Chapter 1

Introduction to Electrocatalysts

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With global energy consumption growing at an unprecedented rate and environmental concerns becoming increasingly acute, the need for clean, sustainable energy conversion and storage systems such as fuel cells, dye-sensitized solar cells, metal-air batteries and Li-CO_2 batteries is of utmost significance. The main reactions involved in these renewable energy technologies are oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), and CO_2 reduction reaction (CO_2RR), which all require catalysts. An electrocatalyst is a surface where chemical energy is electrochemically converted into electrical energy in fuel cells. For the selection of an electrocatalyst and tailoring its characteristics, both stability and selectivity must be assessed. Overall fuel cell performance is mainly determined by the efficiency of the electrocatalyst. Catalysts based on metals are currently widely used, but they suffer from multiple competitive disadvantages, including their low selectivity, poor durability, and negative environmental impact. Hence, it is highly desirable to develop earth-abundant, low-cost, stable, and catalytically active metal-free alternatives for application in renewable energy. Catalysts made from carbon-based metal-free materials possess advantages such as high earth abundance, low cost, high electrical conductivity, structural tunability, good selectivity, and solid stability in acid/alkaline conditions. These characteristics explain why these catalysts are receiving increasing attention in applications related to energy and the environment. Through electrocatalysis without the use of noble metals, numerous carbon-based electrocatalysts have been developed for the storage of clean energy and the protection of the environment. This chapter aims to introduce electrocatalysts and electrocatalysis to the reader. By understanding electrocatalysis and electrocatalysts, the readers will gain a deeper understanding of the concepts. Firstly, the authors will discuss the basics of electrocatalysts, electrocatalysis, types of electrocatalysts, and electrocatalysis, and then they will review some fundamental concepts. Lastly, a brief overview of recent research and

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advancements in non-noble metal free electrocatalysts will be presented by using carbon-based nanomaterials in the context of energy storage and concluded with a remark.

Introduction

With global energy consumption growing at an unprecedented rate and environmental concerns becoming increasingly acute, the need for clean, sustainable energy conversion and storage systems such as fuel cells, dye-sensitized solar cells, metal-air batteries and Li-CO_2 batteries is of utmost significance. The main reactions involved in these renewable energy technologies are oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), and CO_2 reduction reaction (CO_2RR), which all require catalysts. An electrocatalyst is a surface where chemical energy is converted into electrical energy in fuel cells. Both stability and selectivity must be assessed for selecting an electrocatalyst and tailoring its characteristics. Overall, fuel cell performance is mainly determined by the efficiency of the electrocatalyst. Catalysts based on metals are widely used, but they suffer from multiple competitive disadvantages, including low selectivity, poor durability, and negative environmental impact. Hence, it is highly desirable to develop earth-abundant, low-cost, stable, and catalytically active metal-free alternatives for application in renewable energy. Catalysts made from carbon-based metal-free materials possess advantages such as high earth abundance, low cost, high electrical conductivity, structural tunability, good selectivity, and solid stability in acid/alkaline conditions. These characteristics explain why these catalysts are receiving increasing attention in energy and environment applications. Through electrocatalysis without the use of noble metals, numerous carbon-based electrocatalysts have been developed to store clean energy and protect the environment. This chapter aims to introduce electrocatalysts and electrocatalysis to the reader. By understanding electrocatalysis and electrocatalysts, the readers will understand the concepts more deeply. Firstly, the authors will discuss the basics of electrocatalysts, electrocatalysis, types of electrocatalysts, and electrocatalysis, and then they will review some fundamental concepts. Lastly, a brief overview of recent research and advancements in non-noble metal-free electrocatalysts will be presented using carbon-based nanomaterials in the context of energy storage and concluded with a remark.

In this chapter, we will introduce the electro catalyst's role in the fascinating electrochemistry field. We will also briefly go over the fundamental idea to introduce the reader to the underlying ideas governing electrocatalysis and pique their interest in learning more about the enormous variety of electrocatalysts and their uses. In contrast to other books on electrocatalysis's introduction (*1–6*), our chapter provides an in-depth analysis of electrocatalysis's fundamental principles. It also discusses a few instances of the most effective electrocatalysts used in electrochemistry for energy storage application.

Basic Concepts in Electrochemistry

What Is Electrochemistry

The field of chemistry known as "electrochemistry" studies phenomena brought on by the interaction of chemical and electrical forces.

Types of Processes

Two different processes are described below;

1. Electrolytic processes: chemical changes brought on by the movement of an electric current.
2. Galvanic or voltaic processes: produce electric energy through chemical processes. Table 1 lists the main distinctions between galvanic and electrolytic cells.
3. What is an electrochemical cell: Two electronic conductors (electrodes) and an ionic conductor are the typical components of an electrochemical cell (Figure 1). (electrolyte). A cathode and an anode are the typical components of electrochemical cells. While ions move when carrying charges in the electrolyte, electrons or holes, move when carrying charges in the electrodes (both positive and negative). The anode, which represents an electrochemical cell, must always be displayed on the left, and the cathode must always be displayed on the right.

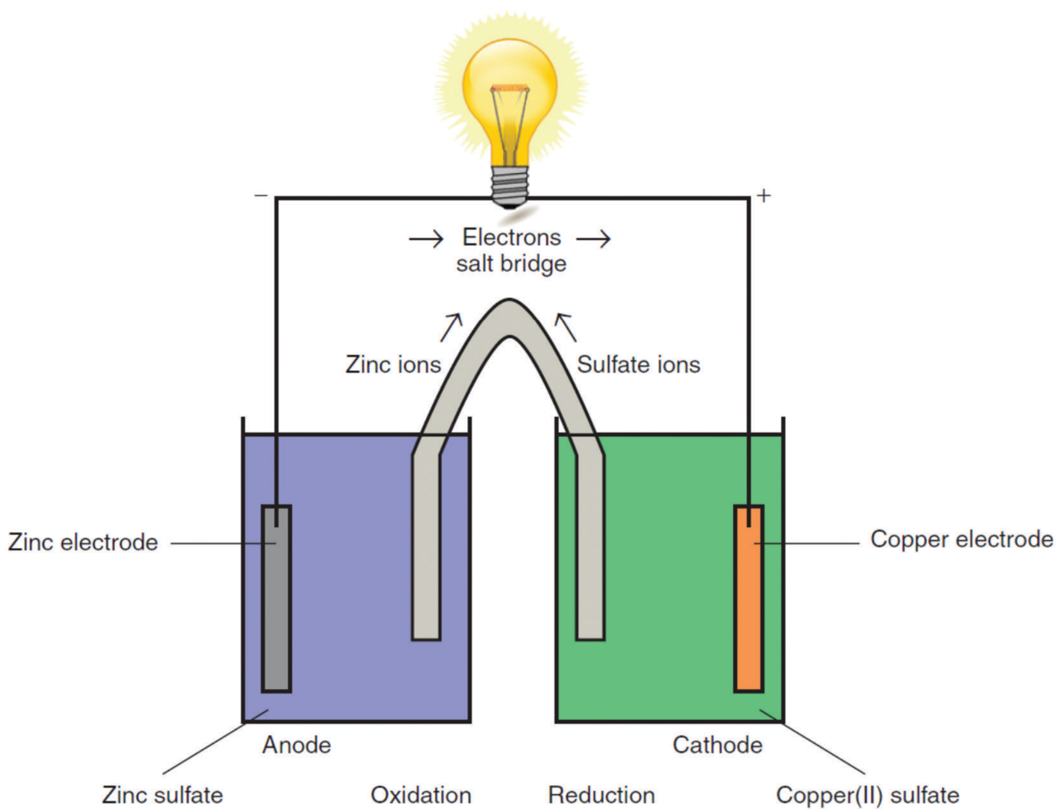

Figure 1. Electrochemical cell. Reproduced with permission from reference (6). Copyright 2009 Elsevier.

Reactions Types

Half-cell reactions: At each electrode, an electrochemical reaction occurs. This reaction is called a half-cell reaction.

Overall reactions: The overall chemical reaction of the cell is given by combining the two individual half-cell reactions.

