Different materials and operating conditions are used in these systems; however, the operating principles are the same. On the basis of different operating temperatures, low and high temperature water electrolysis are also possible.

4.1.1 Alkaline water electrolysis for hydrogen production

Alkaline water electrolysis is one of the most established and widely used methods for hydrogen production. It operates at relatively low temperatures (60–80°C) and utilizes an aqueous solution of KOH (potassium hydroxide) or NaOH (sodium hydroxide) as the electrolyte, with a concentration of approximately 20%–30%. The primary reaction and process to produce hydrogen from AWE are that

the hydrogen is generated at the cathode and oxygen at the anode. The leading product gases are separated by a diaphragm, in which OH^- and water are both penetrable from this media. The anode and cathodes are immersed in an electrolyte. Typically, an electrolyte is a liquid NaOH or KOH. Commonly used electrode materials are cobalt, iron, nickel, in which Ni is most widely used due to its superior electrocatalytic activity and accessibility with inexpensive cost [66].

Key Components and Characteristics:

- Electrodes: Typically made of nickel due to its corrosion resistance and good catalytic properties.
- Diaphragm: Usually asbestos, which separates the generated hydrogen and oxygen while allowing ion conduction.
- Hydrogen Purity: Around 99% but requires additional treatment to remove alkali fog (usually via desorption).
- Current Density: Operates at a maximum of 400 mA/cm^2.
- Energy Consumption: Requires approximately 4.5–5.5 kWh/Nm^3 of hydrogen produced.
- Efficiency: ≃60%.

Despite its relatively high energy demand and moderate efficiency, alkaline electrolysis remains a mature and commercially available technology for hydrogen production. Its main advantages include long operational lifetimes, low-cost catalysts, and scalability. However, it faces challenges such as low current density, slow response to load changes, and the need for large-scale hydrogen storage solutions. To avoid hydrogen/oxygen penetrating the porous asbestos diaphragm resulting in an explosion risk, the pressure between the anode and cathode sides must be balanced. Moreover, alkaline electrolyzers cannot start up quickly, and have a slow loading response. Long start-up preparation makes it difficult to adapt alkaline electrolyzers to the variable nature of renewable energy sources [67].

A Schematic diagram of alkaline water electrolysis (AWE) technique is provided in **Figure 33**.

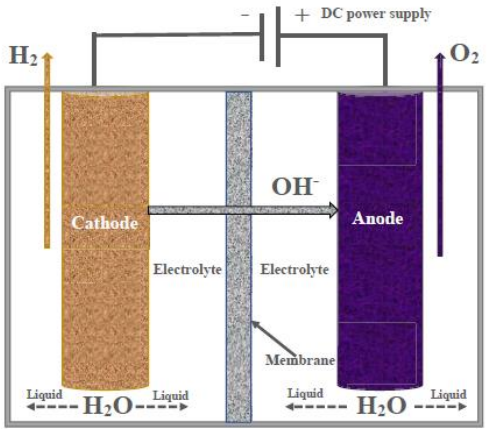

Figure 31: Schematic diagram of alkaline water electrolysis [66].

4.1.2 Solid-oxide electrolysis for hydrogen production (SOE)

Solid-oxide electrolysis (SOE) is an advanced hydrogen production technology that operates at high temperatures (500–1000°C), enabling highly efficient conversion of electrical energy into chemical energy. This process yields ultra-pure hydrogen and has the potential for integration with nuclear reactors due to its high operating temperature.

Key Features of SOE

- Electrolyte: Utilizes a solid ceramic electrolyte (such as yttria-stabilized zirconia, YSZ), which enhances durability and rapid response time.
- Operating Temperature: High temperature (500–1000°C) allows for improved reaction kinetics and lower electrical energy consumption.
- Operating Pressure: Can function at up to 3 MPa, making it suitable for industrial applications.
- Reaction Mechanism: Cathode Side: Water (H_2O) is reduced to form hydrogen (H_2) and oxygen ions (O^{2-}). Anode Side: Oxygen ions (O^{2-}) migrate through the solid electrolyte and are oxidized to produce oxygen gas (O_2).
- Advantages of SOE
    - High efficiency: The use of high temperatures reduces the electrical energy needed, boosting efficiency beyond 80% when integrated with waste heat recovery.
    - Ultra-pure hydrogen: The solid-oxide process minimizes impurities, making it ideal for fuel cell and industrial applications.
    - Integration potential: Can be coupled with nuclear reactors or renewable energy (e.g., solar or geothermal) to maximize efficiency.
- Challenges & Development Needs
    - High-temperature operation: Requires durable materials resistant to thermal stress and degradation.
    - Material limitations: Electrodes and electrolytes must withstand extreme conditions, requiring advanced ceramics.
    - Still under development: Further research is needed for commercial viability and cost reduction.[68]

The schematic diagram of SOE is shown in **Figure 34**

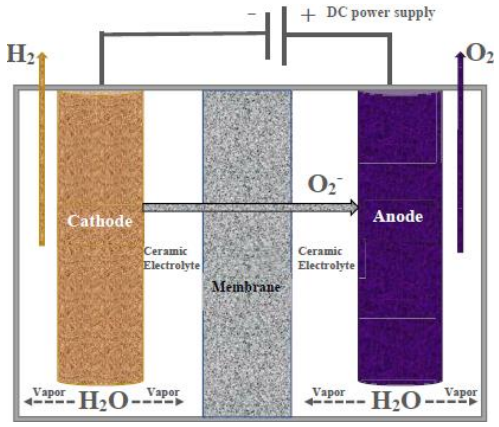

Figure 32: Schematic diagram of solid-oxide electrolysis (SOE)[66].

4.1.3 Proton exchange membrane electrolysis (PEME)

PEME, also known as polymer electrolyte membrane electrolysis, is a highly efficient method for converting renewable energy into pure hydrogen gas. It was first developed in 1966 to overcome the limitations of alkaline water electrolysis and has since become one of the most promising hydrogen production technologies.

Key Features of PEME

- Electrolyte: Uses a solid polymer membrane (such as Nafion) instead of a liquid electrolyte, which prevents gas mixing.
- Operating Temperature: 20–100°C, making it more efficient than alkaline electrolysis in dynamic operation.
- Operating Pressure: Can reach up to 40 MPa, reducing the energy needed for hydrogen compression.

Reaction Mechanism:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (Anode Reaction)} \quad (4.5)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \text{ (Cathode Reaction)} \quad (4.6)$$

- Advantages of PEME
  - High purity hydrogen: The membrane ensures gas separation, producing ultra-pure H_2.
  - Fast response time: Can quickly adjust to fluctuating energy inputs, making it ideal for renewable integration (solar, wind).
  - Compact design: Requires less space than alkaline electrolysis and can operate at higher current densities
  - Lower energy for compression: Produces hydrogen at high pressure (up to 40 MPa), reducing post-production compression costs.
- Challenges & Limitations

- Expensive materials: PEME requires platinum-group metal catalysts (e.g., Pt, Ir, Ru), increasing costs.
- Membrane durability: The polymer membrane degrades over time, requiring periodic replacement.
- Water purity requirement: Needs high-purity water to avoid contamination and performance loss.

Table 9. Comparison between Electrolysis Methods [68].

Feature	PEME	Alkaline Electrolysis	Solid Oxide Electrolysis (SOE)
Operating Temp.	20–100°C	60–80°C	500–1000°C
Electrolyte	Solid polymer membrane	Liquid KOH/NaOH	Solid ceramic
Efficiency	≃70–80%	≃60–70%	≃80–90%
Hydrogen Purity	Very high (99.99%)	High	Very high
Reaction Speed	Fast	Moderate	Slow
Cost	High	Low	High
Commercial	Medium	High	Emerging

4.1.4 Coupled Heat and Power Integration in High-Temperature Electrolysis Systems

The combination of heat and power to high-temperature electrolysis (HTE) systems is a major advance in the development of hydrogen production technology, a concept with a potential to maximize energy efficiency and flexibility of the electrochemical processes at thermodynamically advantageous conditions. High-temperature electrolysis is mainly based around the solid oxide electrolysis cells (SOECs) electrolysis cells, combining electrothermal energy sources to achieve high temperatures of around 800ºC. The electricity needed to split molecules of water is greatly decreased in this working regime, since much of the necessary enthalpy is provided in form of heat. The interconnection of HTE and thermal infrastructure is not only an efficiency increase in electrolysis, but also allows an advanced integration scenario, i.e., reuse of excess heat of power generation or industrial processes. The integration of heat and power into HTE platforms in this context is not just a replacement of energy input, but is part of the complex hybrid systems that can quickly switch between electricity generation, creation of hydrogen and heat recapture based on demand and the availability of resources on the grid.

A good example is that of the 25 kW HTE plant developed at the Idaho National Laboratory (INL) that was developed as an integrated hydrogen generator test bed using solid oxide electrolysis. Both stand-alone SOEC stack testing and full thermally and electrically combined systems with co-located energy systems can be tested in this facility. The capability of such facility on integration is

basis of study of dynamic grid interactions, flexibility in energy distribution and real time control strategies. The architecture of the facility incorporates a high-temperature furnace, a flexible steam production system, and an integrated hydrogen recycle loop that keeps feedstock requirements to a minimal as the plant supports the required reducing conditions in the SOEC cathodes. Within this system a hybrid operating paradigm is illustrated, where heat to drive steam generation is provided electrically and thermally, through a combination of an inductively heated steam generator and a thermal energy distribution system (TEDS). The latter will heat high-temperature heat transfer fluid (Therminol 66) circulating in the latter part of the installation, in order to indirectly produce the steam in a heat-exchanger. The method is an industry benchmark of coupled heat integration, allowing the replacement of large percentages of electrical supply with process heat arising as a byproduct of neighboring thermal plants, e.g., nuclear reactors, industrial waste heat.

The addition of a steam superheater to this design also underlines the need of accurate heat control. As a TEDS only provides steam which is only heated to about 275^{o}C a special superheater is needed to get the steam to the operation temperature of 800^{o}C needed to provide efficient working of the SOEC. The staged heating approach has these advantages besides the need to attain the required thermodynamic condition of working fluid; reduction of thermal stresses and operational safety. In addition, it allows utilization of low quality heat like that provided by intermediate-temperature processes, which is ordinarily not of high quality to use in high efficiency systems. With this interconnection, the plant shows the way in which co-located energy (thermal and electrical) providing can be dynamically adjusted according to the availability of the resources, economy costs, and system performance indicators.

Data on performance of test facility of 25 kW also confirm the technical feasibility of coupled heat and power systems. The SOEC stacks also showed a steady state during long-term operation and the degradation decreased drastically after 450 hours of the test. This allowed long-lasting electrochemical processes as nickel-ceria cermet cathodes and doped lanthanum cobalt ferrite anodes were adopted, and the affinity between the stack material thermal expansion coefficients allowed the life of the stack to be thermally cycled. The said materials and structural characteristics are of the essence to accommodate the variable thermal cycles that characterize the integrated systems and especially when the source of thermal input is variable systems of energy. It is worth mentioning that recycling of electrolytically produced hydrogen, compressed, dehydrated and returned to the system is an executional example of the closed loop energy design philosophy of high-efficiency HTE systems. The direct benefit of this strategy is that it would reduce the use of externally sourced hydrogen feedstocks, increase the system safety by allowing more control of gases and will add system autonomy.

A second study of importance to enhance this level of knowledge further is that high-temperature electrolysis can be applicable to tri-generation systems where hydrogen, heat, and electricity are produced at the same time. The system can be dynamically upsized or downsized to respond to electricity market signals, to the heat demands on the demand side, or to strategies of hydrogen storage by incorporating HTE in combined heat and power (CHP) systems. This three-generation paradigm highlights the inherent flexibility of SOECs that are capable of playing a role as a hydrogen producer as well as power generator depending on their system configuration and the operating mode. The system is scheduled to prefer production of hydrogen through electrolysis during times of low electricity prices, or when great amounts of renewable electricity (when renewable electricity is more than society needs) is present. However, at periods of high demand the system is able to run in fuel cell mode, thus converting previously stored hydrogen back into electricity, thus helping to balance the grid. This two-way capability that is inherent in dynamic energy systems exemplifies how electrochemical platforms might resolve time gaps between energy generation and usages.

Another thermal integration strategy as investigated in the paper is the method of preheating of feed gases using high temperature to raise the exhaust of the electrolysis process through recuperative heat exchange process. This recuperation also decreases the network input to the system and increases efficiency. Notably, the process heat replaces the latent heat of vaporization in traditional electrolysis that contributes more than 10 per cent of total electric energy consumed in the process. Such replacement drastically enhances the round trip effectiveness of hydrogen manufacturing more so in hybrid energy framework scenes where low cost or waste heat exists. An example is that in the case scenario where HTE is incorporated with the light water nuclear power plants or exothermic chemical processing units, the levelized cost of hydrogen is reduced significantly through the implementation of thermal integration. On this basis, high-temperature electrolysis, as a thermally integrated technology, becomes an extremely appealing alternative to producing low-Carbon hydrogen in large volumes, especially in areas with pre-existing infrastructure to support heat-intensive industry.

Additional test-facility and simulation results show that the design behavior of the system is aggregately strong over a wide variety of thermal inputs and operating regimes. Real-time optimization of integrated system behavior can be performed by means of dynamic simulation and control capability configured into the INL DETAIL infrastructure of integrated systems. Simulated coupling with virtual primary systems (like NuScale Integral System Test (NIST) facility) allows high-level experimentation of energy transfer and system response to external perturbation. With a programmable interface the control system is able to effectively reroute thermal energy to the steam generation system thus providing steady cases of electrolyzers operation during a variable thermal supply rate. The feature

allows a high degree of operating resilience, which is very important in the systems that are used in real-world operating conditions, in which energy supply and demand are unpredictable patterns.

In terms of engineering, the modular makeup of the 25 kW system, whose system input can increase to 250 kW, is one example of the design strategy that balances a desire to maintain experimental flexibility and potential commercial scaling. The capability of the system to alternate between the three possible modes of steam production (purely electric, thermally integrated or hybrid) provides a flexible solution on which one can test different integration options. Moreover, the interface of high-fidelity instrumentation located in the same place allows measurement of thermal flows, electrochemical performances, and gas mixtures with high precision and enables strict validation of the performance and possible calibration of models. Such data is essential in identifying techno-economic metrics which can be used to make decisions on the usage of HTE systems in the industrial and energy transition scenario.

Finally, the hybridization of heat and power in high-temperature electrolysis systems is the anchor point of the maturing of hydrogen technologies into increasing efficiency, expanded overall flexibility, and assimilation into large-scale energy systems. It does not only allow utilization of potentially wasted renewable and nuclear heat sources but also encourages synergies between the systems which also help the grid to gain more stability and almost achieve decarbonization objectives. The way forward is to reconsider the application of electrolysis not only as a solution to a single energy problem, but also as a part of a multi-vector energy system, which is being investigated at such facilities as the INL, and which now can serve as a roadmap to subsequent implementation. There are some opportunities to incorporate these systems with chemical production, thermal storage and smart grid management tools and as a result, it might be possible to optimize not only energy consumption but also economic value chains in many sectors.

The integration of electrical and thermal energy sources in high-temperature electrolysis systems creates a new paradigm in the production of hydrogen that is consistent with the more general aim of sustainability, resiliency, and economic efficiency. The two-fold advantage of improved thermodynamics and versatility of application, which has been seen through actual, live systems and testbeds, gives strong evidence as to the need to isolate and advance the coupled HTE technologies and their application. High-temperature electrolysis developed with the help of highly orchestrated system integration, responsive control schemes and novel heat management strategies will become a foundation of the future hydrogen economy [132, 133].

4.2 Electrocatalysts

Water electrolysis consists of two fundamental half-cell reactions: the hydrogen evolution reaction (HER), where water is reduced at the cathode to produce hydrogen (H_2), and the oxygen evolution reaction (OER), where water is oxidized at the anode to generate oxygen (O_2). A major challenge in this process is the high overpotentials required to overcome kinetic barriers, making electrolysis less energy-efficient. To address this issue, catalysts (electrocatalysts) play a crucial role in reducing energy losses and improving reaction rates, ultimately enhancing the efficiency of hydrogen and oxygen production.

There are three main types of electrolysis technologies, each with distinct catalyst requirements. Proton exchange membrane (PEM) electrolysis operates under acidic conditions, offering high efficiency, fast hydrogen production, and low gas permeability. However, it relies on noble metal catalysts such as IrO_2 and RuO_2 for OER and Pt-based catalysts for HER, making the technology expensive. In contrast, alkaline water electrolysis allows for the use of more cost-effective non-noble metal catalysts like nickel, cobalt, and iron-based compounds, but HER in alkaline media is significantly slower than in acidic conditions. Solid oxide electrolysis (SOE) is the most efficient of the three, operating at high temperatures (500–1000°C), which reduces electricity demand by utilizing thermal energy. However, it faces challenges related to high energy consumption, material degradation, and scalability. To make water electrolysis more viable, ongoing research focuses on developing low-cost, high-performance electrocatalysts, such as transition metal carbides, nitrides, and phosphides, as well as nanostructured and single-atom catalysts that improve both HER and OER efficiency.

For electrochemical water splitting reaction, the thermodynamic potential is 1.23 V at 25 °C and 1 atm. However, due to the kinetic barrier for the reaction, water electrolysis requires a higher potential than thermodynamic potential (1.23 V) to overcome the kinetic barrier. The excess potential is also known as overpotential (η) which mainly comes from the intrinsic activation barriers present on both anode and cathode. Overpotential is a very important descriptor to evaluate the activity of the electrocatalysts. Usually, the overpotential value corresponding to the current density of 10 mA/cm^2 is used to compare the activities among different catalysts. This current density corresponds to a 12.3% solar-to-hydrogen efficiency.

The Tafel slope and exchange current are two other parameters to assess the activity from the overpotential vs. kinetic current relationship, which is expressed by the equation: $\eta = a + b \log j$, where η is the overpotential, and j is the current density. In the Tafel plot, the linear correlation yields two important kinetic parameters. One is the Tafel slope b, and the other is the exchange current density j_0 which can be obtained by extracting the current at zero overpotential. The Tafel slope b is related to the catalytic reaction mechanism in terms of electron-transfer kinetics. For

example, a smaller Tafel slope means that there is a significant current density increment as a function of the overpotential change, or in other words, faster electrocatalytic reaction kinetics. The exchange current density describes the intrinsic charge transfer under equilibrium conditions. A higher exchange current density means a greater charge transfer rate and a lower reaction barrier. A lower Tafel slope and a higher exchange current density are expected for a better electrocatalyst.

4.2.1 Noble based electrocatalysts (HER)

Noble metals, such as Pt group metals (PGMs, including Pt, Pd, Ru, Ir, and Rh) show outstanding catalytic performance for HER. Pt ranks at the top of the volcano curve. However, the commercial application of these noble-metal based catalysts is hindered by their scarce storage and high cost. To overcome this challenge, a rational design of catalysts with low metal loading and high metal utilization is necessary. Alloying Pt with transition metal can significantly improve the Pt utilization and the synergistic effect of alloy could modify the electronic environments which significantly promote the HER electroactivity. Sun et al. reported in situ growth of ultrafine PtNi nanoparticle decorated Ni nanosheet array on carbon cloth (PtNi-NiNA/CC) with ultralow loading Pt content (7.7%) which show better HER activity with low overpotential 38 mV in 0.1 M KOH at the current density of 10 mA cm^{-2} than the benchmark Pt/C (20%). Remarkably, it also shows long-term durability with a 90 h catalytic activity test. As a benchmark for Pt electrocatalyst, the activity of HER in alkaline media is usually lower than the activity of HER in acidic media. The reason is the water dissociation on the Pt surface is inefficient which results in poor HER activity. To this end, coupling Pt with water dissociation promoters is the commonly used strategy to boost the alkaline HER activities [69].

Table 10 lists some of the recent examples of studies in developing effective catalysts for HER. These catalysts are compared in terms of the electrocatalytic performance and kinetic parameters under different reaction conditions.

Table 10. Summary of the HER performance of the reported electrocatalysts [69].

Catalysts	Electrolyte	η (mV)	I (mA/cm^2)	Tafel Slope	Stability
PtNi–Ni NA/CC	0.1 M KOH	38	10	42	90h
PtNi–O/C	1 M KOH	39.8	10	78.8	10h
PtNi(N) NW	1 M KOH	13	10	29	10h
Mo_2C-R	1 M KOH	200	30	45	-
Mo_2C-GNR	0.5 M H_2SO_4	167	10	63	3000 cycles
Ni_2P/Ti	0.5 M H_2SO_4	130	20	46	500 cycles
$NiCo_2Px$	1 M KOH	58	10	34.3	5000 cycles
Defect-rich MoS_2	0.5 M H_2SO_4	200	13	50	10,000s
CoS_2 NW	0.5 M H_2SO_4	145	10	51.6	3 h
CoS_2 MW	0.5 M H_2SO_4	158	10	58	41 h
Oxygenated MoS2	0.5 M H_2SO_4	120	Onset	55	3000 cycles

4.2.2 Non-precious metal HER electrocatalysts

The most promising transition metals for hydrogen evolution reaction (HER) catalysts include Fe, Ni, Cu, Mo, the electrocatalytic properties of non-precious metals using a voltametric method, ranking them in the order of Ni > Mo > Co > Fe > Cu for HER performance. Among these, nickel demonstrated superior HER activity in alkaline solutions, making it a widely studied material for non-precious metal catalysts. Additionally, cobalt-based electrocatalysts have shown promising performance in water electrolysis. These non-precious metals offer a viable alternative to expensive noble-metal catalysts, addressing the cost limitations associated with commercial HER applications.

However, while non-precious catalysts are more abundant and cost-effective, they face challenges such as corrosion in strong acidic and alkaline environments and particle aggregation during long-term electrocatalytic cycling. The HER mechanism typically follows either the Volmer-Heyrovsky or Volmer-Tafel pathway, depending on the reaction medium. In the Volmer reaction, a hydrogen atom is adsorbed onto the catalyst surface. This intermediate hydrogen can then either combine with a proton and an electron to form H_2 in the Heyrovsky step or directly recombine with another adsorbed hydrogen atom in the Tafel step. Understanding and optimizing these reaction pathways are essential for enhancing the efficiency and durability of non-precious metal HER catalysts [66].

A schematic diagrams for Volmer step and Heyrovsky step of HER reaction. (a-b) a water molecule attacks the catalyst surface and then dissociates, leaving an adsorbed hydrogen atom and a hydroxyl group. (c-d) Another water molecule attacks the adsorbed hydrogen and form a hydrogen molecule and one more hydroxyl group as shown in **Figure 35**.

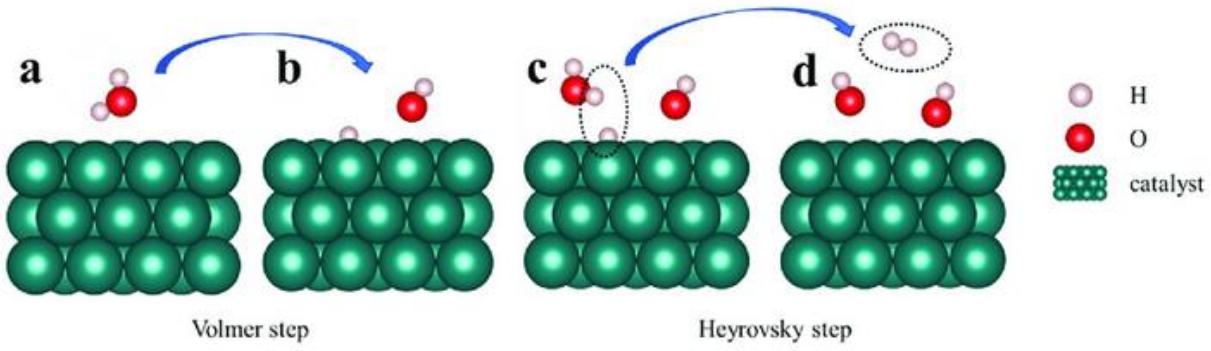

Figure 33: Schematic diagrams for Volmer step and Heyrovsky step of HER reaction

4.2.3 Noble based electrocatalysts (OER)

There are two main types of OER electrocatalysts, noble-metal based electrocatalysts, and non-noble metal based electrocatalysts. For the noble metal based electrocatalysts, Ru and Ir-based catalysts are considered as the state-of-the-art electrocatalyst for OER, especially in the acidic

electrolyte, which has a larger dissolution resistance compared with other metals. To reduce the high price, improve the electrocatalyst activity, stability, and even enforce the dissolution resistance in acidic media, there are several strategies to engineer and optimize the catalyst composition, structure, and morphology. Other than Ir and Ru, other noble metals such as Rh, Au, Pt, and Pd-based catalysts have also been developed as bi- or tri-functional electrocatalysts which show promising performance for OER, HER, and oxygen reduction reaction (ORR) [70].**Table 11** lists some selected OER electrocatalysts in terms of their performance descriptors.

Table 11. Summary of the OER performance of the reported electrocatalysts [69].

Catalysts	Electrolyte	η(mV)	I(mA/cm^2)	Tafel Slope (mV/dec)	Stability
Cu-doped RuO_2	0.5 M H_2SO_4	188	10	43.96	10.000 cycles
IrNi NPNW	0.1 M $HClO_4$	283	10	56.7	200min
IrCo NPNW	0.1 M $HClO_4$	295	10	60.3	-
IrFe NPNW	0.1 M $HClO_4$	302	10	68.5	-
IrNiCu DNF	0.1 M $HClO_4$	300	10	48	2500 cycles
IrO_2 NN	1M H_2SO_4	313	10	57	200 h
$Au_{40}Co_{60}$NPs	0.1 M KOH	175	10	65	1h
G-FeCoW	1 M KOH	191	10		500h
Plasma-engraved CO_3O_4	0.1 M KOH	153	10	68	2000 cycles
NiFe-LDH NPs	0.1 M KOH	151	30	50	10h
$Ni_{0.83}Fe_{0.17}(OH)_2$	1 M KOH	245	10	61	10h
$Ni_xFe_{1-x}Se_2$-DO	1 M KOH	195	10	28	24h

4.2.4 Non-precious metal OER electrocatalysts

Efforts to develop efficient noble-metal-free OER electrocatalysts have focused on optimizing material properties such as texture, composition, morphology, and intermediate binding energies through doping and hybrid structures. A key strategy has been the investigation of transition metals and their compounds as alternatives to noble-metal-based catalysts.

Transition metal compounds, including Fe, Co, and Ni, are widely available, cost-effective, corrosion-resistant, and highly effective as OER electrocatalysts in alkaline solutions. Research by Huang et al. has shown that Ni-based compounds are particularly promising, while Jiang et al. found that the catalytic performance of transition metals follows the trend: Ni > Co > Fe.

Ni-based OER catalysts exist in various forms, such as nickel oxides (NiO), nickel hydroxides ($Ni(OH)_2$), nickel phosphides (NiP), nickel sulfides (NiS), iron-nickel alloys (Ni_3Fe), nickel-iron oxides (NiFe oxides), nickel-iron hydroxides ($NiFe(OH)_2$), nickel cobaltite ($NiCo_2O_4$), and nickel cobalt oxides ($NiCoO_2$).

Additionally, Zhang et al. studied Co-based electrocatalysts for OER in water splitting, demonstrating the electrochemical performance of various cobalt compounds, including cobalt oxides (Co_xO_y),

cobalt sulfides (Co_xS_y), cobalt phosphides (Co_xP_y), cobalt nitrides (Co_xN), and cobalt selenides (CoSe). These findings highlight the potential of transition-metal-based materials in replacing noble metals for OER applications [66].

4.3 Cost-profit analysis of Green Hydrogen

The cost of green hydrogen remains significantly high, reaching up to 15 Euros per kilogram, compared to fossil fuel-based hydrogen production, which historically costs around 1–2 Euros per kilogram. The primary reason for this price gap is the high capital investment required for electrolyzers, along with uncertainties in their future development and cost reduction through scaling and technological advancements. Given these economic challenges, comprehensive cost assessments are necessary to evaluate the current production costs of green hydrogen and to predict when cost parity with gray hydrogen might be achieved.

Additionally, environmental assessments are crucial to verify whether green hydrogen—produced exclusively from renewable electricity in autonomous system configurations—truly results in low greenhouse gas (GHG) emissions. While green hydrogen has the potential to significantly reduce carbon footprints, large-scale deployment may come with trade-offs, such as land and resource use, that need to be carefully analyzed. Understanding these economic and environmental factors is essential for the long-term viability and widespread adoption of green hydrogen as a sustainable energy source.

Future large-scale green hydrogen production could approach environmental boundaries regarding material utilization and land transformation. Second, hydrogen production costs and environmental burdens were usually quantified with static electricity prices and capacity factors, applied to wind and PV electricity generation. Lastly, the assessment of large-scale hydrogen production hubs at favorable hydrogen production locations—such as geographical islands and coastal areas—is currently missing.

4.3.1 Hydrogen production: technologies and system configurations

Different configurations have been explored for hydrogen production, with most literature focusing on smaller systems capable of producing only a few hundred kilograms to several tones of hydrogen per day. However, for large-scale deployment, cost-effective production methods must be prioritized while also considering potential limitations such as material utilization and land transformation. A common goal among these configurations is the production of approximately 10 tons of hydrogen per day, which represents an intermediate scale—higher than most existing techno-economic studies but lower than traditional large-scale hydrogen production methods.

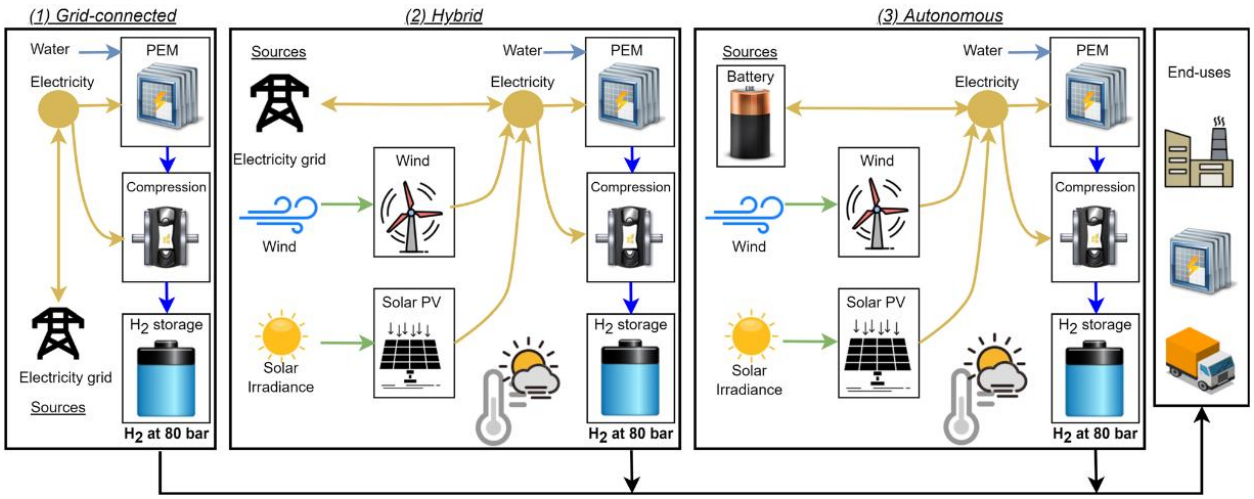

Figure 34: Hydrogen Production Configurations 1) grid-connected, (2) hybrid, and (3) autonomous [71].