Half-Cell Reaction Types

- Oxidation reactions: Oxidation (loss of an electron) is an energetic process and occurs when the electrode's energy dips below the compound's highest occupied molecular orbital.
- Reduction reactions: Reduction is also (gain of an electron) an energetic process and occurs when the energy of the electrode increases above the lowest vacant molecular orbital of the compound.

Half-Cells and Cell Potential

There are two fundamental types of half-cell reactions

- An electrode is dipped in an electrolyte in the two half-cells that make up an electrochemical cell. For both half cells, the same electrolyte may be utilized.
- These two half cells are joined by a salt bridge, which gives rise to ionic contact but prevents them from mixing when filter paper is dipped in a potassium nitrate or sodium chloride solution.
- A salt bridge is created. Electrons are lost in one of the electrochemical cell's half cells through oxidation, while electrons are gained in the other half cell through reduction. It should be noted that both half cells undergo an equilibrium reaction; when equilibrium is reached, the net voltage equals zero, and the cell ceases to function as a generator of electricity.
- An electrode's electrode potential describes the propensity of an electrode in contact with an electrolyte to lose or gain electrons. It is possible to forecast the overall cell potential using the values of these potentials. The standard hydrogen electrode is typically used as a reference electrode when measuring electrode potentials (an electrode of known potential).

Primary and Secondary Cells

- Galvanic cells used in primary cells are essentially disposable. In these cells, electrochemical processes occur that are inherently irreversible. As a result, the reactants are used to create electrical energy, and the cell stops producing current once all of the reactants have been used up.
- Secondary cells also referred to as rechargeable batteries, are electrochemical cells with a reversible reaction or the ability to operate as electrolytic and galvanic cells. The difference between the Galvanic and electrolytic cells are given below in Table 1.

Most primary batteries, consisting of multiple cells connected in series, parallel, or a combination of the two, are viewed as wasteful and damaging to the environment. This is because they use 50 times more energy during production than during production. They are regarded as hazardous waste and contain a lot of toxic metals.

Table 1. The Critical Differences between Galvanic Cells and Electrolytic Cells

Voltaic Cell /Galvanic Cell	*Electrolytic Cell*
These electrochemical cells convert chemical energy into electrical energy.	In these cells, electrical energy is converted to chemical energy.
These cells undergo entirely spontaneous redox reactions.	The redox reactions in these cells are not spontaneous; instead, energy input is necessary for them to occur.
The anode and cathode in these electrochemical cells are both negatively charged.	These cells have a cathode that is negatively charged and an anode that is positively charged.
The source of the electrons is the species that is oxidized.	Electrons come from an outside source (such as a battery).

Applications of Electrochemical Cells

- Many non-ferrous metals are electro-refined using electrolytic cells. To electro wine these metals, they are also utilized.
- Electrolytic cells produce lead, zinc, aluminum, and copper that are highly pure.
- Melted sodium chloride can be used to produce metallic sodium by putting it in an electrolytic cell and running an electric current through it.
- Galvanic cells are a common component of many widely used commercial batteries, including lead-acid batteries.

In many remote locations, fuel cells, a significant class of electrochemical cells, provide clean energy.

Electrocatalyst and Electrocatalysis

Because traditional fuels are still used, mainly in transportation and electricity generation, greenhouse gas emissions are causing dangerous climate change. To solve scientific problems, energy sources with high capacity like metal-air batteries and fuel cells have been developed to address clean energy requirements in transportation applications as well as the usage of renewable energies (*7*, *8*). Redox reactions in electrochemistry like OER, ORR, HER, and others take place in the energy storage devices' electrodes. An electrochemical redox reaction processes have several roadblocks. HER, ORR and OER, and all play a role in clean and sustainable energy technologies like water splitting devices, transition metal-air batteries, and fuel cells. To improve the reaction of Oxygen reduction in fuel cell technology for conversion of energy, the Oxygen evolution in transition metal-air batteries for storing energy, as well as HER in solar water splitting for hydrogen fuel production, catalysts are necessary. In these processes, noble metals like Ir (iridium), Pd (palladium), Pt (platinum), and oxides of metals are commonly utilized as catalysts.

On the other hand, catalysts based on noble metals have several drawbacks, including Gas poisoning sensitivity, poor stability, expensive demand, limited selectivity, restricted availability, and so on, all of which have hampered the commercialization of those energy solutions. To keep costs down of precious metals and their oxides, scientists have worked hard to build electrodes with metal-free and Pt-free catalysts that are effectively for Oxygen reduction reaction (*9–12*), Oxygen evolution reaction (*13*, *14*), Hydrogen evolution reaction (*15*, *16*), and other processes. Moreover, a variety of metal-free electrocatalysts are outstanding two functional electrocatalysts for OER/ORR in recyclable transition metal-based-air batteries (*17*, *18*), as well as OER/HER in water electrolysis reaction (*19*) as well regeneration fuel cells (*20*). Electrocatalysts with Three functional and multifunctional (OER, ORR and HER) have recently been identified (*21*, *22*).

What Is Catalyst in Chemistry

Catalysts are chemicals that modify the reaction pathway to change the rate of a reaction. Any catalyst is utilized to accelerate the reaction rates. On the other hand, they are utilized to rebuild or destroy bonds between the atoms in particular compounds' molecules or elements. Catalysts, in essence, promote atoms to react, making the entire chemical reaction process more accessible and practical. The following are a few of the essential characteristics of catalysts:

- A catalyst isn't the one that starts a chemical reaction.
- There is no consumption of a catalyst in the reaction. This means that it is not used up in the reaction. It must, however, take part in the reaction.
- Catalysts have a propensity for reacting with reactants to develop intermediates while assisting in forming a final byproduct. After the complete procedure, a catalyst can reproduce.

Catalysts come in three forms in nature: solid, liquid, and gaseous. Solid catalysts include metals or metal oxides, like halides and sulphides. Catalysts include semi-metallic elements such as B (boron), Al (aluminum), and Si (silicon). The Catalysts can also be completely pure liquid or gaseous materials. These components can sometimes be mixed with suitable solvents or carriers. A catalytic reaction arises when a catalyst is present in the system. In other words, catalytic activity is a chemical reaction combining a reactant and a catalyst. As a result, intermediates in chemical reactions are developed, which can interact easily with one another or another reactant to produce a product. The catalyst, however, is regenerated when the intermediates in chemical reactions and the reactants react. The reaction modes between the reactants and catalysts are typically different and even more complicated with solid catalysts. Processes of oxidation and reduction, acid-base reactions, free radical production and the development of complex coordination are some examples of reactions. Surface properties and electrical crystal structures strongly influence the reaction pathway of solid catalysts. Some solid catalysts, such as polyfunctional catalysts, have several reactions with the reactants.

Types of Catalysts

Depending on the necessity or demand of the chemical reaction, many types of catalysts might be utilized. The following are the details:

Positive Catalysts

Positive catalysts increase the rate at which a chemical reaction occurs. It increases the product yield percentage by lowering the activation energy barriers, permitting many reactive molecules to be transformed into products.

Negative Catalysts

Negative catalysts are those that slow the rate of a chemical reaction. It slows the reaction rate by increasing the activation energy barrier, which lowers the number of reactant molecules that can be converted to products and hence delays the reaction.

Promoter or Accelerators

A promoter or accelerator is a chemical that boosts the catalytic activity.

Catalyst Poisons or Inhibitors

Catalyst poisons or inhibitors are substances that reduce the action of the catalyst.

What Is Electrocatalyst

An electrocatalyst is a catalyst that engages in electrochemical processes. Electrocatalysts are a kind of catalyst that operates on electrode surfaces or is the electrode surface itself in some situations. Heterogeneous electrocatalysts include platinized electrodes. A homogeneous electrocatalyst enables the transfer of electrons between an electrode and the reactants and produces a chemical reaction characterized by a half-reaction (*23*).

Background and Theory

A catalyst is a material that accelerates a chemical reaction without even being consumed in the process. Thermodynamically, a catalyst lowers the activation energy needed for a chemical reaction. When an electrochemical process is initiated, an electrocatalyst will impact the activation energy of the reaction. Figure 2 depicts the activation energy of chemical processes as a function of the energies of products and reactants. The activation energy of electrochemical reactions is proportional to the potential or voltage at which the reaction occurs.