To support the transition toward large-scale hydrogen production, a cradle-to-gate analysis is conducted to assess the feasibility of supplying hydrogen at the production gate. The system boundaries include the production of all components necessary for generating and delivering hydrogen at a pressure of 80 bar. This approach ensures a comprehensive evaluation of material, energy, and cost factors, ultimately contributing to the development of more efficient and scalable hydrogen production technologies. The three considered hydrogen production configurations are explained in the following sections and are visualized in Figure 36.

A polymer electrolyte membrane (PEM) electrolyzer is utilized for hydrogen and oxygen production from water, offering several advantages such as operational flexibility, rapid response times, and quick start-up capabilities. These characteristics make PEM electrolyzers particularly suitable for integration with intermittent renewable energy sources, ensuring efficient hydrogen production even with variable power inputs. Due to their adaptability and performance, PEM electrolyzers are the preferred choice in those configurations, supporting the transition to sustainable hydrogen production at a larger scale.

The grid-connected configuration involves an electrolyzer that is directly linked to the national electricity grid. This setup is chosen primarily because selected European locations have access to their respective electricity grids. The capacity of the electrolyzer is determined based on the targeted hydrogen production rate and an optimization problem. An energy management system regulates the amount of electricity purchased for hydrogen production, ensuring a consistent daily output of 10 tons of hydrogen. Once produced, the hydrogen is stored in a pressure tank with a one-day storage capacity at 80 bar pressure, facilitating a stable and continuous supply.

The hybrid configuration integrates both a grid connection and a direct link to renewable energy sources, such as photovoltaic (PV) solar, onshore wind, and offshore wind electricity. This

setup is designed to take advantage of low-cost renewable energy while using the electricity grid as a backup for storage and supply. By leveraging the grid during periods of low or even negative electricity prices, the system ensures continuous electrolyzer operation, thereby reducing the necessary installed capacity. This hybrid approach has the potential to lower both costs and environmental impacts, particularly when connected to a low greenhouse gas (GHG) intensive electricity grid. An optimization model determines the ideal balance between electrolyzer capacity and renewable generation, ensuring hydrogen is produced at the lowest possible annualized cost or with minimal life cycle GHG emissions. However, the installation of PV or wind generators is not mandatory and depends on the specific site conditions.

The autonomous configuration operates independently from the electricity grid, relying entirely on locally available renewable energy sources such as photovoltaic (PV) panels, onshore wind, and offshore wind turbines. This setup is particularly suited for geographical islands or remote locations where access to the national electricity grid is unavailable. In this scenario, the electrolyzer is powered exclusively by renewable electricity, ensuring a self-sufficient hydrogen production system. However, one challenge of this configuration is the potential curtailment of renewable electricity to balance power supply and demand. This could lead to wasted renewable energy and the need for oversized energy technologies to ensure consistent hydrogen production [71].

4.3.2 Economic Assessment

We include all costs during the lifetime of the different system configurations. To achieve this, investments, operation costs, fixed operation & maintenance as well as replacement costs are considered in this cost assessment.

The cost analysis for hydrogen production includes three scenarios: pessimistic, average, and optimistic. These scenarios represent different cost projections based on variations in technology and grid costs. The optimistic scenario assumes the lowest costs for technology and electricity, reflecting potential advancements and economies of scale. Conversely, the pessimistic scenario represents the highest costs, accounting for possible challenges such as expensive grid electricity and slower technological progress. The average scenario provides a balanced estimate between the two extremes. The costs can be expressed mathematically as:

$$CH_2 = \frac{C_{inv,an}+C_{op}+C_{om}+C_{rep,an}}{MH_2} \quad (4.7)$$

Where MH_2 represents the total annual hydrogen production the $C_{inv,an}$ the annualized investment costs, the C_{op} includes the operational costs, including potential revenues from grid electricity

injection. The C_{om} accounts for fixed operation and maintenance costs and lastly the $C_{rep,an}$ represents the annualized replacement costs.

By dividing the total annual costs by the total annual hydrogen production, this economic indicator provides insight into the cost competitiveness of different hydrogen production configurations [71].

Another method presented for the cost estimation of H_2 production is the presented below.

The net present value (NPV) calculation accounts for the time value of money by discounting all expected future cash flows to their present value. This approach allows for an accurate assessment of a project's financial viability over its lifetime. The NPV is determined by summing the discounted cash flows from the plant's operation while considering a given discount rate. A positive NPV indicates that the project is financially feasible and expected to generate profit, whereas a negative NPV suggests that the costs outweigh the benefits, making the investment less attractive.

Similarly, the levelized cost of hydrogen (LCOH) is an essential economic indicator that measures the cost per kilogram of hydrogen produced over the entire plant lifecycle. It accounts for capital expenditures, operational and maintenance costs, energy expenses, and replacement costs, ensuring a comprehensive financial evaluation of hydrogen production systems. By comparing LCOH across different production methods and scenarios, investors and policymakers can identify the most cost-effective and sustainable hydrogen production pathways.

$$NPV = \sum_{n=0}^{N} \frac{CF_n}{(1+r)^n} = \sum_{n=1}^{N} \frac{CF_n}{(1+r)^n} - I_0 \quad (4.8)$$

where *N* is the project period in years, CFn is the net cash flow at operating year *n*, I_0 is the capital expenditure (CAPEX), and *r* is the discount rate or calculating a change in cash value, which typically applies 4–9% to energy industry facilities. The discount rate reflects the opportunity cost of the invested capital, the project's riskiness, and the inflation level.

The net present value (NPV) serves as a crucial metric for assessing business feasibility, indicating whether a project is financially viable. When the NPV is positive, it suggests that revenues exceed expenditures, making the project a worthwhile investment. Additionally, the point at which NPV turns positive can be used to estimate the payback period, which is essential for investors to gauge the time required to recover their initial investment. NPV also aids in comparing multiple investment opportunities, helping investors select the most profitable option.

However, NPV alone does not fully account for differences in investment sizes across projects. To address this limitation, the internal rate of return (IRR) is often analyzed. The IRR is the discount rate at which the NPV becomes zero, meaning that the project breaks even in terms of discounted cash flows. A higher IRR indicates a more attractive investment, as it reflects a greater return relative to

the cost of capital. The IRR is particularly useful when comparing projects with varying scales of investment, providing a normalized measure of profitability.

The IRR can be derived as follows:

$$\sum_{n=0}^{N} \frac{CFn}{(1+IRR)^n} = 0 \tag{4.9}$$

The internal rate of return (IRR) must exceed the discount rate for a project to generate revenue, making it a key indicator of investment competitiveness. A higher IRR suggests a more financially attractive project, as it implies greater profitability relative to the investment cost. While NPV remains the primary factor for evaluating economic feasibility, incorporating IRR analysis allows for more effective comparisons between projects, enabling better decision-making.

In addition to NPV and IRR, the levelized cost of hydrogen (LCOH) serves as a crucial metric for assessing the overall cost-effectiveness of hydrogen production. LCOH is calculated based on the defined cost and revenue components, providing a comprehensive measure of the cost per unit of hydrogen over the project's lifetime. This metric helps investors and policymakers determine the economic viability of hydrogen production technologies and compare them with alternative energy sources.

$$LCOH = \frac{TotalLifetimeCost}{TotalLifetime H_2 Production} = \frac{CAPEX + \sum_{n=1}^{N} \frac{OPEX_n}{(1+r)^n} + TR \sum_{n=1}^{N} \frac{REVH_n}{(1+r)^n}}{\sum_{n=1}^{N} \frac{MH_2(1-SRD)^n}{(1+r)^n}} \tag{4.10}$$

where *SRD* is a degradation rate that accounts for a loss of hydrogen production efficiency.

This study aims to determine the most cost-effective method for producing green hydrogen by conducting a techno-economic analysis of four different water electrolysis technologies: alkaline water electrolysis (AWE), proton exchange membrane electrolysis (PEMEC), solid oxide electrolysis with electric heaters (SOEC (E.H)), and solid oxide electrolysis combined with a waste heat source (SOEC (W.H)). Each of these technologies has unique advantages and challenges in terms of efficiency, cost, and feasibility for large-scale hydrogen production.

The analysis considers factors such as capital investment, operational costs, energy efficiency, and integration with renewable energy sources. While AWE and PEMEC are well-established technologies with lower initial costs, SOEC systems, especially when combined with waste heat, offer higher efficiency but require higher upfront investments. The study aims to provide insights into which of these methods offers the best balance between cost-effectiveness and sustainability for large-scale green hydrogen production.

The study calculated the cost of producing 1 kg of hydrogen using different electrolysis technologies in a 1 MWel plant. The costs were found to be $7.60 for AWE, $8.55 for PEMEC, $10.16

for SOEC (E.H), and $7.16 for SOEC (W.H). Among these, SOEC combined with waste heat (SOEC (W.H)) proved to be the most economical option.

According to the NPV analysis, when hydrogen is sold at $7.50, $8.00, and $9.00 per kg, the SOEC (W.H) case consistently generated profit. In contrast, AWE and PEMEC only became profitable at $8.00 and $9.00 per kg, respectively, while SOEC (E.H) never reached a positive NPV even at the highest price. The U.S. Department of Energy (DOE) has set a target production cost of $5/kg$H_2$ to meet a supply price of **$10/kg$H_2$.** To achieve this, electricity costs must be reduced by more than half, and if both electricity costs and taxes are cut in half, production costs would fall below $5/kg$H_2$ for all cases except SOEC (E.H). In the long term, significant reductions in investment costs will be necessary to make green hydrogen production more viable [72][73].

4.4 Transition Metal Phosphides (TMPs) and Nitrides as Low-Cost HER/OER Catalysts

4.4.1 Cobalt-Based Phosphides with Tailored Morphology

Of interest as promising alternative materials to noble metal based catalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are transition metal phosphides (TMPs) such as nickel phosphide (Ni_2P) & cobalt phosphide (CoP). Of these, cobalt based compounds have attracted much attention because of their abundance, stability and high intrinsic activity at various pH values. As per the doctoral research work done by Kakkarakunnel Jose Vishal [74], hollow ternary $NiCo_2Px$ electrocatalysts modified at surface showed unparalleled bifunctional catalytic performance for water splitting in acidic, neutral and alkaline electrolyte. In the study, controlling the catalyst morphology, introducing multi-branched, spike covered hollow structures was found to greatly increase density of exposed active sites, which in turn increased overall catalytic activity.

In particular, two other types of surface morphologies were synthesized: one of them consisting of smooth spherical particles, and the other consisting of branched spike covered hollow spheres. The ECSA was higher for the latter, which along with improved charge transfer kinetics was primarily attributed to its morphological superiority. Electrochemical tests show that an overpotential of 170 mV for HER and 390 mV for OER was achieved in 1 M KOH with favorable Tafel slopes for the optimized $NiCo_2Px$ catalyst. In addition, this catalyst showed stable performance in an alkaline electrolyzer setup [74] with only 10 mA/cm² degradation over 50 hr (no collapse), which is noticeable as this catalyst ran for 1000 continuous cycles.

However, the origin of the enhancement in bifunctional activity was attributed not only to the increase in surface area, but also to synergistic interactions between nickel and cobalt within the phosphide matrix. It is anticipated that cobalt inclusion would enhance conductivity and

improve electron transport and nickel inclusion will enhance HER kinetics, especially in alkaline environments. These results present that careful management of the morphology and elemental composition of the TMPs can have a big impression on the electrocatalytic exercise, and subsequently, create them a powerful prospect for cost effective and environment pleasant water electrolysis functions.

4.4.2 Transition Metal Nitrides: Structure and Activity Insights

Among the transition metal nitrides (TMNs), molybdenum nitride (MoN) and vanadium nitride (VN) have been studied in detail due to their capacity for use in place of noble metal catalysts in electrochemical energy conversion systems. As stated by Zheng et al [75], nitrogen atoms are located in interstitial sites with metallic lattice in TMNs, and those have unique electronic structure. Here we show that this configuration increases the metal-metal atomic spacing, changes the d-band center, and increases the Fermi level density of the material to improve adsorption characteristics and catalytic activity. Importantly, these changes make the TMNs' surface character very close to the properties of platinum group metals such as their ability to enhance processes such as HER and OER.

Zheng et al. [75] reviewed that nanostructuring of TMNs could further improve the performance by elevating surface area and exposing more active sites. However, synthesis of highly porous TMN structures by nitriding transition metal oxides (TMOs) or by MOF derived nitrides has been enabled by various synthesis strategies. In these nanocrystalline materials, conductivity and corrosion resistance improve to this harsh reaction condition. Mesoporous Mo_3N_2 nanowires prepared from MoO_3 precursors treated using ammonia were found to be highly active and stable as an electrocatalyst due to their porosity and large surface area [75].

Additionally, TMNs enjoy robust chemical strength and tolerance against poisoning effects associated with poisoning in precious metal based system. TMNs including TiN, VN, and Mo_2N have been proved capable of applied to HER/OER in both acidic and alkaline circumstances with good onset potential, current density, and stability. Recent progress in co-doping and heteroatom substitution of multi-metallic TMNs leading to fine tuning of electronic structure and the promotion of metal center synergies was also highlighted by the review. This strategy enhances reaction kinetics and also long term durability and makes TMNs viable candidates for next generation low cost electrolysis systems [75].

4.4.3 Single-Atom Catalysts and Composition-Tuned TMP Systems

Recent advances in the design of catalysts have been, in particular, in the realm of atomically engineering the catalyst structure, by using very fine details such as single atom catalysts. These materials maximize the utilization of atoms, which means that the need to use the least amount of metal material necessary can be substantially improved while still retaining or even improving the catalytic performance. Fang et al. [76] studied a composition tuning strategy for developing a quaternary $Co_{0.7}Ni_{0.3}S_{0.5}Se_{1.5}$ electrocatalyst with outstanding bifunctional activity for both HER and OER. Structural reorganization and electronic tuning of incorporating Ni and S into $CoSe_2$ matrix not only led to more catalytically active sites exposed, but also enhanced the material's intrinsic conductivity.

For HER and OER, the optimized CoNiSSe composition (x = 0.3) offers reaction kinetics and achieves Tafel slope of 42.1 mV dec and 65.5 mV dec, respectively. The enhanced performance was rationalized to be due to synergistic interactions between the doped Ni and S atoms that tunneled the electron density around the cobalt centers. In addition, as a benefit of the flower like network structure of the catalyst, the electrolyte penetration and gas diffusion were efficient, and this was favorable to the observed enhancement of catalytic activity and stability. It showed little degradation under long-term cycling tests [76].

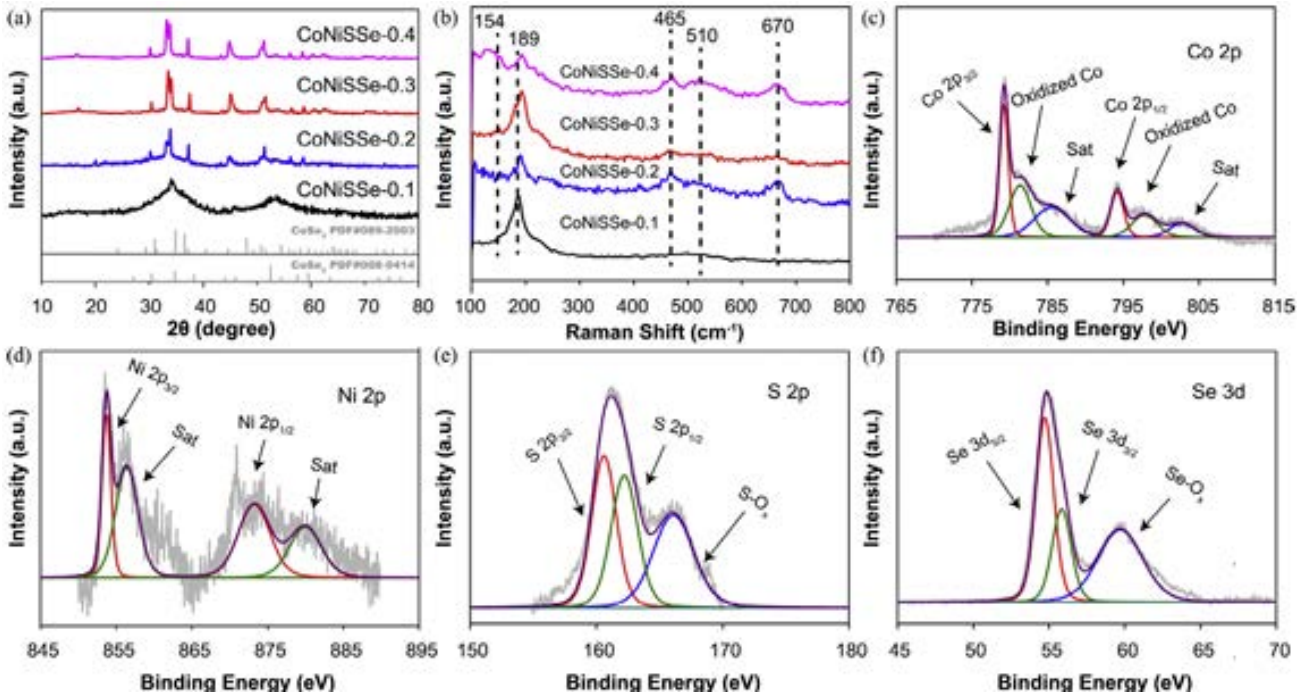

Figure 35: Structural and spectroscopic characterization of $Co_{0.7}Ni_{0.3}S_{0.5}Se_{1.5}$. XRD (a) and Raman (b) spectra confirm phase formation and vibrational modes across various compositions. High-resolution XPS spectra of the Co 2p (c), Ni 2p (d), S 2p (e), and Se 3d (f) regions for CoNiSSe-0.3 reveal the oxidation states and bonding environments of the elements [76].

Finally, this study also focused on the role of electronic structure tuning for optimizing catalytic activity. Through the application of electrochemical impedance spectroscopy (EIS), shifts in binding energies, charge transfer resistance, and so on, were verified, from X-ray photoelectron spectroscopy (XPS), to confirm heteroatom doping. This is confirmed by structural and spectroscopic analyses in **Figure 37**, consisting of XRD, Raman and high-resolution XPS spectral characterizations to indicate the phase purity, lattice vibrational modes and elemental chemical states of the $Co_{0.7}Ni_{0.3}S_{0.5}Se_{1.5}$ system.

In addition, structural characterization indicates a cubic pyrite type lattice that is both electronically suitable and allows for active site exposure. Thus, the $CoSe_2$ system decorated with Ni and S epitomizes how a composition tuned TMPS may lead to high performance electrocatalysts competitive in performance with precious metal counterparts.

Parallel research on SACs made from the support of a carbon based matrix shows that isolated cobalt or nickel atoms anchored on nitrogen doped carbon can replicate the coordination environment of active sites found in noble metal catalysts. Besides the reduction of metal usage, these systems also improve the catalyst selectivity and stability, which are two major challenges in today's HER/OER catalyst development.

4.5 Metal-Organic Frameworks (MOFs) and Derivatives in Electrolysis

4.5.1 MOFs as Precursors for Porous Carbon-Based Metal Catalysts

Due to their tunable composition, highly porous structure and structural versatility, metal–organic frameworks (MOFs) have been investigated as precursors for advanced electrocatalysts. The system possesses a unique framework made of metal nodes that are linked with organic linkers, and presents an approach towards controlled transformation into catalytically active species embedded in carbon based materials. Recently, considerable effort has been devoted to utilize MOF pristine or after transformation to metal/carbon hybrid nanostructures that possess promising electrocatalytic activity for hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR).

From a work of Wang et al. [77], carbon based metal catalysts from MOF have high conductivity, large specific surface area but optimal exposure of active sites critical for efficient electrochemical reactions. Pyrolysis of MOFs results in formation of the metal centers as nanoparticles or single atoms anchored in excess carbon matrix which serves as a matrix for nitrogen or other heteroatom doping from the organic linkers. We schematically illustrate the MOFs to single

atom and metal nanoparticle embedded in a carbon framework via pyrolysis in **Figure 38**, and then apply them to various electrocatalytic applications.

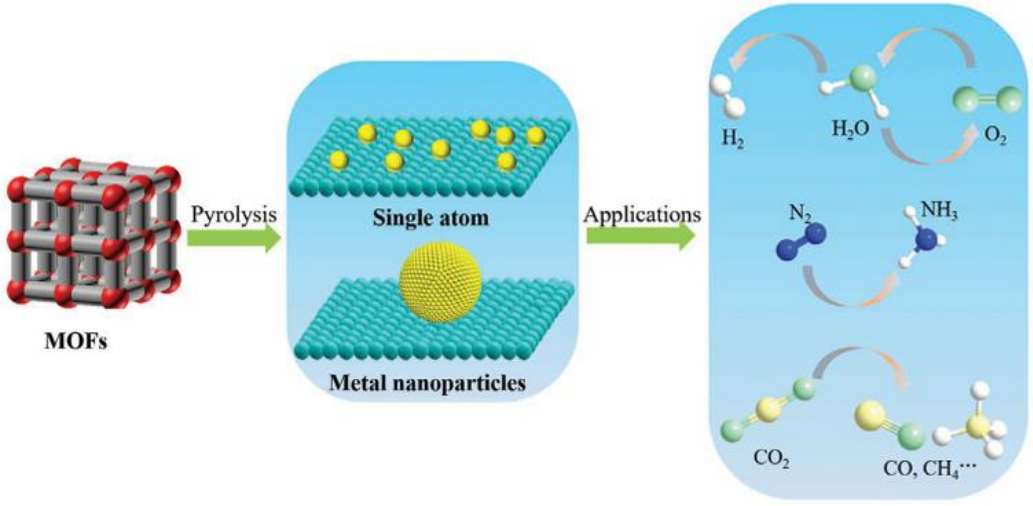

Figure 36: Schematic illustration of the design and application of MOF-derived electrocatalysts. Pyrolysis of MOFs produces single atoms or metal nanoparticles anchored on conductive carbon matrices, enabling efficient HER, OER, ORR, and other energy-related catalytic reactions [77].

Through this strategy, single atom catalysts (SACs) which are characterized by highly efficient metal utilization and atomically dispersed active center can be made. The authors emphasize that metal ions spatial arrangement in MOFs are exactly placed within the framework that makes them perfectly suitable precursors for yielding such SACs, with the investigations of transition metals (Co, Fe, and Ni) being the most frequently established.

Moreover, the MOF derived electrocatalysts are not restricted to formation of nanoparticles. Researchers have been able to control the morphology of the resulting carbon matrix through sacrificial templates or through gas-migration synthesis methods to provide hollow nanospheres, 1D nanotubes, or other morphologies by optimizing mass transport and access to active sites during catalytic operation [77]. This represents a major step forward in the rational design of the low cost and efficient HER or OER catalytic materials, in both acidic media and alkaline media.

4.5.2 Tunable Conductivity and Charge Transfer in MOFs

Nevertheless, because of their structural advantages, one of the inherent limitations in pristine MOFs for direct utilization as electrocatalysts is their poor electrical conductivity. In principle, various strategies have been employed by researchers to address this issue through intrinsic and extrinsic modifications of MOFs to increase their electronic conductivity. According to Saha et al. [78], MOF conductivity can be improved by utilizing redox active ligands, extended π-conjugated systems, mixed-valence metal centers, or by guest metal nanoclusters or conducting polymers.

Conductive MOFs are divided into the intrinsically conductive and the extrinsically conductive types by the authors. **Figure 39** illustrates the graphical representation of these enhancement strategies of MOF's conductivity based on intrinsic (e.g. redox active ligands, extended conjugation) and extrinsic (e.g. conjugation polymer modification, π–π stacking guest) traits.

Figure 37: Schematic representation of intrinsic and extrinsic strategies for enhancing the electrical conductivity of MOFs. The left side highlights molecular-level design approaches, including redox-active ligands, mixed-valence cations, and soft donor atoms. The right side illustrates extrinsic methods such as π–π stacking, conducting guest molecules, and incorporation of metal nanoclusters. Color code: C = gray, S = yellow, Se = pink, N = blue, O = red, Cl = green [78].

The former transport is charged dependent through the framework itself by included mechanisms, through bond or through layer, while the latter transport is charged independent involving conductive guest in the porous matrix. For example, the soft donor atoms sulfur and selenium have been used in concert with transition metals to promote better metal–ligand orbital overlap and hence through bond charge transport.

Additionally, additional levers for modulating conductivity are also available such as redox hopping and dimensional control (1D, 2D, or 3D architectures). Using experimental evidence, the study shows that conductivity can be substantially improved by adjusting the metal-to-ligand ratio or using a mixed ligand system in order to design MOF derived materials which can operate at industrially relevant current densities [78]. These results highlight this need of tuning electronic properties of MOFs for their use in devices for electrocatalysis.

4.5.3 MOF-Derived Electrocatalysts for Oxygen Evolution Reaction (OER)

In terms of the oxygen evolution reaction, when applied as electrocatalysts, MOF derived materials have shown auspicious promise owing to their structural flexibility and compositional

availability. **Figure 40** shows the framework structure of MOFs which originates from the fact that metal ions and organic linkers assemble to form highly ordered frameworks through coordination bonding.

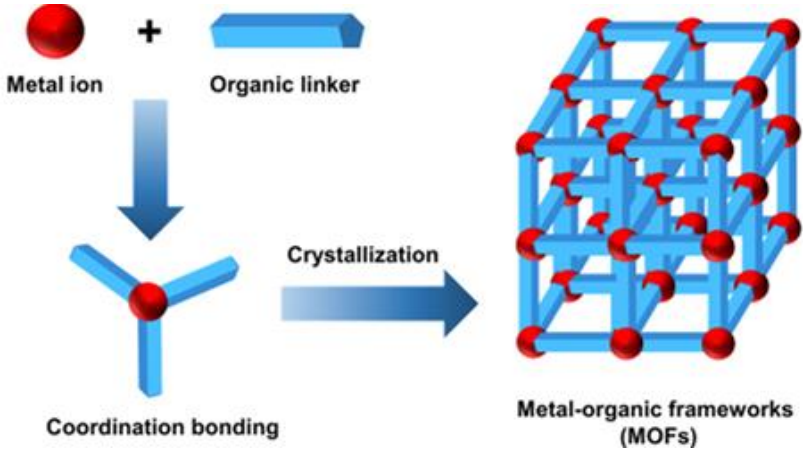

Figure 38: Schematic representation of the fundamental formation process of metal–organic frameworks (MOFs), involving the coordination of metal ions and organic linkers into crystalline porous networks [79].

According to Qin et al. [79], MOFs present as excellent templates to generate a series of multimetallic. By applying different thermal treatments under particular atmospheres, researchers can alter the transformation from the MOF to the active species of Co_3O_4, CoP, or $CoSe_2$, each of which has both high activity and high stability in alkaline OER.

In the end, there are several examples provided, such as MOF-derived Co_9S_8/N, S co-doped carbon nanofibers and ZIF-67 derived CoS_2 nanosheets, with low overpotentials and superior cycling stability. A significant strategy relates to the preparation of actiniae like carbon nanotube arrays that possess a large surface area and hierarchical porosity for improving the catalytic kinetics and gas evolution during OER. Meanwhile, the authors stress that using MOFs as precursors affords accurate control over the final catalysts morphology and elemental composition factors, which are requisite to controlling the electronic structure and reaction pathway of the catalyst.

Beyond placing them into a structural control, the doping of dopants like nitrogen, phosphorus or sulfur in the carbon matrix triggers the electron redistribution and increase the defect density, which also augment the catalytic performance. The idea of tailoring MOFs as more generic material design for making a variety of water splitting and relevant electrochemical catalysts is the highest level of this approach [79].

4.5.4 In Situ Grown MOF-Based Electrodes for Direct Application

Beyond pyrolyzed MOF derivatives, the reoccurring theme is using the MOFs in their native form as functional electrocatalysts without carbonization to high temperature. Li et al. [80] have developed an in situ grown Cu based MOF [$Cu(OH)_2$]/CF for oxygen evolution reaction in this area. They chemically converted the $Cu(OH)_2$ nanowire arrays on a copper substrate into a Cu-based MOF through

solvothermal treatment. The 3D porous electrode with excellent OER performance (overpotential 330 mV at 10 mA/cm2) and durability under alkaline condition was obtained through this strategy.

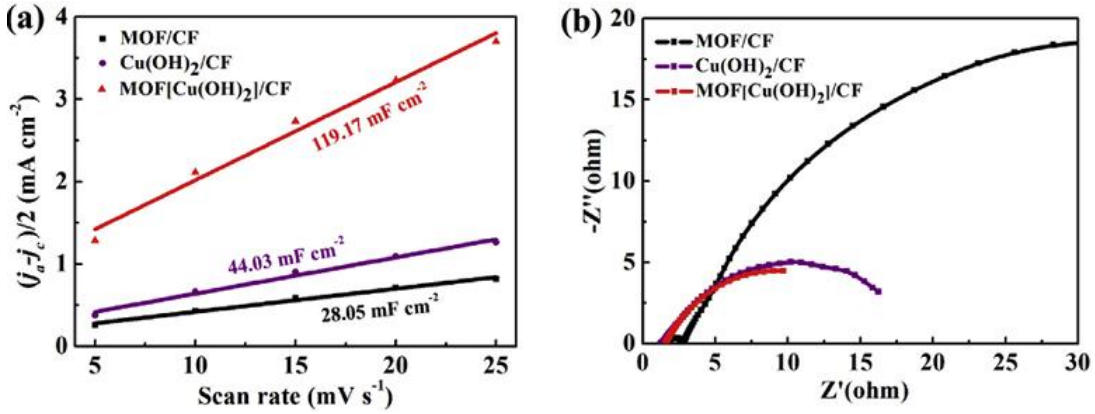

Figure 39: (a) Double-layer capacitance (C_{dl}) extracted from linear scan voltammetry at 1.17 V vs. RHE for MOF/CF, $Cu(OH)_2$/CF, and MOF [$Cu(OH)_2$]/CF, indicating enhanced surface area for the latter. (b) Nyquist plots from electrochemical impedance spectroscopy (EIS) at 1.5 V show lower charge-transfer resistance for MOF [$Cu(OH)_2$]/CF, validating improved interfacial electron kinetics [80].

It eliminates the need for corrosive polymer binders or an additional carbon support to reduce interface resistance and maximize accessible active sites. Additionally, the direct growth of MOFs on conductive scaffolds, e.g., metal foams, provides strong mechanical adhesion and great potential to minimize the performance degradation with prolonged electrolysis processes. $Cu_3(BTC)_2$ was confirmed by XRD and XPS to be formed and converted to catalytically active CuO during operation. Furthermore, further electrochemical analysis (**Figure 41**) is done on the in situ grown MOF [$Cu(OH)_2$]/CF electrode and it is found that the electrode shows superior capacitive behavior and charge transfer characteristics. Its high OER activity and stability stems from a larger electrochemically active surface area and enhanced interfacial conductivity due to the significantly increased (Cdl) and decreased (Rct). The study demonstrates MOF precursors can also serve as functional catalysts when in situ growth processes are carefully engineered [80].