Consequently, electrocatalysts typically modify the voltage where reduction and oxidation occur. In contrast, an electrocatalyst promotes a chemical reaction on the surface of an electrode (*24*). Because electrons are transferred from one chemical species to another during electrochemical reactions, suitable electrode surface contacts allow electrochemical transformations to occur, lowering the voltage needed to carry out these transformations (*24*). Stability, selectivity and activity are three factors that can be utilized to evaluate electrocatalysts. For a particular applied voltage, it is possible to quantify the electrocatalyst's activity by calculating the quantity of current density generated and, consequently, the reaction rate. The Tafel equation characterizes this relationship. Crucial to assessing the stability of electrocatalysts is their capacity to withstand the conversion potentials. Electrocatalyst selectivity is the interaction of electrocatalysts with particular substrates and the formation of a specific product (*25*). The selectivity coefficient, which compares the material's reaction to the target substrate to the response to certain other interferents, can be utilized to evaluate selectivity (*23*).

High activation barriers could be negative in several electrochemical systems, such as galvanic cells, fuel cells, and many types of electrochemical cells. The energy used to overcome such activation barriers is converted to heat. In most exothermic combustion processes, this heat catalyzes the reaction's progression. In an electrochemical redox reaction, this heat is a waste product that is wasted by the system. High overpotentials and low faradaic efficiency are commonly used to characterize the additional energy needed to overcome kinetic barriers. Each of the two electrodes and their corresponding half-cells would necessitate its unique electrocatalyst in all of these systems. In their total chemical transformations, multiple electron transfers, half-reactions comprising many stages, and the production or consumption of greenhouse gases will typically have significant kinetic barriers. Furthermore, at the surface of an electrode, there are frequently many potential reactions. During water electrolysis, the anode, for example, can oxidize water using a two-electron process to produce hydrogen peroxide or a four-electron process to produce oxygen. An electrocatalyst can make either reaction path easier.

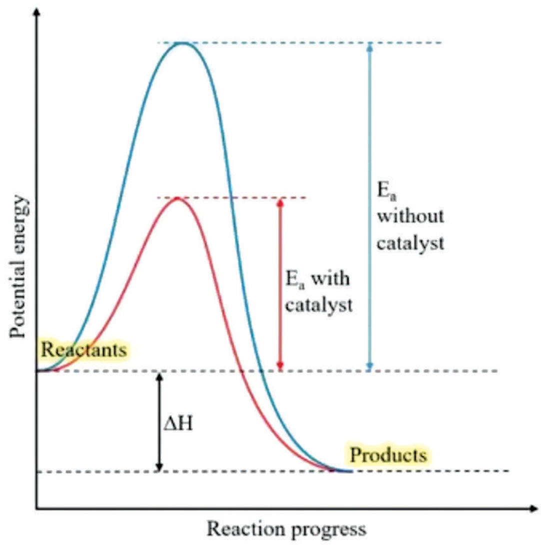

Figure 2. Diagram of the potential energy of a chemical reaction in the presence and absence of a catalyst. Catalysts can accelerate chemical reactions by reducing their activation energies since they remain unaffected by the reaction. An electrocatalyst reduces electrochemical activation energy by reducing an electric voltage where it takes place. Reproduced with permission from reference (25)*. Copyright 2020 MDPI.*

Features of Electrocatalysts

The features of electrocatalysts include:
High activity
High surface area
Good electrical conductivity
Long term stability

High Activity

Strongly depends on the physicochemical properties of the electrocatalyst surface and the electrode-electrolyte interaction**.** It must effectively lower the energy barriers of the electrocatalytic reaction and increase the electron transfer rate.

High Surface Area and Good Electrical Conductivity

These can be achieved by structuring conductive supports/substrates at the nanoscale.

Long-Term Stability

It is significant for practical applications. For example, in the ORR process, Pt-based catalysts have a low tolerance to byproducts such as Methanol/CO, resulting in a limited operating life of the devices.

What Is Catalysis

One of the core technologies in our current world is catalysis. It is widely used in industries for manufacturing and in the cleanup of waste to remove pollutants. Even internal biological mechanisms in our body frequently use catalysis. There must be enzymatic catalysis for all living things. Photosynthesis, considered the most crucial catalytic process, is in most of the most basic and primitive forms of life. The general definition of catalysis is the action of a catalyst, an agent that speeds up a chemical reaction while remaining unaffected by it. Catalysis can be divided into two main groups:

Catalysis Types: What Are They

A catalyst can be divided into three types depending on the material and its physical state.

- Homogeneous
- Heterogeneous
- Autocatalysis

Homogeneous Catalysis

It is referred to as homogeneous catalysis when a catalyst and a reactant occur in the same form of matter. Homogeneous catalysts operate in almost the same step as the reactants. Typically, homogeneous catalysts or substrates are dissolved in an appropriate solvent. The formation of methyl acetate ($C_3H_6O_2$) from acetic acid (CH_3COOH) and methanol with the influence of H+ is an example of homogeneous catalysis.

Oxidation of Sulfur Dioxide (SO_2) in Lead Chambers

Sulphuric acid can be produced using the lead chamber process. The catalyst used in this procedure is nitric oxide (gas).

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{\text{NO (g)}} 2SO_3\ (g) \tag{1}$$

It is homogeneous catalysis because SO_2 and O_2, as well as the catalyst NO, are all gases in the above reaction.

Photocatalysts (Homogeneous Catalysis)

This is known as photocatalysis, when a catalyst accepts light and is then elevated to an excited state.

Autocatalysis

In this catalytic reaction, no special catalyst is utilized. However, one of the products acts as a catalyst, accelerating the production process. In autocatalysis, one of the outcomes of the reaction is what speeds up the reaction. One of the easiest ways to see this is when a solution of ethane dioic acid (oxalic acid) is oxidized by a solution of potassium manganate (VII) that has been made acidic (potassium permanganate).

$$2MnO_4^- + 6H^+ + 5\begin{matrix}COOH\\|\\COOH\end{matrix} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \qquad (2)$$

At ambient temperature, the process moves very slowly. It serves as titration to discover how much potassium manganate (VII) solution there is, usually done at around 60°C. Even though it starts pretty slowly. Manganese (II) ions help speed up the reaction. Since none of these things is there before the reaction begins, it begins very slowly at ambient temperature. But if you look at the equation, you'll see that one of the products is manganese (II) ions. When the reaction goes on, a more significant amount of catalyst is made, which makes the reaction go faster.

Heterogeneous Catalysis

In this type of catalysis, the reacting molecules and the catalyst utilized in the reaction are not in the same state of matter. Since surface catalysis primarily occurs between a solid surface and a gas, it is frequently referred to as surface catalysis. Generally, this process is comprised of three stages:

- adsorption of reactants on the catalyst surface
- chemical reaction on the surface
- desorption of products from the catalyst surface.