4.5.5 Bimetallic MOF-Derived Catalysts with Local Structural Modulation for Enhanced HER/OER

Liquid-phase modulation of the bimetallic MF-derived catalysts has been developed as a very potential approach toward the augmentation of the electrocatalytic performance and stability of the materials that are employed in the hydrogen evolution reaction (HER) as well as oxygen evolution reaction (OER). The strategy takes advantage of the unique properties of MOFs e.g. control porosity, large surface area, and ability to accommodate more than one metal site within the same well-defined structure; to produce multifunctional electrocatalysts with synergism. Specifically, control of the local coordination environment of metal active sites in the transformation of MOF to derivatives takes center

stage in optimizing their electronic structures, defect concentrations, and catalytic kinetics, factors that have direct impacts on their usage in water electrolysis systems.

Lately there has been activity concentrated on the methodical development of bimetallic catalysts, in which the transition metal based units perform completely diverse but synergistic aspects. In one exemplary study the series of Co-Fe-based MOF-derived catalysts were prepared with a fine control of the Fe coordination environment, resulting in the formation of Fe-N_4 motifs dispersed in a porous carbon-rich in cobalt nanoparticles. This structural modulation was enabled by a pyrolysis reaction that preserved the atomically dispersed state of Fe, but caused the generation of metallic Co clusters, avoiding a monodisperse state that would result in a monosite architecture and instead leading to a two-site configuration well suited to overall water splitting. Fe-N_4 substituents further improved the catalytic activity, through further optimization of the local charge distribution and through acceleration of kinetics of charge transfer. Such two-site structure allowed to tune binding energies of H* and OH* intermediates that play significant roles in accelerating HER and OER, respectively.

Electrochemical screening of the CoFe-based materials showed better catalytic activity in alkaline environment, and also low overpotential was needed to attain current densities relevant to industrial applications. It showed OER overpotential of 295 mV at 10 mA/cm^2 and HER overpotential of 134 mV at the same condition, outdoing monometallic analogs and the reference noble metal catalysts. Also, Tafel slope analyses showed positive kinetics and smaller slopes reflected the energy efficient properties of the electron transfer. Stability experiments were carried out to validate the long-term stability of at least 30 days in excessively long chronoamperometric monitoring, where little degradation in the electrocatalysts was observed as evidence of the structural stability the MOF-derived carbon network and synergetic coupling between the metals could provide. The material also showed a good Faradaic efficiency and charge- transfer resistance implying the optimized interfacial interactions between catalyst surface and the electrolyte.

The local modulation of the bimetallic sites related to the creation of attractive catalytic enhancement effect inherent in these systems. Spectroscopic investigations, composed of X-ray absorption fine structure (XAFS) and X-ray photoelectron spectroscopy (XPS), confirmed the Co-Fe coordination bond between Fe and N_4, and partial electron transfer of Co to Fe. This electronic redistribution had an important role in aligning the d-band center of the metal sites, and thus enhanced adsorption energies of reaction intermediates. Furthermore, encapsulation of Co nanoparticles in graphitized carbon shells not only attributed to electrical conductive property but also guaranteed a corrosion-free environment and had self-assembling properties so that the particles are unlikely to

aggregate. Fe sites composed of atomically dispersed Fe and Co clusters, each playing a specific role in the mechanism, is a completely new paradigm of designing bifunctional electrocatalysts.

Building hierarchical porous structures to optimize access of active sites and mass transport is another important breakthrough in this field. Similarly, a one-pot solvothermal differentiation and a controlled pyrolysis were used to make NiFe bimetallic MOF-derived nanosheets. The resulting electrocatalysts featured ultrathin morphologies and three dimensional structures, thus offering vast degrees of edge sites and reduced electrolyte diffusion routes. Among these morphological structures, and the local tuning of Ni-O-Fe connections and defect design were factors that played important roles in exceptional electrocatalytic activities. The NiFe-based catalyst recorded a low OER and HER overpotential of 270 and 125 mV at 10 mA/cm^2 in 1.0 M KOH, respectively, and compared favorably to much of the catalog of MOF-derived systems. Significantly, the finding of this paper is that the adjustment in coordination of Fe between the octahedral and tetrahedral across the course of pyrolysis played a key role in the creation of highly active electronically unsaturated sites.

The mechanisms of the observed catalytic enhancements were further explained with help of density functional theory (DFT) calculations. through FeONi couplings it was demonstrated that the energy barrier towards O bond creation during OER was reduced, and in addition it manipulated the electronic states of spatially neighboring Ni atoms and made them accessible to hydrogen adsorption in HER. These synergistic coupling between the Ni and Fe atoms in a customized coordination motif indicated the significance of atomic control of materials derived of MOFs. There was also an enlightenment on the use of carbon defects and making use of heteroatoms like nitrogen to enhance conductivity and the possibility of more anchoring sites being available to metal species. The intrinsic activity originated not only by acting only as the conductive framework, but also by enabling the defect-rich carbon matrix to control the charges surrounding the active site.

In a synthetic approach to study, scaling and reproduction of bimetallic MOF derived catalysts has been sought by optimizing the precursor choice, pyrolysis conditions, and the post-treatment. A high level of composition homogeneous and spatial control over metal distributions can be achieved using bimetallic organic linkers or pre-assembled bimetallic clusters as well. Subsequent acid leaching and annealing processes also can do additional removal of inactive components and increase crystallinity, which is important to practical deployment. All these methods together work to have the derived materials with consistent catalytic qualities across batches, which is a key prerequisite to an industrial scale.

Electrolyzer devices have also been suggested to incorporate bimetallic MOF-derived catalysts especially in the design of membrane electrode assemblies (MEAs), both of alkaline and

anion exchange membrane (AEM) electrolyzers. Their higher activity and stability in the operational conditions show that these materials can be used elsewhere, not only in laboratory-scale experiments. Introduced in MEAs, CoFe- and NiFe- based catalysts came maintained significant current densities when low voltage requirements were required even in long-term operations. The poser ability to mix with normal ionomers along with their inability to degrade over cyclic voltammetry trials make them quite appropriate in the next generation electrolysis units.

Further, custom porosity and surface chemistry of MOF-derived materials can lead to tunnelable wettability and gas diffusion capabilities, which are crucial in controlling the formation and suppressing bubble formation, as well as in efficient access to reactants. This becomes even more important at high current densities when performance is normally limited by mass transport. Hierarchical morphologies given by MOF precursors, particularly those formed in presence of templating agent or hard sacrificial templates, have interlocked pores, which considerably decrease diffusion resistances. Such design principles are essential in improving real-life usefulness of MOF based catalysts in practical electrolysis use.

Regarding the long-term performance, further degradation tests revealed that bimetallic MOF-derived catalysts lost less than 10 percent of its initial activity upon exceeding 100 hours of continuous operation. Post-stability analysis by structural means indicated that most of the initial core-shell architectures and chartizied carbon structures were still intact yet the active metal sites were left accessible and intact in terms of chemistry. Such toughness is explained by annealing temperature and creation of strong metal-carbon and metal-nitrogen bonds, which are thermodynamically stable. This system has very dynamic adaptability on operating conditions, which emphasizes sound material engineering of catalysts.

The second important benefit of local structural modulation in bimetallic MOF-derived catalysts concerns the possibility of breaking conventional scaling laws in electrocatalysis. With electronically and geometrically engineered active sites, the binding energies of intermediates (e.g. *OH, *O, and *OOH in OER, or *H in HER) can be decoupled. This versatility permits to tune reaction kinetics and thermodynamics simultaneously which is normally a great challenge in single metal systems. Multi-step reaction chemistries and stabilization of reaction intermediates is easier with the dual-site set-ups provided by bimetallic systems, especially those that are supported on defect-engineered carbon matrices, leading to increased turnover frequencies and enhanced energy efficiencies.

The discipline is also evolving with the addition of the in situ and operando characterization methods that give real-time information about catalyst behavior under actual working conditions. In situ Raman spectroscopy, X-ray absorption spectroscopy and electrochemical impedance spectroscopy are

gaining popularity as a means of interrogating phase changes, changes in oxidation state and interfacial charge redistribution. Coupled with the possible topographical change on interface, these studies show the flexibility of active site and the structural flexibilities in preserving activities under variable electrochemical conditions. By way of example, operation-induced reconfiguration and partial oxidation of metal centers have been correlated with temporary enhancement of activity, implying that dynamic restructuring could be an essential characteristic of high performance electrocatalysts.

The intelligent design of bimetallic MOF-derived catalysts that provides local structural modulation promises to provide an effective pathway to the next-generation water electrolysis materials. Rational design at the atomic-level brings the ability to design electrocatalysts that not only always exceed the activity and stability of classical materials but whose properties can also be altered, to be suitable to different electrochemical contexts. Synergistic effects of the bimetallic cooperation, defect engineering and optimization of morphology lead towards the achievements of strict criteria of industrial-scale of hydrogen generation. The incorporation of such new high-performance catalysts in practicable electrolysis systems is an important development path to energy-sustainable and economically feasible hydrogen energy systems [134, 135].

4.6 2D Catalysts and MXenes in Water Electrolysis

4.6.1 Transition Metal Dichalcogenides as Efficient Electrocatalysts

Many two-dimensional (2D) materials, one being molybdenum disulfide (MOS_2) and tungsten disulfide (WS_2) that belong to the transition metal dichalcogenides (TMDs) family, have attracted much interest in applications in electrocatalysis for water splitting. As a result of their unique layered structures, they provide abundant exposed active sites especially at the edges, and high surface area interaction with electrolyte species. In addition, they have tunable electronic structure and physicochemical stability to act as good candidates for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in harsh acidic and alkaline environments.

As described by Wang et al. [81], the catalytic behavior of MoS_2 has been promising with proper engineering, due to its optimal hydrogen adsorption energy and semi metallicity. The authors note that catalytic activity is greatly enhanced in defect rich or doped nanostructured MoS_2 like nanoplates and nanotubes as the charge transport is improved and more active edge are exposed. As an example, HER showed lower overpotentials and better long term stability in oxygenated MoS_2 with surface defects, which was outperforming many other alternatives based on non-noble metals.

As concerns the reaction media, MoS_2 and WS_2 based electrocatalysts work well in both acidic and alkaline electrolytes. Additionally, in acidic conditions, their HER performance is

significantly improved by more favorable hydrogen adsorption energetics. Nevertheless, a number of studies have shown that these catalysts, combined with conductive support, such as carbon nanotubes or doped graphene, still retain high catalytic activity under alkaline conditions in which water dissociation is usually a rate-limiting step. Thus, by utilizing low cost 2D dichalcogenides, efficient, low cost hydrogen production technologies over a broad pH range are possible [81].

The critical factor for the practical use of MoS_2 and WS_2 has also been their stability. After prolonged electrochemical cycling, nanostructured TMDs also remained morphologically intact and showed effective chemical degradation resistance, in experimental setups. Due to this characteristic, along with being intrinsically abundant and cost effective, these materials are thought to serve as a solid alternative to platinum group metals in water electrolysis systems. **Figure 42** shows a summary of the fundamental performance parameters for HER/OER evaluation such as activation energy, overpotential, Tafel slope, durability, Faradaic efficiency and turnover frequency. These criteria are important in benchmarking the performance of MoS_2 and WS_2–based electrocatalysts.

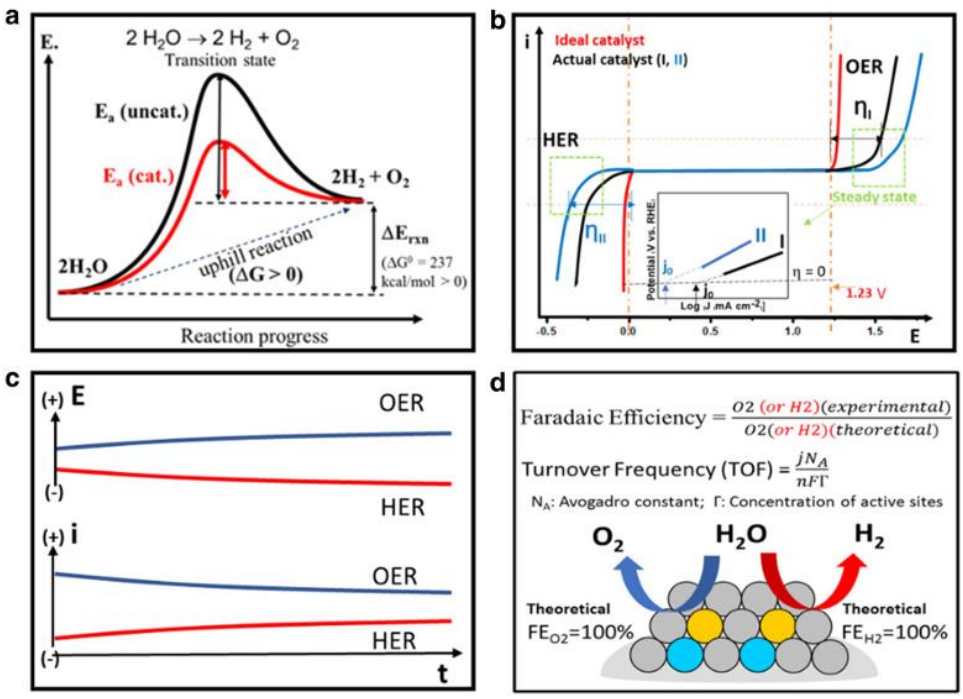

Figure 40: Schematic overview of key electrocatalytic performance indicators. (a) The catalyst's role in lowering the activation energy barrier. (b) Overpotential and Tafel behavior of real vs. ideal catalysts. (c) Stability profiles based on current and potential trends over time. (d) Faradaic efficiency and turnover frequency (TOF) expressions, both critical for evaluating catalytic utilization and selectivity [81].

4.6.2 MXenes and Their Derivatives in Electrochemical Water Splitting

Another new promising class of materials for electrocatalysis is the family of MXenes, 2D transition metal carbides and nitrides with the general formula Mn+1XnTx. Of these, Ti_3C_2Tx is the most studied because it has metallic conductivity, a hydrophilic surface, and mechanical flexibility. The purpose of these

materials is their layered morphology as in graphene and their enhanced electrochemical functionality associated with surface terminations of –OH, –F and =O. These surface groups are able to be controlled in order to tune the electronic structure and catalytic behavior of MXenes.

According to Anwar et al. [82], properly engineered MXenes have shown large catalytic activity on HER and OER. For instance, the modification of Ti_3C_2Tx with transition metal species or heteroatom results in low overpotentials and favorable Tafel slopes at a variety of current densities. As such, the authors pointed out that MXene composite structures, where the MXenes are combined with other conductive or catalytic components (i.e. Ni, Co or Mo compounds), lead to synergistic effects that enhance charge transfer and active site exposure.

Perhaps the most significant advantage for practical deployment purposes is that MXenes can potently work in both acidic and alkaline environments. Their metal conductivity in acidic media favors fast electron transfer whereas, in alkaline media, their surface chemistry can be designed to promote water dissociation. According to Anwar et al. [82], doped strategies and the nanostructuring approaches like forming ultrathin nanosheets or defect engineering will open new paths to further improve the MXene performance. Electroactive surface area is increased, the binding energy for hydrogen is optimized, and long term operational stability is improved.

Besides good electrocatalytic performance, MXenes are distinguished for scalable syntheses and the ability to be processed with the current electrode fabrication technologies. Integrating them into flexible and lightweight electrodes in order to use them for portable and wearable hydrogen generation devices has been explored. Such flexibility along with excellent environmental stability and low cost of the raw materials put MXenes at the forefront of the next generation of electrocatalyst design.

4.6.3 2D Catalyst Performance Across Electrolytic Media

First, a comparative overview of 2D catalysts—MoS_2, WS_2, and MXenes—is given, they possess excellent bifunctional catalytic performances under various electrochemical conditions. Transition metal dichalcogenides and MXenes were reported [83] to work well in acidic and alkaline media (where alkaline water electrolysis (AWE), proton exchange membrane electrolysis (PEME), and solid oxide electrolysis (SOE) are used), which is important for their use in different electrolysis systems.

The authors stress that the morphology, composition and interaction with the support materials are very influential to the performance of 2D catalysts. For instance, because the nanosheets' unsaturated metal centers at edges exhibited enhanced adsorption and desorption

kinetics that are needed for catalytic turnover. 2D catalysts are also mechanically stable and maintain their structural integrity in high current density environments due to their high mechanical stability and high sintering and corrosion resistance, which are common failure modes.

Also, Song et al. [83] pointed out the need for optimization of the catalysts for a specific electrolysis system. In PEME systems, acidic environments exist, resulting in catalysts that are required to be robust against oxidative degradation, while the proton conductivity should be high. Doping or combination of MoS_2 and its derivatives with conductive polymers has shown promise in such applications. Alternatively, layered materials like MXenes are conducive and chemically active enough to promote OER efficiently in alkaline systems where oxygen evolution is sluggish.

It discussed cost benefits associated with the use of 2D materials as well. While noble metals, such as platinum, iridium, and ruthenium, are plagued with a scarcity and high price, the aforementioned electrolyzer components are made from MoS_2, WS_2, and MXenes, which are synthesized from earth abundant elements limiting the material cost of electrolyzer components. In addition, their potential of solution based processing methods results in low energy, large capacity manufacturing, which is in line with the economic goals of green hydrogen technologies [83].

In general, the integration of 2D catalysts into water electrolysis systems is a convergence among high catalytic performance, structural stability and economic aspect. It is expected that future research will be directed towards heterostructure engineering, in situ characterization of catalytic sites and system level integration for efficiency and durability enhancement.

4.6.4 Janus 2D Catalysts and Their Anisotropic Charge Transfer Behavior in Electrolysis

Recent developments of Janus two-dimensional (2D) catalysts have developed a transformative strategy in the area of electrocatalysis in water splitting systems, especially the ability to utilize their inherent anisotropic electronic transfer activity. Such materials consist of atoms with asymmetric arrangements across the two opposite sides of a monolayer, and have non-conventional physicochemical properties that are accessible otherwise to symmetric 2D materials. Such asymmetry also results in an inherent dipole out of plane and inversion symmetry breaking that can generate directional charge redistribution and its associated increase in interfacial reactivity. Those properties are especially favourable in case of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) since the best adsorption energies and fast kinetics can be controlled by the electronic structure of the catalyst/electrolyte interface. Janus 2D materials thus design and fabrication are a strategic path towards charge transfer dynamics and catalytic performance tailoring in water electrolysis applications.

A very important contribution in this area has been the synthesis of Janus transition metal dichalcogenides (TMDs), including MoSSe, that contain chemically distinct chalcogen planes (sulfur and selenium) on opposite sides of a molecule. This imbalance in the symmetry of the composition results in a natural electric field between the monolayers, which favors anisotropic charge separation and greater directional carrier mobility. The better HER activity of Janus MoSSe monolayer than its symmetric counterparts (MoS_2 and $MoSe_2$) have been proved by experimental studies and first-principles calculations, which is ascribed to the increased charge polarization and changed d-band electronic structure. The face terminated with a sulfur will provide more favorable adsorption sites having protons and the side consisting of selenium will help in providing better electrical conductivity and delocalizing of charge. Such dual functioning (appearing as the result of the Janus architecture) is capable of spatially specific catalytic activity and greater optimization of the active surface. Electrochemical and spectroscopic techniques have been also used to explicitly define asymmetric ejective charge transfer in Janus materials, where the asymmetry can be attributed to asymmetric ion diffusion and potential-dependent values of polarization because of asymmetric electric double-layers. Such phenomena are crucial in producing low overpotentials and high exchange current densities especially on acidic and alkaline milieu. The Janus structure also determines the orientation of dipole moments, resulting in a modulation of interaction with solvated ions in addition to altering interface water structure that is essential in HER and OER kinetics. Specifically, the anisotropic electronic environment controls the stability of the intermediate compounds such as *H and *OH, making their formation and desorption activation barriers lower. This brings quicker reaction rates and lower energy losses into account and so, Janus 2D catalysts are particularly appropriate with integrated electrolysis applications, such as photoelectrochemical and two-terminal water-splitting systems.

Recently, the research team produced a Janus MoSSe monolayer through a two-step annealing process of thermal annealing with adjustable chalcogen substitution. The emerging material had the strong vertical dipole and a substantial difference in the work function values on its front- and back-sides as validated with Kelvin probe force microscopy and ultraviolet photoelectron spectroscopy. This resulted in the next step of this anisotropic catalytic performance wherein the S-terminated side displayed stronger HER activity by virtue of its smaller hydrogen adsorption Gibbs free energy (AG H to zero) and the Se-terminated side retained electronic activity to facilitate the movement of charge. Moreover, the paper revealed that the Janus architecture could retain its structural durability and activity of the catalytic activity through long-term electrochemical cycling, which indicates the high sturdiness of the systems under realistic situations.

A yet different milestone study examined Janus MXenes, which are a somewhat older subclass of 2D materials formed via selective etching of layered MAX phases with the distinction of having an asymmetric surface termination. Such substances as Ti_2CST and Mo_2CTe possess a highly conductive metallic core with asymmetrically (re)arranged functional groups (- O, -S, -Se, -Te) on their surfaces. The built-in potential gradient imposed on the stack of atomic layers by the Janus property of MXenes was shown by density functional theory (DFT) simulations to lead to separation of charge carriers and to directional electron flow. This internal electric field is very important in electrolysis of water leading to rapid and selective migration of charge to active sites and, thereby, promoting the reaction kinetics during electrolysis of both HER and OER.

Janus MXenes are also tunable in terms of band structure and surface chemistry leading to the ability to specifically tune the adsorption energy of key intermediates. In the case of HER, the optimal situation would be when one gets from 0 a 0 in terms of 0G H displaying a perfect hydrogen binding procedure. Janus MXenes Ti_2CST and Mo_2CTe have been demonstrated to achieve this thermodynamic optimum due to selective termination of chalcogen atoms on one only side of the structure effectively balancing the electronics of the surface. Symmetric charge build-up is not possible in OER because both surfaces have terminations, enabling asymmetric charge accumulation, promoted rates and stabilization of *OOH intermediates, which are generally a rate-limiting step, in alkaline media. This dual reactivity presents opportunities to bifunctional catalysis, with potentially the same material catalyzing both HER and OER at the same time, resulting in the design of compact and efficient electrolyzers.

Computational studies also help elucidate the electrochemical heterogeneity of Janus 2D catalysts by the distribution of the electric field, the charge density distributions, and reaction mechanisms on asymmetric surfaces. This modeling has shown the internal dipole moment changes the potential energy landscape of adsorbed systems giving rise to directional adsorptions and desorptions. The overall effect is to lower the energy barriers to proton-coupled electron transfer (PCET) reactions that are the key to water splitting. The spatial registration of the frontier orbitals further, provides that the activity is localized at discrete atomic sites, increasing turnover frequency, and reducing the parasitic side reactions. This kind of atomic-precision is crucial when attempting to optimize 2D materials intrinsic activity, as well as remain scalable and replicable.

Unlike the existing materials, the Janus 2D catalysts boast an additional benefit over their base constituents; that of improved interfacial compatibility with both supporting substrates and electrode designs. The internal electrical field favors good interfacial attachment and limits contact resistance and lowers mechanical stability against operating stress. Heterostructures and hybrid

electrodes can use these materials, where anisotropy properties can form synergistic links with co-catalysts, scaffolding conducting materials, and ionomer binders. As an example, Janus MoSSe intergrown on a carbon nanotube substrate showed increased current density and decreased overpotential when compared with its non-Janus equivalents which can be attributed to the directional charge transport and better electrolyte access due to the asymmetric surface chemistry.

Also contributing to its potential and adaptive catalysis is the dynamic nature of Janus catalysts in reaction conditions. The local electronic environment around the Janus materials has been demonstrated through operando Raman spectroscopy and X-ray absorption to change in the course of HER and OER thereby activating initially inert sites. This dynamic responsiveness is the result of the unusual electronic environment formed by the Janus arrangement in which redistribution of charge and surface reconstruction is directed by the internal electric field. This reactivity allows self-optimization on long runs of electrolysis, minimizing catalyst deactivation and increasing operational life-times.

One of the factors leading to the practical application of Janus 2D catalysts is their scalability in terms of synthesis as well as their structural stability. New procedures in vapor-phase chalcogen substitution, molecular beam epitaxy and chemical vapor deposition have allowed generating high-quality Janus monolayers and few-layer films with well-defined thickness and domain orientation. The techniques guarantee the reproducibility of the dipole strength, the composition of the surface, as well as crystallinity, which is all important to provide the uniform behavior in the electro-catalysis. Moreover, the thermal, chemical stability of Janus materials proved well in severe electrochemical conditions, such as acidic or alkaline solutions at high temperatures, which allows applying them in case of commercial electrolyzers.

Another area where the strategies of defect engineering come in handy is in the design of Janus-type catalysts, since in this case vacancies, edge terminations, and substitutional dopants can be introduced to customize catalytic activity. Any combination of these two degrees of freedom associated with the interplay between structural defects and dipolar asymmetry gives more degrees of freedom to tailor activity and selectivity. As an example, creating sulfur vacancies in Janus MoSSe enhances the activity density of active sites and facilitates water dissociation, which boosts kinetics of HER. Likewise, OER-relevant electronic structure can also be altered by doping with transition metals, including Fe or Co. These changes like that they are compatible with the intrinsic anisotropy of Janus materials and can make possible multidimensional tuning of the catalytic characteristics.

Their structural and electronic features which make Janus 2D catalysts uniquely positioned make them a force of materials used in water electrolysis. In addition to unprecedented control over

interfacial reaction due to their inherent dipole moments and anisotropic charge transport processes and mechanisms, they are highly active catalysts, highly selective, and stable. The combination Janus architectures with 2D material platforms, such as TMDs and MXenes, allows one to envisage innovative electrolysis systems with multifunctional adaptive and efficient designs. Janus catalysts can take on these problems by exploiting their directional reactivity and tunable surface chemistry, and point the way to more sustainable and cost-effective energy conversion technologies. Their further study with regard to their synthesis, mechanistic properties and integration with devices will become critical in translating these novel materials beyond their discovery to an actual industrial use [136, 137].

4.7 Catalyst Support Engineering & Conductive Substrates

4.7.1 Conductive Substrate Effects on Adsorbate Binding and Catalysis

The conduction substrates have been of increased interest in electrocatalytic systems in technology since they can affect adsorbate binding energies, charge transfer kinetics, and catalytic activity levels. However, use of conductive supports like metals and doped carbons, especially in oxygen evolution and reduction reactions (OER/ORR), can have a strong effect on the performance of the catalyst layer. Li and Nørskov (2020) showed that there is a remarkable enhancement in adsorption of important reaction intermediate species, O*, HO*, and HOO* on the wide bandgap TMOs, such as ZrO_2 and HfO_2 co-incorporated with metallic support [84].

Density functional theory (DFT) theoretical analysis shows that the oxygen containing species bind more strongly on thin TMO layers supported on gold surfaces than their unsupported versions. Charge transfer from the metal support to adsorbate layer leads to a redistribution of electronic density and an improvement of the adsorbate stabilization, a factor which contributes to this enhancement. Furthermore, it is thickness dependent. For example, support induced effects become insignificant when oxide layer of the ZrO_2/Au systems exceeds roughly 8 nm, suggesting that the interfacial proximity plays a crucial part in support engineering.

The conductive substrate is additionally confirmed by Bader charge analysis and projected density of states (PDOS) that they promote the efficiencies of direct electron transfer to the adsorbed intermediates, which enhance the binding energies. The donation of this electron, alongside dipole formation within the oxide metal interface causes work function shift within the system, providing conditions which favor electrocatalysis. Interestingly, the support effect is strong when it comes to wide gap TMOs, but very little for oxides like SnO_2 and PdO_2 where the intrinsic conductivity is high enough so that one can maintain sufficient charge mobility [84].

This reveals that substrate engineering is not only a structural option, but also a functional design criterion. In doing so, the kinetics of redox reactions can be manipulated and greatly reduced overpotential for HER/OER processes can be achieved by tailoring the thickness and electronic properties of the catalyst support interface.

4.7.2 Transition Metal Carbides as Alternative Support Frameworks

Transition metal carbides (TMCs) have recently attracted much attention as next generation carbon supports in electrocatalytic systems. The ability to be robust and interactive substrates for H2 and O2 evolution reactions is due to their chemical stability, metallic conductivity and Pt − like electronic properties. As per Tackett et al.[85], it is reported that the combination of platinum group metals (PGMs) with TMC supports leads to stronger metal–substrate interactions, other than having the benefit of reducing PGM loading requirements, also contributing to improving catalytic durability and performance at elevated pH range.

The abundancy of carbon with high surface area and conductivity, makes it widely used a traditional support for electrocatalysts. Although it is subject to corrosion under electrochemical conditions resulting in catalyst detachment and performance loss. On the other hand, TMCs including TiC, WC and NbC provide better stability and stronger metal-support bonding to prevent active particle agglomeration and detachment. Furthermore, TMCs also facilitate tunability of surface d band centers which makes possible convenient manipulation of adsorbate binding energies. In particular, electronic structure of the support can greatly affect HER and ORR activity, and so optimization of this parameter is paramount.

For instance, Pt monolayers borrow the benefit of surface engineering and are deposited on TMCs that exhibit similar activity as bulk Pt, but at much reduced material consumption. It is demonstrated through DFT calculations that the HBE can be adjusted via the TMC support choice, such that HER activity is enhanced and catalyst cost reduced. Furthermore, the CO poisoning resistance in fuel cell applications is improved in these hybrid systems, which together provide additional evidence to support this strategic shift toward PGM/TMC composites for the next generation energy devices [85].

A notable point is that TMC–based supports are also active under both acidic and alkaline environments, essential features to make universal electrolyzers and fuel cells. It has already been experimentally demonstrated that WC@Pt and Pt@WC hybrid systems exhibit outstanding superiority in terms of catalytic activity and stability, due to the synergistic effects arisen at the metal–carbide

interface. In addition to being a materials innovation, integration of TMCs into catalyst design falls in line with efforts to reduce the use of critical raw materials in clean energy technologies.

4.7.3 MoS_2-Supported Platinum Nanostructures: Enhancing Charge Transport and Utilization

MoS_2 has emerged as a promising support material for platinum-based catalysts in hydrogen evolution reactions due to its unique structural and electronic characteristics. This layered transition metal dichalcogenide possesses a high specific surface area and abundant edge sites, both of which are critical in stabilizing dispersed platinum nanoparticles and enhancing their electrocatalytic activity. In a recent study by Li et al. [86], edge-enriched MoS_2 thin films were utilized as supports for platinum nanoparticles, resulting in a hybrid electrocatalyst that exhibited remarkable performance in the hydrogen evolution reaction. The vertically aligned MoS_2 nanosheets not only provided chemically active edge sites but also established a robust conductive framework that stabilized the platinum nanocrystals, facilitating enhanced catalytic activity and charge transport.