The following considerations regarding catalyst action must be made. The thermodynamics of the reactions are not changed by catalysts first. Any catalyst does not support a thermodynamically impossible reaction. Therefore, even without the catalyst, the reaction would still occur, albeit perhaps too slowly, to be noticed or valuable in a particular situation. Additionally, because a catalyst increases both the forward and reverse reaction rates equally, it does not affect the equilibrium composition. This raises the question of why it is claimed that a catalyst's selectivity is its most important quality from a practical standpoint since a catalyst cannot alter the state of equilibrium. It is essential to remember that if there is a complex reaction network, which is frequently the case, the catalyst may have a different impact on each reaction, changing the overall reaction selectivity. Adsorption of reactants occurs on the catalyst surface in heterogeneous catalysis. In the catalytic reaction, chemical bonds between reactants weaken, forming new compounds. Compounds (products) with weaker bonds to the catalyst are released. Heterogeneous catalysis is shown by the industrial production of ammonia (shown below), which needs solid catalysts to speed up the reaction between nitrogen and hydrogen at such a significant rate:

$$N_2\,(gas) \rightarrow N_2(ads) \qquad \text{(Taking in nitrogen on the surface of the catalyst)} \qquad (3)$$

$$N_2\,(ads) \rightarrow 2N(ads) \qquad \text{(Nitrogen dissociation)} \qquad (4)$$

$$H_2\,(gas) \rightarrow H_2(ads) \qquad \text{(Hydrogen is absorbed on catalyst surface)} \qquad (5)$$

$$H_2\,(ads) \rightarrow 2H(ads) \qquad \text{(Hydrogen Dissociation)} \tag{6}$$

$$\mathrm{N}(ads) + 3H(ads) \rightarrow NH_3(ads) \qquad \text{(reaction to form ammonia adsorbed)} \tag{7}$$

$$NH_3\,(ads) \rightarrow NH_3(g) \qquad \text{(Desorption of ammonia)} \tag{8}$$

It should be observed that reactant adsorption is frequently not uniform across the catalyst surface. Active sites are specific favourable regions on a surface where adsorption and consequently catalysis primarily occurs. In environmental chemistry, catalysts are crucial for degrading pollutants like industrial and automobile exhausts.

Electrocatalysts (Heterogeneous Catalysis)

Several forms of metal-containing catalysts are employed in electrochemistry, mainly when dealing with fuel cell engineering. The primary purpose of these catalysts is to speed up the half-reactions rate in a fuel cell. Most of the time, a popular electrocatalyst employed in a fuel cell is based on platinum nanoparticles. Slightly larger carbon particles now support these. Platinum accelerates the oxygen reduction rates to hydroxide or water when it interacts with one of the fuel electrodes of the cell (also hydrogen peroxide).

Types of 2D Nanomaterials-Based Electrocatalyst for an Energy Conversion Application

There are different types of catalysts used for energy conversion, and some of those are listed below in Table 2.

- Metal-free 2D nanomaterials
    - Graphene (e.g., N-doped Graphene)
    - Graphene
    - Graphitic carbon nitride (g-C_3N_4)
    - Hexagonal boron nitrite (h-BN)
    - Black phosphorus
- 2D Transition-metal oxides and hydroxides
    - Transition metal oxides
    - Layered transition metal hydroxides
- 2D metals chalcogenides
    - Transition metal dichalcogenides (MoS_2)
    - Non-layered metal chalcogenides
- MXenes and non-layered transition metal carbides and nitrides
- Transition metal catalyst
- Metal-organic frameworks (MOFs)

Engineering Protocols for Efficient Catalysts Design

Protocols include the following:

- Heteroatom doping
- Defect engineering
- Lateral size and thickness regulation
- Strain and phase engineering
- Interface engineering

Table 2. OER Electrochemical Data of Carbon, Cobalt, Iron, Nickel, Manganese, Zinc, and Copper-Based Compounds

S. No	*Catalyst used*	*Electrolyte*	*Electrode*	*Ref*
1	N, P co-doped Mesoporous carbon (NPMC-1000)	6 M KOH	GCE	(*26*)
2	g-C_3N_4 NS–CNT	0.1M KOH	GCE	(*27*)
3	S-doped CNT	1 M KOH	Pyrolytic graphite electrode	(*28*)
4	N doped graphite	0.1 M KOH	GCE	(*29*)
5	echo-MWCNTs	1MKOH	GCE	(*30*)
6	Cobalt oxide nano rods	1 M KOH	CFP	(*31*)
7	Amorphous Co_3O_4 Film	1 M KOH	Au substrate	(*32*)
8	Co_3O_4/N-m rGO	1 M KOH	Ni foam	(*33*)
9	Co_3O_4/N-CNTs grafted carbon polyhedron	1 M KOH	GCE	(*34*)
10	Co_2–Fe–B	1 M KOH	Cu substrate	(*35*)
11	FeNi LDH/ graphene	1 M KOH	Nickel foam	(*36*)
12	Fe doped NiO	0.5 M KOH	Gold electrode	(*37*)
13	Fe-Ni_3S_2/NF	1 M KOH	Nickel foam	(*38*)
14	$ZnCo_2O_4$/ NCNTs	0.1 M KOH	RDE	(*39*)
15	IrO_2-ZnO	1 M KOH	GCE	(*40*)
16	NiO/TiO_2	1 M KOH	GCE	(*41*)
17	NiO/Fe saturated	0.1 M KOH	FTO	(*42*)
18	C-NiOx/polypyrole	1 M KOH	Carbon electrode	(*43*)
19	Ni–Bi/RGO	1M KOH	GCE	(*44*)
20	Ni-Fe-P	1 M KOH	Ni foam	(*45*)

Table 2. (Continued). OER Electrochemical Data of Carbon, Cobalt, Iron, Nickel, Manganese, Zinc, and Copper-Based Compounds

S. No	*Catalyst used*	*Electrolyte*	*Electrode*	*Ref*
21	Mn_2O_3	0.1 M KOH	GCE	(*46*)
22	α-MnO_2	0.1 M KOH	Pyrolytic graphite carbon	(*47*)
23	Mn-CoO/NCNTs	0.1 M KOH	RDE	(*48*)
24	Mn-Ni nanoplates/rGO	1 M KOH	GCE	(*49*)
25	$MnFe_2O_4$ NFs	0.1 M KOH	GCE	(*50*)

What Is Electrocatalysis

Electrocatalysis is a critical process in fuel cells and electrolysis devices. In electrocatalysis, bonds are broken and formed by electron (e^-) and ion transport at electrode surfaces. The availability of renewable electricity increases electrochemical devices' ability to convert chemical to electrical forms, enabling electrical energy to be stored in electricity-driven conversions or manufactured as chemical molecules. The Carnot limit is a term that refers to a limit that applies to thermal processes and is avoided when chemical and electrical energy are converted directly. Electrocatalytic processes that promote chemical or electrical interconversions are necessary to facilitate ecologically acceptable and renewable energy technologies, which contribute to the long-term infrastructure for energy. Electrocatalytic activities occur in electrolysis devices and fuel cells at both cathode and anode. Fuel cells use an exergonic reaction to transform chemical energy directly into electricity. Fuel cells typically consist of an anode that oxidizes the fuel and a cathode that reduces oxygen, producing electrical energy. Anode electrocatalytic processes can oxidize various fuels, including methane, ammonia, alcohols, hydrogen and sugars. Other oxidants, such as hydrogen peroxide (H_2O_2), can also be used on the cathode side. However, oxygen reduction from the air offers the most practical alternative for large-scale fuel cell applications. Within a proton exchange membrane fuel cell system (Figure 3A), hydrogen is oxidized at the anode to generate electrons and protons, while oxygen is reduced to H_2O at the cathode (*51*).

Electrolysis technologies use electrical work to drive endergonic reactions. Water electrolysis in a hydrogen fuel cell (Figure 3B) flips the chemistry by oxidizing water to oxygen at the anode and reducing protons at the cathode to produce hydrogen gas. Additional electrocatalysts of interest in electrolysis applications include the conversion of carbon dioxide to hydrocarbons or carbon monoxide (*52*), the exchange of oxygen from biomass (*25*), nitrate to nitrogen and ammonia, and nitrate to nitrite. Water oxidation might be the anodic reaction for all these reduction processes, allowing the overall process to input electrical energy and water to aid chemical reduction. The complete electrochemical reaction successfully achieves hydrogenation in the case of hydrogen oxidation as an anodic reaction. Electrochemical devices operating at ambient temperatures to 1300 K can perform the electrocatalytic actions outlined above. Solid ion conductors are used in high-temperature equipment/devices.