The synthesis of the platinum-decorated MoS_2 hybrid electrocatalyst involved careful control of thermal annealing parameters, including spin speed, duration, and precursor concentration. These parameters were precisely tuned to manipulate the size, spatial distribution, and surface density of the platinum nanostructures, ensuring uniform deposition across the MoS_2 support. This meticulous engineering of the catalyst architecture was pivotal in achieving an optimized hybrid structure that demonstrated an exceptionally low overpotential of 9 mV at a current density of 10 mA/cm^2. The corresponding Tafel slope of 44 mV/decade indicated favorable charge transfer kinetics and a catalytic mechanism conducive to rapid hydrogen evolution. Importantly, the integration of platinum nanoparticles with the MoS_2 framework did not compromise the structural stability of the system, as evidenced by consistent catalytic performance over 10,000 electrochemical cycles, highlighting the long-term durability of the hybrid catalyst.

The synergy observed between platinum and MoS_2 in this hybrid system arises from complementary structural and electronic interactions. The inherent high surface area and edge-rich morphology of MoS_2 serve as ideal nucleation sites for platinum nanoparticle formation, effectively mitigating particle aggregation and promoting uniform distribution. This uniformity is crucial in maintaining a high electrochemically active surface area, a key factor in achieving sustained high catalytic activity. Furthermore, the intimate electronic coupling between the platinum nanoparticles and the sulfur atoms in the MoS_2 lattice facilitates efficient charge transfer across the interface. This electronic interaction is instrumental in lowering the energy barrier for proton reduction, thereby accelerating the kinetics of the hydrogen evolution reaction.

The superaerophobic nature of the MoS_2 scaffold further contributes to the superior performance of the hybrid catalyst. During water electrolysis, gas bubbles formed at the catalyst surface can hinder active site accessibility and impede charge transfer, leading to a decline in catalytic activity. The superaerophobic property of MoS_2 enables rapid gas bubble detachment from the catalyst surface, maintaining consistent exposure of active sites and stable catalytic activity even at elevated current densities. This characteristic is particularly advantageous in high-rate electrolysis applications where gas bubble management is critical for process efficiency.

In contrast to traditional carbon-based supports, which are widely used for platinum nanoparticles in electrocatalytic applications, MoS_2 offers several distinct advantages. Beyond its role as a physical support, MoS_2 itself exhibits catalytic activity toward the hydrogen evolution reaction, thereby contributing to the overall activity of the hybrid catalyst. Moreover, the chemical robustness of MoS_2 under harsh electrochemical conditions ensures long-term stability, a feature that carbon supports often lack due to their susceptibility to oxidation and structural degradation. The compatibility of MoS_2 with scalable fabrication techniques such as chemical vapor deposition further underscores its potential for industrial deployment, enabling the production of large-area electrodes with consistent performance characteristics.

The findings of Li et al. [86] underscore the importance of substrate engineering in the design of high-performance electrocatalysts. The optimization of the catalyst support extends beyond considerations of electrical conductivity and surface area, incorporating the atomic-scale interactions that govern catalyst stability and activity. In the Pt/MoS_2 system, the atomic-level synergy between platinum and sulfur sites enhances the intrinsic activity of the catalyst while simultaneously stabilizing the nanoparticle morphology against agglomeration and degradation.

The structural integrity of the MoS_2 framework is maintained during extended operation, providing a mechanically robust platform for platinum nanoparticle anchoring. The layered structure of MoS_2 accommodates the mechanical stresses associated with gas evolution and electrode cycling, preventing catalyst detachment and preserving the high dispersion of platinum nanoparticles. This mechanical stability, coupled with the inherent chemical inertness of MoS_2 in acidic electrolytes, positions the Pt/MoS_2 hybrid catalyst as a compelling candidate for practical hydrogen production applications.

From an electronic standpoint, the interaction between platinum nanoparticles and the MoS_2 support modulates the electronic structure of the active sites, optimizing the binding energies of reaction intermediates and enhancing the turnover frequency of hydrogen evolution. This electronic modulation is a consequence of charge redistribution at the metal-support interface,

which influences the adsorption and desorption behavior of protons and hydrogen molecules. Such atomic-level interactions are essential for achieving low overpotentials and high exchange current densities, key performance metrics in electrocatalytic hydrogen production.

The versatility of MoS_2 as a catalyst support extends to its ability to accommodate various nanoparticle deposition strategies, including wet chemical reduction, atomic layer deposition, and electrodeposition. Each of these techniques offers distinct advantages in controlling the morphology and distribution of platinum nanoparticles, providing opportunities to further tailor the catalytic properties of the hybrid system. Such flexibility is crucial for optimizing performance across different electrochemical environments and for meeting the diverse requirements of hydrogen production technologies.

The implications of these findings are significant for the broader field of electrocatalysis and hydrogen production. By demonstrating that the optimization of catalyst supports can lead to substantial enhancements in catalytic performance, this research highlights a pathway for improving the efficiency and durability of electrochemical hydrogen production systems. The insights gained from the Pt/MoS_2 hybrid system also inform the design of other hybrid catalysts that leverage the unique properties of two-dimensional materials and noble metal nanoparticles.

The engineering of MoS_2-supported platinum nanostructures exemplifies a sophisticated approach to catalyst design, where the interplay between structural morphology, electronic properties, and interfacial interactions defines the overall performance of the system. The work of Li et al. [86] demonstrates that by harnessing the synergistic effects at the atomic level, it is possible to achieve electrocatalysts with exceptional activity, stability, and scalability. Continued exploration of such hybrid systems, informed by both experimental and theoretical studies, will be essential for advancing the field of hydrogen production and for realizing the potential of electrochemical water splitting as a cornerstone of sustainable energy systems.

4.8 Stability and Lifetime Challenges in Low-Cost Catalysts

4.8.1 Degradation Pathways and Performance Decay in Non-Precious Metal Catalysts

Transition metals including nickel, cobalt, and iron, low cost electrocatalysts, proved to be potential alternatives to the Pt group metals in water electrolysis. However, one of the major shortcoming of using these materials has been their insufficient long term durability. The materials, though having the advantages of availability and cost, are typically chemically unstable, having structural degradation, and losing an active site under operating conditions, especially in an alkaline medium [87], as Kazemi et al in 2024, have mentioned.

Corrosion is one of the primary degradation mechanisms as such active material is dissolved or structurally reorganized. It is especially manifested at high pH conditions, where metal hydroxides are able to form and undergo redox cycling. Moreover, high overpotentials and variable reaction conditions further deteriorate mechanical stress and particle detachment from substrate. Therefore, there is a drop in the electrochemical surface area (ECSA), thus leading to a decrease in the catalytic activity. Localized heating and pH fluctuations are often accelerated by the generation and accumulation of gas bubbles.

The stability is quantified with chronoamperometric and chronopotentiometric techniques, or in conjunction with long term cyclic voltammetry (CV). Take for example, the quantity referred to as relatively stable catalyst is defined as one maintaining the same current density with insignificant overpotential change for a duration of 240 hours, however, industrial targets demand catalyst functionality over thousands of hours. Additionally, Kazemi et al. point out the necessity for HER electrocatalysts to remain structural integrity under acidic and alkaline conditions and with high Faradaic efficiency and insignificant degradation of the Tafel slope [87].

This means that improving the stability more is not achieved solely by increasing catalytic activity. Relevant aspects include improving hydrogen binding energy (HBE), creation of surface protective layers, and utilizing pseudocapacitive effects to alleviate rapid potential fluctuations. Together these factors not only affect the immediate electrochemical response, but also the long term reliability and lifetime for operation in motion.

4.8.2 Stability Enhancement through Defect Engineering and Surface Structuring

The recent literature has adopted the use of defect engineering as a strategy to improve the stability of low cost electrocatalysts. According to Wang et al. (24), high current densities come with the risk of rapid electron transfer, bubble accumulation, catalyst detachment, which negatively affect the long term stability of HER catalysts. Through the deliberate incorporation of defects such as vacancies, heteroatom doping and dislocation networks, researches have been able to adjust the electronic structure and the mechanical resilience of the materials [88].

For instance, it was shown that the creation of oxygen vacancies in Bi_2O_3 nanosheets provided more exposed active sites as well as better charge transfer for more effective hydrogen adsorption and evolution. An important caveat is that defects are stable only when there is an optimum concentration of such defects; when vacancy formation is excessive, it creates instability and collapse of structural framework, which ultimately decreased the performance. The integration

of dislocation networks in PtNi nanoparticles lowered the water dissociation energy barrier and strengthened surface atoms by mitigating current density induced destabilization as well.

Alternatively, the development of core–shell morphology, that is a robust inner core surrounding an active outer shell, is another effective approach. In addition to being a mechanical strength provider, this architecture also enables the growth of favourable interfacial properties, which buffer the catalyst from dissolving. Improved mechanical integrity is further contributed by alloying and amorphization. A high-entropy alloy based on Ni, Co, Fe, Mn, and Mo reached a current density 1000 mA cm^{-2} at 150 mV overpotential and retain its activity over prolonged cycles [88].

In addition, heterostructures, e.g. $Ni_2P@Cu_3P$ and Ru@P,O – NiFe LDH/NF, have great potential to improve the charge transfer and structural adhesion. Unidirectional electron flow is propelled by the built-in electric fields at these interfaces and charges accumulation and thermal stress, two important mechanisms for limiting the lifetime of the PV system. The key significance of the present findings pertains to the bulk catalyst material but also to the interfaces and surface engineering for increasing catalyst life under real®, industrial operating conditions [88].

4.8.3 Core-Shell Architectures and Protective Layers for Durable Operation

Core–shell architectures and protective layers have garnered significant attention as highly effective strategies to address the longstanding challenges of chemical and mechanical stability in low-cost water electrolysis catalysts, particularly under the demanding conditions associated with industrially relevant current densities. These design approaches combine a conductive and mechanically robust core with a catalytically active and protective shell, establishing a structural synergy that enhances both catalytic activity and durability. Zang et al. (2024) have reported substantial improvements in corrosion resistance, adhesion to substrates, and tolerance to thermal and electrochemical stress in catalysts engineered with such core–shell configurations, underscoring their promise for bridging the gap between laboratory-scale innovations and practical, scalable hydrogen production systems [89].

In these composite structures, the core component typically consists of conductive and chemically stable transition metal carbides, nitrides, or phosphides, chosen for their excellent electrical conductivity and mechanical strength. These cores act as efficient electron pathways that sustain high current densities while resisting structural deformation. The shell, often composed of a noble metal or other catalytically active phase, performs the dual function of facilitating the hydrogen evolution or oxygen evolution reactions while simultaneously serving as a protective barrier for the underlying core. This arrangement effectively mitigates the direct exposure of the

core material to the corrosive electrochemical environment, reducing dissolution and prolonging the operational lifespan of the catalyst.

One exemplary system illustrating the benefits of this design philosophy involves the CoPt-Pt single atom (PtSA) architecture confined within a nitrogen-doped carbon framework. In this configuration, the platinum shell demonstrates high dispersion across the surface, maximizing the number of catalytically active sites while leveraging the strong metal–support interactions to suppress nanoparticle agglomeration and detachment. Such structural optimization has been shown to achieve impressive performance metrics, with overpotentials as low as 63 mV at current densities exceeding 1 A/cm² and sustained catalytic activity over hundreds of hours [89]. The protective nature of the platinum shell is critical in maintaining the electrochemical integrity of the active layer under aggressive operating conditions, highlighting the effectiveness of core–shell designs in industrial applications.

Beyond the inherent benefits of layered structures, amorphous or disordered surface coatings have been demonstrated to further enhance catalyst resilience by diffusing mechanical strain uniformly across the active layer. In particular, materials such as molybdenum-doped $NiS_{0.5}Se_{0.5}$ exhibit disordered surface structures that function as mechanical buffers during hydrogen evolution cycles. These amorphous layers accommodate the repeated expansion and contraction of the catalyst during operation, preventing localized stress accumulation that can lead to cracking, delamination, or other structural failures. This attribute is particularly critical in maintaining catalytic performance over extended lifetimes, especially in industrially relevant electrolysis conditions where mechanical integrity is as vital as chemical stability.

Protective coatings also play an essential role in preventing catalyst sintering, swelling, or cracking—phenomena that are exacerbated under the high thermal and electrochemical stresses typical of industrial electrolysis environments. Such degradation pathways are often responsible for the decline in catalyst performance and lifetime in practical systems, as they compromise the structural coherence of the active layer and reduce the number of accessible catalytic sites. The incorporation of protective layers not only shields the catalyst core from aggressive conditions but also preserves the high surface area and active site density that are critical for maintaining high catalytic activity over prolonged operational periods.

The dual functionality of core–shell structures and protective coatings emerges as a key advantage in the development of electrocatalysts capable of meeting the rigorous demands of commercial water electrolysis systems. On one hand, the catalytically active shell ensures high turnover frequencies and efficient charge transfer for the target reactions, directly contributing to

system efficiency. On the other hand, the protective function of the shell or coating safeguards the underlying core against chemical attack, mechanical deformation, and phase instability, thereby preserving the long-term integrity of the catalyst structure. This dual role is indispensable for transitioning innovative catalyst designs from laboratory experiments to large-scale deployment in water electrolysis plants, where durability and stability under fluctuating load conditions are as critical as catalytic activity.

Moreover, the interface between the core and shell in these architectures facilitates unique electronic interactions that modulate the electronic structure of the active sites, often leading to enhanced intrinsic activity. These interfacial effects can adjust the adsorption energies of key intermediates, such as hydrogen and hydroxyl species, thereby improving the reaction kinetics and lowering the energy barriers associated with the electrochemical processes. The atomic-scale tuning of electronic properties at the core–shell interface thus provides a powerful lever for optimizing both activity and stability in low-cost catalyst systems.

The selection and optimization of materials for both the core and the protective shell remain central to the success of these architectures. Transition metal carbides and nitrides, for example, offer a favorable combination of electrical conductivity and mechanical robustness, while noble metals and metal oxides serve as highly active and corrosion-resistant shell materials. Strategies for synthesizing these structures, such as atomic layer deposition, electrodeposition, and chemical vapor deposition, provide precise control over shell thickness and composition, enabling the fine-tuning of interfacial properties and ensuring the uniformity necessary for consistent catalytic performance.

The findings reported by Zang et al. [89] underscore the practical potential of core–shell and protective layer designs in advancing the durability and operational lifetime of low-cost electrocatalysts. These insights highlight the importance of moving beyond the traditional focus on catalyst activity alone and embracing a holistic approach that considers mechanical, thermal, and chemical stability as integral components of catalyst design. In doing so, the gap between laboratory research and industrial application can be effectively narrowed, paving the way for the deployment of water electrolysis systems that meet the dual imperatives of performance and durability.

The development of core–shell architectures and protective layers represents a significant advance in the field of water electrolysis catalysts, offering a robust solution to the stability and lifetime challenges inherent in low-cost catalyst systems. By combining structural engineering with interfacial electronic modulation, these strategies deliver catalysts that are not only highly active but also resilient under the harsh conditions of industrial operation. Future efforts to expand the

range of materials, refine fabrication methods, and elucidate the fundamental mechanisms governing stability will be crucial in fully realizing the potential of these advanced catalyst designs. Such developments will play a vital role in supporting the global transition to sustainable hydrogen production and the broader deployment of clean energy technologies.

4.8.4 Dynamic Catalyst Reconstruction and Self-Healing Phenomena During Electrolysis

Dynamical reconstruction of catalysts under electrochemical conditions and self-healing processes have taken center stage in the quest toward high functioning, low-cost electrocatalysts of water electrolysis. In contrast to the classical paradigm of static catalyst models in which one assumes that the structural integrity of the active phase during operation does not alter, there is now convincing evidence that a large number of electrocatalysts exhibit dramatic structural and compositional transformations during operation. It is not that such dynamic changes are passive degradative processes, rather in some cases they actively result in the creation of more catalytically active or stable phases, or spontaneous regeneration of activity following initial deactivation. Such bipolar reconstruction-self-healing is especially evident in transition metal-based materials (in particular, perovskite oxides and layered double hydroxides) currently increasingly used as low-cost alternatives to five-metal-based catalysts in alkaline and neutral water electrolysis.