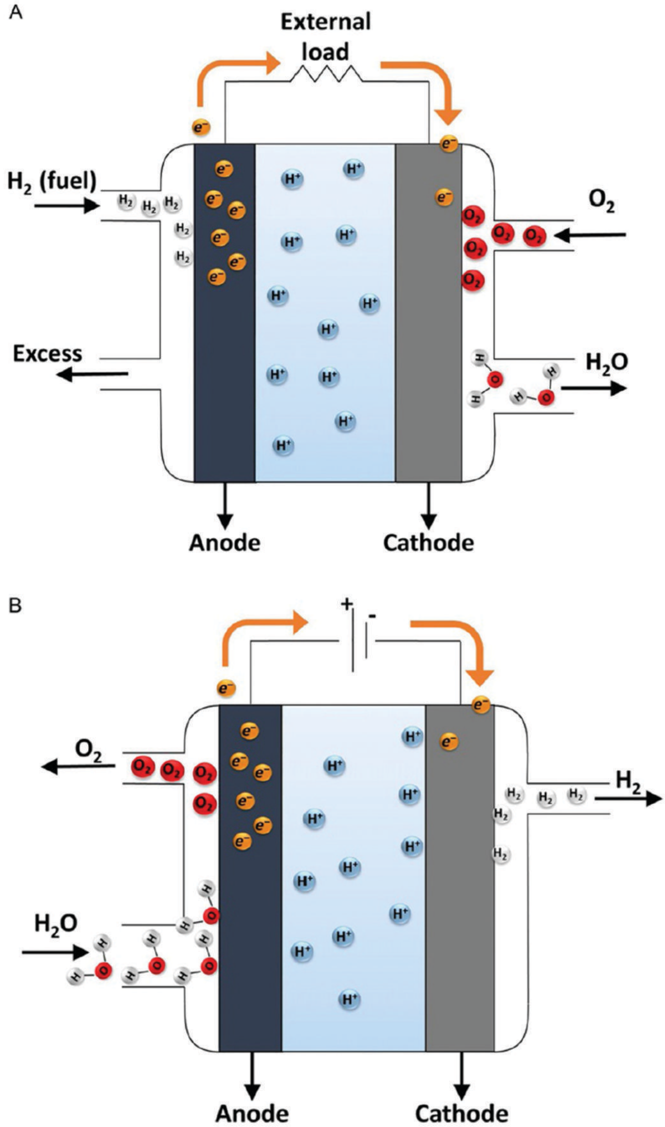

Figure 3. Diagrams of a fuel cell system that converts exergonic H_2 and O_2 to water (A) and a Hydrogen derived from endergonic water electrolysis (B). Reproduced with permission from reference (51). Copyright 2018 Elsevier.

In contrast, hydrated polymeric membrane components are used in low-temperature equipment/devices to allow the transport of ions between anode and cathode. Hydroxide or Proton conducting polymeric membranes can be used in hydrogen fuel cells to operate at low temperatures. In high-temperature fuel cells, solid oxygen ions or proton conductors can be utilized, with the high temperatures facilitating the conduction of ions in solid. In addition, hydrogen fuel cells can operate between 400 and 1300 K by using liquid H_3PO_4 as an electrolyte. The performance of an electrochemical device is affected by its reaction kinetics, product transport, reactant and ion transport, and electron conduction (Figure 4). Materials' composition, interfacial structures, and single-phase behavior affect these processes. Electrochemical reactions accelerate exponentially as the cell moves away from its equilibrium potential. Electrochemical devices are often limited by the reaction rate at the electrode surface, as they are intended to perform with a slight deviation from the reaction equilibrium potential. Electrocatalyst materials need to be designed to facilitate efficient operation near equilibrium potential. Electrocatalysis occurs at the electrode-electrolyte interface, where reactants, ions, and products move between these components. Electrocatalysis is a chemical reaction in a "homogeneous" system when the electrolyte breaks and forms bonds, with electrons transferred to or from an inert electrode to complete the process.

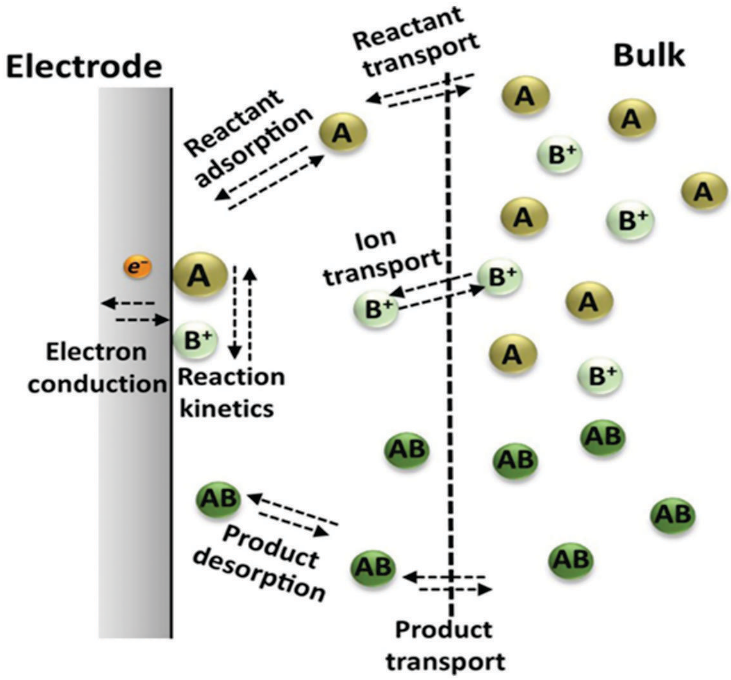

Figure 4. The mobility of species and ions, electrochemical reactions, and electron conduction near the electrode surface are significant factors in an electrochemical reaction. Reproduced with permission from reference (51). Copyright 2018 Elsevier.

Brief History of Electrocatalysis

The history of electrocatalysis begins with the history of electrochemistry. Faraday discovered the rules of electrocatalysis between 1833 and 1836 (*53*). Gardner Cottrell established the Cottrell equation (*54*, *55*), which governs the relationship between the kinetics of electrodes and mass transfer. Bowden and Rideal pioneered electrocatalysis in the 1920s when they developed a variety of metals for measuring the (HER) (*56*). Pt-group metals exhibit the highest HER activity, including Pt, Ir, Pd, Rh, and others. The overpotential will be significantly reduced by minimizing the Set off potential and Tafel slope of the Pt electrocatalyst (0.2–0.4V). In 1923, the electrochemical basis hypothesis for how acids and bases act was published (*57*). The term electrocatalysis was invented by N. Kobosev and W. Monblanowa in 1931 (*58*). Electrocatalytic water splitting is the method of hydrogen synthesis via electrocatalysis that has generated the most interest. The catalyst is essential to the reaction, and depending on the semiconductor type, it can behave as an anode or a cathode (n or p-type). The electrocatalytic CO_2 reduction reaction (CO_2RR) has been studied for over a century. In 1870, formic acid was the only product of the CO_2RR reaction. The H atom–metal interaction and proton discharge activation energy relationship were published in 1935 by J. Horiuti and M.

Polanyi (*59*) released another critical study in 1981. CO_2RR, HM $(CO)_5$ where M = Mo, Cr, or W has been shown to have carbonyl anionic metal hydrides. The behaviours of RuO_2-doped Ni/Co_3O_4 electrodes were examined by Krstajic et al. (*60*). It is shown that RuO_2 in a Co_3O_4 matrix with less than 10 mol% RuO_2 has the same electrocatalytic response as pure RuO_2. At 65 degrees Celsius, propane was electrochemically destroyed in fuel cells, releasing CO_2 as the main carbonaceous product. The rate of electro-oxidation would, of course, increase with higher temperatures.

As propane temperature rises above 65°C, however, the cracking process on platinum catalysts and other transition metal catalysts accelerates noticeably, producing enormous methane volumes. Methane is inert in fuel cells, unlike other hydrocarbons. Due to the breaking reaction producing so much inert methane, it appears the propane fuel cell is stuck: the higher temperatures required for faster oxidation of electrochemical reaction may cause halting of propane electrochemical oxidation. According to current research, propane electrochemical oxidation at platinum catalyzed fuel cell anode now interacts with propane gas-surface cracking. Cracking is prevented when the fuel cell is under demand for electrical power. In an open circuit, cracking happens the same way in standard gas surface exams. Combining a fuel cell and a chromatographic gas analyzer led to these unexpected results.

Electrocatalysis in Fuel Cell

An electrochemical fuel cell is a device in which electrons arrive at the cathode from the anode via an external circuit, generating electrical work. Positive and negative ions are displaced through the conducting media to the cathodic and anodic regions resulting from this process. Electrochemistry and catalysis expertise are combined to study the kinetics and mechanisms of anodic and cathodic reactions in homogeneous and heterogeneous systems. N. Nakamura created the phrase "electrocatalysis." W. and Kobosev In 1934, Monblanowa (*58*) W. T. Grubb produced the first link between HER kinetic data on numerous metals and their related characteristics, such as metal–hydrogen bond energy and metal sublimation enthalpy (*61*).

"Electrocatalysis" refers to electrochemical reactions that begin with dissociative chemisorption or include the electrode surface. The electronic structure of the substrate (electrode) is essential; (ii) Interactions between the substrate and the adsorbate as a result of reactants or products are significant; (iii) Both the aspect ratio of catalyst particles and the mean coordination number of surface atoms affect rate processes; and (iv) The lifetime of an electrocatalyst is determined by poisoning effects caused by byproduct accumulation, as well as particle surface sintering and ripening events. At low temperatures, the electrode potential, on the other hand, is a significant variable that can dramatically change the rate of electrocatalytic reactions. This allows for precision potential control at the electrochemical interface when dealing with electrocatalytic processes' selectivity.

Review of Fundamental Concepts

A catalyst's geometric/electronic structure and catalytic activity are highly correlated. This knowledge of the structure-activity relationship will aid in the creation of new electrocatalytic materials that are highly efficient.

Free Energy Diagram for an Electrochemical Reaction

A diagram showing the free energy of an electrochemical process is the plot showing Gibb's free energy of a chemical reaction as the reaction proceeds at various potentials. It is crucial to determine if it's thermodynamically spontaneous. A similar method can even be applied to predict the performance of engineered materials, as it can be used to determine the viability of chemical reactions and processes that utilize specific materials as electrode surfaces.

Several critical electrocatalytic chemical reactions involve the transfer of protons and electrons, including the CO_2RR, HER, OER, and oxygen reduction reactions.

$$X^{*} + H^{+}_{(aq)} + e^{-} \rightarrow XH \tag{9}$$

X^{*} Indicates X which substance is adsorbing on the electrode. To draw the free energy plots, we have to calculate the free energies of each product and intermediates as they are formed during the reaction. Under these conditions, the free energy change would be as follows:

$$\Delta G = G(XH) - G(X^{*}) - G\left(H^{+}\right) - G(e^{-}) \tag{10}$$

The Computational Hydrogen Electrode (CHE) model is used for the calculation of proton and electron free energies for processes involving transfers of electron and proton. The CHE model considers the standard hydrogen electrode (SHE) as a reference when dealing with protons and electrons' free energy. For the SHE to work, the following reaction must be in equilibrium:

$$H^{+}_{(aq)} + e^{-} \rightleftarrows \ 1/2H_2(\,g) \tag{11}$$

Under standard or equilibrium conditions, both the and reaction terms have the same chemical potential, i.e., the H^+ concentration is 1M, and 0 V potential, 1bar for the H^2 gas at room temperature. Let μ (X) be the chemical potentials of X, then,

$$\mu\left(H^{+}\right) + \mu(e^{-}) = 0.5\ \mu(H_{2(\,g)}) \tag{12}$$

Therefore, the free energy of H_2 (g) can be utilized instead of the free energy of electrons and protons. The following is free energy change in the chemical process.

$$\Delta G = G(XH) - G(X^{*}) - 0.5G(H_{2(\,g)}) \tag{13}$$

It should be noted that while the equation above applies to standard conditions (at 0 V potential and pH = 0), it must be modified to account for the effects of applied voltage and pH:

To include the applied voltage bias: $+eU$, is added; here, e indicates the charge of the electron, U represents an applied potential concerning standard hydrogen electrode

To include variations in the pH: $+k_BT\ log(10)pH$, T indicates the temperature, where k_B indicates the Boltzmann constant.

To fully understand the CHE model, it is imperative to note that it considers the following:

- In the presence of an electrostatic field, the adsorption energy of intermediates on an electrode surface does not depend on it
- There is equilibrium among the electrolytes
- There is equilibrium between the electrodes and the electrolyte bulk at the surface where the reactions occur.

Therefore, it ignores how electrostatic potential may influence adsorption energies at double layers - an effect that can be very significant to molecules with strong dipoles. Furthermore, it disregards activation barriers, so the results obtained by using CHE are solely thermodynamic.

Theory of Density Functionality

The Schrodinger equation provides all the information about the energy state of every chemical system, hence defining its properties. Because solving the Schrodinger equation is difficult for all but the most elementary systems, like the hydrogen atom, several approaches can be used to solve it. One of these approximations is Density Functional Theory (DFT). According to the Hohenberg-Kohn theorem, any system's ground-state properties are controlled by its electron density, and the total system energy may be estimated using electron density functionals. Due to the low computing cost and accuracy balance, DFT computational methods are popularly employed in research for investigating molecules, solids, heterogeneous reactions, and so on (*62*).

DFT Analysis

To demonstrate DFT analysis, DFT calculations to get the OER's free energy diagram on a simple metallic surface are discussed below. OER involves the following steps:

$$OH^- + * \rightarrow OH^* + e^- \tag{14}$$

$$OH^* + OH^- \rightarrow O^* + H_2O(l) + e^- \tag{15}$$

$$O^* + OH^- \rightarrow OOH^* + e^- \tag{16}$$

$$OOH^* + OH^- \rightarrow * + O_2(g) + H_2O(l) + e^- \tag{17}$$

In terms of Gibbs free energy, these stages can be described

$$\Delta G_1 = G_{OH^*} + \mu_{e^-} - \left(\mu_{OH^-_-} + G_*\right) = (G_{OH^*} - G_*) + (\mu_e^0 - \mu_{OH^-}^0 - eU) \tag{18}$$

$$\Delta G_2 = G_{O^*} + \mu_{H_2O(l)} + \mu_{e^-} - (G_{OH^*} + \mu_{OH^-}) = \left(G_{O^*} + \mu_{H_2O(l)} - G_{OH^*}\right) + (\mu_e^0 - \mu_{OH^-}^0 - eU) \tag{19}$$

$$\Delta G_3 = G_{OOH^*} + \mu_{e^-} - (G_{O^*} + \mu_{OH^-}) = (G_{OOH^*} - G_{O^*}) + (\mu_e^0 - \mu_{OH^-}^0 - eU)\ \Delta G_4 \tag{20}$$

$$= G_* + \mu_{O_2(g)} + \mu_{H_2O(l)} + \mu_{e^-} - \left(G_{OOH^*} + \mu_{OH^-_-}\right) \tag{21}$$

$$= \left(G_* + \mu_{O_2(g)} + \mu_{H_2O(l)} - G_{OOH^*}\right) + (\mu_e^0 - \mu_{OH^-}^0 - eU) \tag{22}$$

where $\mu_e^0, \mu_{OH^-}^0$ are the potentials of electron and OH at standard conditions.

The free energies of $O*$, $OH*$ and $OOH*$ on the catalyst, the surface is corrected by $T\Delta S$ and ZPE (zero-point energy) and the sum of ΔG_1, ΔG_2, ΔG_3, and ΔG_4 can be calculated to be $1.608eV$.

The rate-determining step is the simplest reaction with the lowest reaction free energy, whereas the overpotential is the potential that corresponds to it (*63*).

$$\mathrm{G}^{\mathrm{OER}} = \min\{\Delta\mathrm{G}_1,\ \Delta\mathrm{G}_2,\ \Delta\mathrm{G}_3,\ \Delta\mathrm{G}_4\} \tag{23}$$

The free energy at 0 V is expressed as follows: It can be used to determine the overpotential.

$$\eta = (max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e) - E_{eq} \tag{24}$$

The free energy relations of any chemical reaction can also be explained using above mentioned method.

We use the famous thermodynamic equation to compute the free energy of these terms:

$$\Delta G = \Delta H - T\Delta S \tag{25}$$

The following equation shows the adsorption free energy (ΔG) of products and reactants adsorbing on catalyst surfaces.