The most recent contribution was made to the thorough overview of these processes by the research of self-healing oxygen evolution catalyst based on CoFe layered double hydroxides (LDHs). Operando studies have indicated that during anodic polarization these materials undergo high rates of oxidation of Co 2+ to Co 3 + and Co 4 + with the concurrent formation of a catalytically active oxyhydroxide phase. This stage is however, intrinsically metastable and decays through oxidation of species of Fe into the electrolyte. What sets those LDHs apart is that they can constantly re-incorporate Fe 3+ ions of the electrolyte as local concentration gradients and electrostatic attraction redistribute those at the reconstructed lattice. This regeneration process is more or less a self-healing process which maintains the surface Fe/Co ratio which is vital in optimal catalytic activity. This dynamic interaction between the soluble and lattice-bound iron forms a stable active surface during the long time scale of electrolysis despite a competitive dissolution and redeposition process kinetics. The interesting fact is that this method does not involve external forces or follow up cures, and this way represents the adaption capability of that kind of catalysts.

The electrochemically coupled mechanism is also stabilization mechanism. After all, the presence of electric potential differences between the double layer allows enhancing the insertion of Fe3+ into Co-based matrices via field-assisted diffusion. Such interaction is also backed with

thermodynamic preferability in high pH conditions where Fe(OH) 4 -rich predominates and has the potential to be added easily to the deficiencies in the oxyhydroxide lattice. This defect-healing effect maintains the redox-active Fe centers that are active synergistically with Co to reduce the overpotential of oxygen evolution reaction (OER). The synergy also leads to the development of a positive trade-off between conductivity and catalytic turnover rate, in the sense that Co framework sustains electron mobility whereas Fe helps to modulate the binding energies of OER intermediates. Consequently, their self-healing abilities not only imply structural but also electronic self-healing which has far-reaching consequences on the lifetime as well as operating efficiency of non-precious metal electrocatalysts.

The dynamism of catalyst surfaces under working conditions has also been done elegantly in the case of the perovskite oxides especially those spotted with Barium, strontium, cobalt and iron. It has recently been demonstrated that such materials amorphize at their surface, and order and reorder in extended electrochemical cycling, transforming between crystalline perovskites structures and disordered but catalytically active amorphous layers. Although such transformations have been attributed to degradation in the past, the study of these amorphous phases by increased methods of operando characterization, such as X-ray absorption spectroscopy or in situ electron microscopy has shown that these can possess superior activity owing to higher unsaturated coordination sites density and flexible local structure, appropriate to form OER intermediates.

Very interesting work was carried out on the self-healing properties of the Ba 0.5Sr 0.5Co 0.8Fe 0.2O 3 - 8 (BSCF) perovskite in the OER regime. It is through progressive surface reconstruction during electrolysis that this material is able to restructure its surface into a mixed Co Fe oxyhydroxide phase, the outermost atomic layers of which were intimately interconnected on to the underlying perovskite lattice. Interestingly, upon exposure at times to possible cycling or short durations of open-circuit relaxation, the surface layer spontaneously re-crystallized into a partially ordered structure rather similar to the original perovskite motif. This two-way transformation was explained by an active process of lattice oxygen and metal cations exchange, facilitated by local pH and redox variation of the surfaces in catalyst-electrolyte interface. The mechanism essentially constituted a feedback loop in which disorder within the structure, caused by the operating rate, enhanced the catalytic rate whereas relaxation enabled a re-gain in order and stability even though to a limited extent. The dynamics between these two regimes is at the core of a self-healing chain reaction that leads to long life catalytic performance with long operation time.

Such dynamic reconstruction is not restricted to mere surface atoms only but subsurface layers are also involved thus, posing a piecemeal compositional and electronic properties across the

active region. HAADF-STEM time-resolved experiments have observed that Co atoms migrate in the anodic bias to the surface, and then some will flow back to the bulk in the resting periods. This ensuring of regeneration of fresh active site and surface defect recovery helps in reducing the obtention of irreversible degradation. The system will therefore be a quasi-open catalytic cycle such that the structural flux will not be a decay but rather, it will be a reproduction process.

These self-reconstructing systems have unusual stability profiles with regard to electrochemical behavior. In contrast to monotonic loss of current density with time, common to most low cost catalysts, instead in BSCF and other perovskite oxides, the current density may stabilize at a relatively high level, or actually increase at low current densities with time, at least during the first few electrolysis hours. Such an activation process can be associated with the process of reconstructing the surface layer to form it and, therefore, the most favorable catalytic state is not actually obtained in the process of synthesis, but in the operating process itself. The practical implication is that steps like cyclic voltammetry or galvanostatic activation as pre-conditioning steps can be employed in order to shape the active surface structure in situ so that pre-conditioning by high temperature or chemical complexation become unnecessary as the active surface can be shaped prior to reaction. There has already been integration of these findings into catalyst design and this fact is already making an impact on the design of next generation low cost materials. A new approach is molecular engineering of perovskite precursors with a mobile A-site cations and redox-flexible B-site metal to enable moving-on and moving-off surface. At the same time, electrolyte formulations are also being refined to add trace metal ions that may be incorporated selectively into the catalyst matrix during operation that would further enhance the self-healing mechanism. The underlying mechanism of this electrochemical doping method is to take the advantage of nondestructive surfaces reconstruction to provide continuous activity renewal, which does not require extrinsic regeneration schemes. Indicatively, OER activity and stability have been improved in cobalt-based catalysts through doping their sites with Ni 2+ or Mn 2+ species during operation with such ions occupying lattice vacancy inherited in the reconstruction process.

Dynamic changes of the oxidation state of surfaces are likewise victimized by the phenomenon of catalyst reconstruction. In in operando X-ray absorption near-edge structure (XANES) studies of BSCF and other similar surface Co-bearing oxides, it was observed that the average oxidation state of surface Co varied alternately between Co3 + and Co4+ with applied potential. Structural distortions accompany these redox states which varies the local electronic environment and affect the adsorption energies of oxygen intermediates. Reversibility of the transitions in oxidation state is also very important in order to retain activity because complete over-

oxidation or reduction is deactivating. In that way, the capability of the catalyst to withstand repeated redox processes without the irreversible loss of activity is the hallmark of its self-healing ability. Even more, the practical applicability of these discoveries can be further reinforced by the fact that dynamic self-healing materials can be compatible with industrial scale electrolyzer designs. The structural plasticity and compositional robustness of reconstructed catalysts makes them well-suited to use in devices that have to run at changing current densities, work stop/start, or different pH and temperature regimes. Further, the fact that they handle the presence of electrolytic impurities or mechanical perturbations strongly, makes it less necessary to have frequent replacements or maintenance that are cost-saving factors in the large-scale production of hydrogen. It was found that the BSCF-based systems have a high promise of being commercially adopted with a lifetime of more than 200 hours at high current densities that retain over 90 percent of initial activity.

Lastly, the grasp of dynamic reconstruction and self-healing is being exploited to guide machine-learning-guided catalytic discovery. With encoded structural descriptors relevant to reconstruction propensity, defect mobility, and redox cycling capacity captured in predictive models, researchers can now use those models to screen compositional spaces of large volumes to identify materials likely to exhibit self-healing behavior. This method closes the empirical experimentation and theoretical design and allows the rapid synthesis of stable strong-performing electrocatalysts. The new paradigm therefore does not place catalyst reconstruction in the category of liabilities that must be repressed, but rather a working characteristic that can be made use of, making a conventional difficulty to a pillar of electrocatalysis in the contemporary world.

Collectively, the observed phenomena of dynamic catalyst reconstruction and self-healing serves as a conceptual transformation in the way catalyst stability is being framed in the framework of the low-cost water electrolysis implementation. In place of the inflexible systems that cannot modify themselves in any way, researchers are currently adopting the fluxional systems, which accommodate the environmental conditions in which they operate, maintaining or even improving their performance. These observations open the road to the future of catalytic materials that regenerate themselves without external assistance, are stable at industrial temperatures, and be optimized by a trial-and-error balanced with computational analysis and design. These systems are set to be the key in the sustainable scaling of hydrogen technologies in the decades to come [138, 139].

Chapter 5 CONCLUSIONS – SUGGESTIONS FOR FURTHER STUDY

Sustainable and decarbonized energy transition depends crucially on the development of clean and scalable hydrogen production technologies. However, water electrolysis is by far the most environmentally friendly option, whereby hydrogen is created using water and renewable electricity only, with oxygen being the only byproduct. As presented in this study, water splitting for hydrogen production faced challenges and emerging strategies have been covered in detail, including technological advances in the electrolysis system, electrocatalyst engineering, materials science and economic assessment.

5.1 Technological Advancements in Electrolysis Systems

Alkaline water electrolysis (AWE), proton exchange membrane electrolysis (PEME) and solid oxide electrolysis (SOE) technologies have their own advantages as well as limitations for water electrolysis. The most mature and commercially available technique continues to be alkaline electrolysis, because of the use of low cost materials and robust operation. It can however be disadvantageous owing to its relatively slow response time and lower current densities which are unsuitable for dynamic operation during the use of renewable energy sources.

However, PEME allows quicker reaction kinetics, and higher current densities, with more compact system design, but they depend greatly on expensive noble metal catalysts (Pt, Ir, Ru), and are determined by the use of highly pure water in order to prevent degradation of membrane. At elevated temperatures, SOE has the greatest potential electrical efficiency since it harvests both thermal and electrical energy. However, SOE is still in a developmental stage and also suffers from other material and durability challenges.

However, comparing different methods in detail, it is shown that no one method is best suited for all situations. They should rather be selected according to the specific application, scale and integration with energy sources. Decentralized green hydrogen production can be made possible with the aid of electrolyzers in conjunction with renewable sources in hybrid or autonomous configurations.

5.2 Innovations in Electrocatalyst Design

In the case of water electrolysis, the two electrocatalysts that drive the two half reactions, namely, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), play a central role. However, these reactions proceed with low kinetics, and high overpotentials are required in order

for them to take place, leading to low system efficiency. Significant work of this thesis was devoted to advances in noble metal based and non-noble metal based catalysts.

Noble metal catalysts like Pt and IrO_2 offer unmatched activity and stability, particularly in acidic conditions. Yet, these are scarce and pricey, and that calls for substitutes. Alloying noble metals with base metals for higher utilization, engineering of single atom catalysts (SACs) for atom efficient utilization, or development of core–shell structures with higher activity but sufficient durability will likely provide the best solutions.

In spite of being non-precious, Ni, Co, Mo and their compounds (e.g., Mo_2C, Ni_2P, CoS_2) have exhibited competitive performance under alkaline conditions with HER. It was found that NiFe and Co based systems are also viable alternatives for OER. With improved electronic properties, charge transfer and active site exposure, unmated morphologies, heteroatom doping and defect control, transition metal phosphides (TMPs), nitrides (TMNs) and dichalcogenides have been engineered.

Nanostructured or porous electrocatalysts can be derived from metal organic frameworks (MOFs) and their derivatives. Thus, the ordered arrangement of metal nodes and organic linkers in MOFs is used to convert MOFs to SACs or metal–carbon hybrids with high catalytic efficiency. Furthermore, the creation of intrinsically conductive MOFs and direct in situ MOF–based electrodes leads to a new avenue for the following generation electrocatalyst development.

5.3 Stability and Durability: A Critical Barrier

A major challenge for such non-precious metal systems remains catalyst stability under prolonged operation. However, both activity and lifetime are compromised by degradation mechanisms, including corrosion, particle agglomeration structural collapse, and delamination, etc. To deal with these problems, innovation in the material design, including defect engineering, the introduce of oxygen vacancies, and the construction of robust core–shell architectures with protection layers is needed.

It has been demonstrated, by studies on integrating conductive supports such as transition metal carbides (TMCs), MXenes, or 2D materials (i.e., MoS_2, WS_2), that they can greatly improve the stability and charge transfer of the catalyst. Better dispersion of active species is facilitated by these substrates; the substrates provide mechanical and thermal stress buffer. To further promote unidirectional electron flow and thereby enhance catalyst efficiency while avoiding charge accumulation and consequent thermal degradation, heterostructures with such built in electric fields can be employed.

In reality, a stable behavior must not be treated as an afterthought, but as a primary design objective. Valuable for reliable long-term hydrogen production are multifunctional materials that possess the abilities to be catalytic active, corrosion resistant, and structurally resilient.

5.4 Techno-Economic Considerations

However, the price of green hydrogen is still a major obstacle for its widespread adoption despite much technological progress. In addition, high energy input and limited system lifetimes contribute to a levelized cost of hydrogen (LCOH) that is still several times higher than that of gray hydrogen based on fossil fuels. The current economic gap needs to be addressed through the improvement in efficiency, reduction of materials cost and the scaling up of the production systems.

Under current assumptions, solid oxide electrolysis technology with waste heat integration (SOEC W.H.) will be most economical compared with other electrolysis technologies, according to the study's cost analysis for different scenarios (pessimistic, average, and optimistic) of electrolysis technologies. PEME and AWE, on the other hand, face competitive conditions under lower electricity prices and optimized operation of the system. Importantly, the management will use tools like net present value (NPV), internal rate of return (IRR) and low levelized cost of heat (LCOH) to evaluate financial feasibility and investment attractiveness.

With such a configuration, hybrid (grid + renewables) and autonomous (off-grid) models come to offer flexibility in terms of both geography and economics. These must not only be evaluated based on cost, but also on the nonproportionality of the environmental impact, land use, and the sustainability of materials.

5.5 Suggestions for Further Study

The complexity and multi-disciplinary nature of water electrolysis and green hydrogen production make possible many future promising directions for investigation. An area of particular importance is the ability to provide advanced in situ characterization during the electrocatalyst behavior under near real conditions. Studies such as potential induced surface restructuring, phase transitions in operation, and processes that take place during the course of reaction cycles will be of significance as they would provide an understanding of the degradation mechanisms and improving catalyst stability.

The second critical research direction involves the synthesis of single atom and nanostructured catalysts, and their scalable synthesis. Cost effective methods that allow a lab scale success to be successfully scaled up without thereby sacrificing material performance are required to bridge the gap between laboratory scale successes and industrial deployment. Special attention should be paid

to low temperature and solution processing compatible with continuous roll to roll manufacturing platforms.

Besides materials and processing innovations, hydrogen production integration with energy storage systems, smart electrical grids, and large industrial applications, e.g., ammonia synthesis and steel production provides further potential to increase the overall energy system efficiency. Such synergies could lead to new value chains and help decarbonize our grids across multiple sectors.

Another avenue for further exploration of hybrid material systems is that of composites between perovskite and MOF materials, and also the development of dual phase electrolytes that can lead to transformative progress in conductivity, catalytic performance and the long term operational stability of these devices. In future, these novel materials could provide for more efficient and robust electrocatalytic processes than are currently available for the new energy demands that are required.

The environmental impact of hydrogen technologies will have to be assessed by the development of comprehensive lifecycle and circular economy framework. This requires these tools to evaluate sustainability in greenhouse emissions as well as other critical drivers like raw material sourcing, recyclability, and end of life. They should be embedded from the technologies' early stages to ensure long term viability based on some sustainable design principles.

Finally, there exists great promise for artificial intelligence and machine learning for speeding innovation as well. It can be employed to discover new catalyst candidates, project degradation pathways, as well as optimize system performance in real time. AI based approaches will make possible to accelerate timelines of development and reduce costs of operation by way of data driven materials discoveries and system control.

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