The following equation can obtain the reactant's adsorption free energy (ΔG) and product molecules adsorbed on the catalyst surface. Accordingly, the enthalpy term depends on the adsorption energies of the adsorbate on electrode surface E and the change in zero-point energy (i.e., the lowest possible energy that a quantum mechanical system may have (ZPE)).

$$\Delta G_i = \Delta E_i + \Delta ZPE_i - T\Delta S_i \tag{26}$$

where

- ΔE_i indicates the adsorption binding energy,
- ΔZPE_i, The ZPE of each species of adsorbate or free molecule, is calculated based on its vibrational frequency,
- T represents the temperature,
- ΔS_i denotes the change of entropy.

Because the contribution of an adsorbed species is negligible, as ΔSi for $*$, $OH*$, $O*$, $OOH*$ is $0eV$, entropic terms can be found in thermodynamic tables. DFT calculations employing vibrational characteristics can yield zero-point energies.

The energy of the entire system is calculated using DFT calculations. Surface OH adsorption on water (H_2O and H_2) results in an energy change that may be measured using $E\ (OH)*$ and a gas-phase reference system's total energy (E). The free energy change for each intermediate of the OER reaction is then calculated similarly, and the free energy plots can be generated from that data.

Calculating the Free Energy Diagram at Various Potentials

An eU term for each reaction step can be used to calculate the diagram at various potentials from CHE model's free energy plots at 0 V.

$$\Delta G_i(U \text{ as a function of } RHE) = \Delta G_i(0\ V \text{ vs } RHE) - eU \tag{27}$$

Thus, free energy diagrams at various applied potentials can be calculated. DFT is used to predict new catalysts based on this.

Sabatier Principle

According to the Sabatier principle, heterogeneous catalysis uses quality concepts developed by chemist Paul Sabatier. A catalyst should interact with a substrate that is "just right"; that is, it should not be too weak or too strong. When interactions are weak, molecules do not attach to catalysts, and the reaction does not occur. In contrast, a strong interaction will prevent a product from being dissociated.

Visualizing a chemical reaction versus a property such as the heat of adsorption of a chemical reactant onto the catalyst can illustrate this principle. Since of their shape, such plots are dubbed volcano plots because they go through a maximum and resemble an inverted parabola or a triangle. Similar three-dimensional graphs against two separate properties, like the reacting species' adsorption temperatures in 2 different reactions, can also be constructed. In that situation, the plot is known as a volcano surface and is typically displayed as a contour plot. Balandin is the creator of volcano plans (*62*, *64*).

The volcano map in Figure 5 depicts the breakdown of formic acid using several transition metal catalysts. The heat of synthesis (Hf) of the metal format salt was employed as the x-axis in this example because tests confirmed that the intermediate chemical reaction was a surface format. To maintain the traditional "volcano" shape, the y axis is plotted reverse to represent the specific temperature at which the chemical reaction reaches the specified rate. Due to the slow rate of adsorption when ΔH_f is low (To put it another way, higher temperatures are needed), the chemical reaction is slow (To put it another way, higher temperatures are needed). The desorption process becomes rate-limiting at high values of ΔH_f. ΔH_f is an intermediate value for the maximum rate in the platinum group metals in this case, with the rate a result of the combination of absorption and desorption rates.

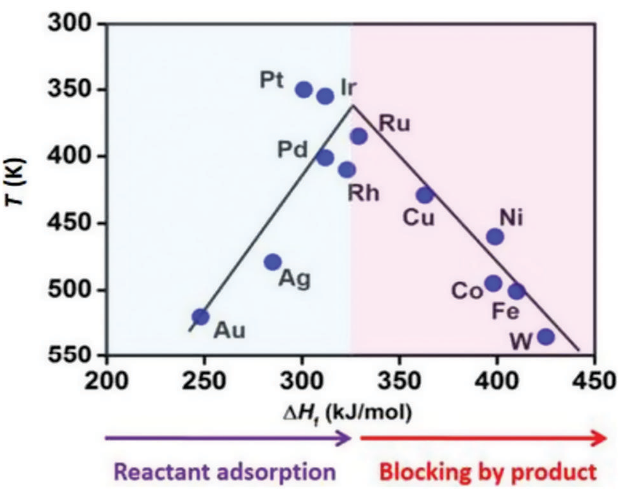

Figure 5. Formic acid volcano plot in the presence of transition metals. Reproduced with permission from reference (62). Copyright 2015 Elsevier.

Volcano Curves in Electrochemistry

The plot between the exchange current density and hydrogen's binding energy is known as Sabatier or volcano curves for the HER. Sabatier (*65*) pointed out that while some bonding is required for catalysis, significant bonding with the catalyst would block the surface and impede the reaction. When developing novel catalysts, the Sabatier principle is crucial. According to the Sabatier principle, the best HER catalysts have an ideal hydrogen binding energy (reactivity), as shown by the Volcano curve. The reaction rate as a function of the strength of the intermediate-catalyst bond generates a curve with a maximum, known as the volcano plot.

Tafel Equation

In electrochemical kinetics, the Tafel equation is a relationship between the overpotential and electrochemical reaction rates (Figure 6). An example of a simple, unimolecular redox process is that the voltage differential between an electrode and a bulk electrolyte affects the electrical current flowing through that electrode. The Tafel equation is applied to each electrode individually if an electrochemical reaction takes place over two electrodes in half reactions. The Tafel equation for a single electrode is as follows:

$$\eta = \pm A \times log_{10}\left(\frac{i}{i_o}\right) \tag{28}$$

- An anodic reaction is denoted by a plus sign under the exponent, while a minus sign denotes a cathodic reaction.
- η is the overpotential, (V)
- A is the Tafel slope, (V)
- *I* is the current density (A/m$^{2)}$
- i_0 is the current exchange density (A/m^2).

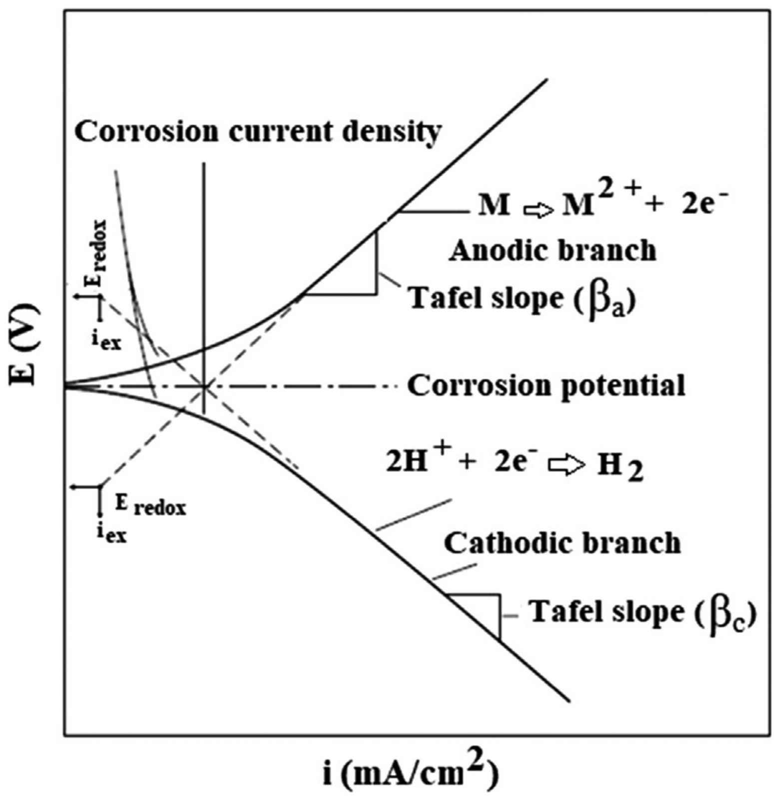

Figure 6. Tafel diagram for an anodic reaction (oxidation). Reproduced with permission from reference (66). Copyright 2019 Elsevier.

This equation's proof and more explanation can also be found here (*66*, *67*). The Tafel equation approximates the Butler–Volmer equation in the scenario of |η| > 0.1

Using the Tafel equation, the current can be expressed solely as a function of potential since the concentrations inside the bulk electrolyte and just at the electrode are almost the same. As another way of stating this, the electrode mass transfer rate is expected to be much higher than the reaction rate, and the slower rates will dominate the reaction. Furthermore, the Tafel equation implies that for a given electrode, the reverse half rate of the chemical reaction is small compared to the forward rate of the chemical reaction.

Overview of the Terms

Exchange current describes the movement of electrons from reduced and oxidized species to the electrode. To put it another way, the reaction rate at reversible potential is represented by current exchange density (by definition, A zero overpotential is one where there is no overpotential by the). Forward and reverse reactions are performed at equal rates at reversible potential, meaning there is equilibrium in the reaction. The density of the exchange current is measured at this rate.

Experimentation is used to determine the slope of the Tafel. A single transfer of electrons is theoretically possible when the dominating reaction mechanism is just a one-electron transfer.

$$\lambda k_B T / e < A \tag{29}$$

Where A can be expressed as below:

$$\mathrm{A} = \lambda \mathrm{k_B}\, T / \mathrm{e}\alpha = \lambda V_T / \alpha$$

Where

- $\lambda = 2.302585 = \ln(10)$
- k_B represents the Boltzmann's constant,
- T represents an absolute temperature,
- e represents the electron's electric elementary charge,
- $V_T = k_B\, T/e$ is the thermal voltage, and
- Coefficient of charge transfer (α): this value of the charge transfer coefficient must fall within the range of zero to one.

Mass Transfer Equation in the Case of Non-Negligible Electrode Mass

To put it another way, in a broader sense

The expanded Butler–Volmer equation is deduced in the following way, based on the work of Faulkner and Bard, Thomas-Alyea and Newman, A function of concentration and potential is used to calculate the current (as in simple form). Although the mass-transfer rate is minimal, it has only one consequence on the chemical process: it changes the concentrations (provided). Concentrations depend on potential.

In another way, the Tafel formula could be written as:

$$i = nkFC\, exp\, (\pm\, \alpha F\, (\eta/RT)) \tag{30}$$

Here

- $\cdot n$ denotes the number of exchanged electrons, as in Nernst's equation,
- k represents the electrode reaction rate in s^{-1},

- F represents the Faraday constant,
- C represents the concentration of reactive species at the electrode surface in mol/m^2,
- An anodic reaction is indicated by a plus sign under the exponent, whereas a negative sign shows a cathodic reaction,
- R stands for the universal gas constant.

Equation in the Situation of Low Polarization Values

Another equation applies when the polarization values are low |η| ≈ V. In this scenario, the relationship between polarization and current is usually linear (rather than logarithmic):

$$i = i_0\,(nF/\,RT)\,\Delta E \tag{31}$$

The linear region is known as polarization resistance because it resembles Ohm's law formally.

Nernst Equation

The potential, as well as the redox process, are linked by the Nernst equation, which results in zero current flow. It denotes the equilibrium potential (V) of redox reaction with zero DC flow in an electrolytic cell solution:

The Nernst equation $$V = V_0 + \left(\frac{RT}{nF}\right) \ln\left(\frac{a_{ox}}{a_{red}}\right) \tag{32}$$

Here,

- V_0 stands for the standard electrode potential of redox systems,
- n represents the number of electrons involved in the unit reaction,
- R refers to the universal gas constant as opposed to resistance,
- F represents the Faraday constant.
- Activities are a_{red} and a_{ox} and a = γc: here γ represents the activity coefficient, and c is the concentration. When concentrations are low (when there are no interactions of an ion), γ = 1, but at high concentrations, γ <1 is used. The half-cell potentials are also standardized conditions, implying that another electrode is a standard hydrogen electrode.

Additionally, the Nernst concept can be applied to semipermeable membranes containing different concentrations on the two sides.

The RT/nF factor of the Nernst equation can be substituted with a common logarithm at room temperature instead of a natural logarithm for the Nernst equation. In this case, the Nernst equation is:

$$V = V_0 - 0.061 \log\left(\frac{a_{ox}}{a_{red}}\right) \tag{33}$$

Nernst equations assume that reactions are reversible: they should proceed reasonably quickly in both directions. As a result, the surface's concentration of products and reactants is maintained near their equilibrium value. If the reaction rate of the electrode is weak in any direction, it is impossible to reverse the reactions at the electrode surface. As a result, the Nernst equation is incorrect, and the electrode concentration is not in equilibrium.

Butler–Volmer Equation

The Erdey–Grz–Volmer equation, commonly known as the Butler–Volmer equation, is one of the most fundamental electrochemical kinetics equations/relationships. A simple, one-molecule redox reaction demonstrates why and how the voltage difference between the electrode and the bulk electrolyte affects the current that goes through the electrode. It also takes into account the fact that anodic and cathodic reactions can happen within the same electrode (*67*):

The butler-Volmer equation can be expressed as follows:

$$j = j_0 \cdot \{\exp\left[\frac{\alpha_a zF}{RT}\left(E - E_{eq}\right)\right] - \exp\left[-\frac{\alpha_c zF}{RT}\left(E - E_{eq}\right)\right]\} \quad (34)$$

Here:

- j is the current density at the electrode, dimension: A/m^2 (where j = I/S)
- j_0 stands for current density exchange, dimension: A/m^2
- *E potential* of the electrode, dimension: V
- E_{eq} stands for an equilibrium potential, dimension: V
- T represents the temperature, K
- z denotes the number of electrons within electrode reaction
- F represents the Faraday constant
- R is the universal gas constant
- α_c stands for the charge transfer coefficient at the cathode, and it has no dimensions.
- α_a stands for the charge transfer coefficient at the anode, and it does not have any dimensions
- η is the activation overpotential (where $\eta = E - E_{eq}$).

Limiting Circumstances

Butler–Volmer's equation has two limiting cases, and they have written below:

- The simplified Butler–Volmer equation can be expressed as follows:

$$j = j_0 \frac{zF}{RT}\left(E - E_{eq}\right) \quad (35)$$

  when $E \approx E_{eq}$, the low overpotential zone is what it's termed (also known as polarization resistance).

$$j = j_0 \frac{zF}{RT}\left(E - E_{eq}\right)$$

- Butler–Volmer equations simplify Tafel equations in the area of high overpotential.
- $(E - E_{eq}) >> 0$, shows the first term as dominant, while $(E - E_{eq}) >> 0$, shows the second term as dominant.

  At the cathodic reaction, $E - E_{eq} = a_c - b_c \log j$, for $E << E_{eq}$, or

  At anodic reaction, $E - E_{eq} = a_a + b_a \log j$, for $E >> E_{eq}$

For the Tafel equation, b and a are constants related to the chemical reaction (for a given temperature and reaction). There are differences between cathodic and anodic constants of the Tafel equation. The slope b of the Tafel, on the other hand, can be described as follows:

$$b = \left[\left(\frac{\partial E}{\partial \ln|I_F|} \right)_{Ci,T,p} \right] \tag{36}$$

I_F is the faradaic current, with $I_F = I_c + I_a$, I_c being the cathodic current, and Ia being the anodic current.

Applications

Water Splitting

Hydrogen can be produced as a clean energy source by splitting water into H_2 and O_2 on a semiconductor photocatalyst. Heterogeneous photocatalysts for water splitting have been developed from various materials. As shown in Figure 7, there are three stages to the water splitting reaction: (1) The photons are absorbed by a semiconductor photocatalyst, which then releases electron-hole pairs. To transfer the generated carriers to the semiconductor surface, (2). Three, electrons and holes can reduce and oxidize H_2O. Cocatalysts made from deposited metal or metal oxide nanoparticles on the surface of the semiconductor photocatalyst aid in the final step, which consists of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) (*68*).

For instance, it is widely known that adding Pt nanoparticles to the surface of various photocatalysts, such as TiO_2 and $SrTiO_3$, can improve the HER. Such surface properties can also improve the OER. To increase the overall effectiveness of photocatalytic water splitting, it is essential to create nanoparticle cocatalysts.

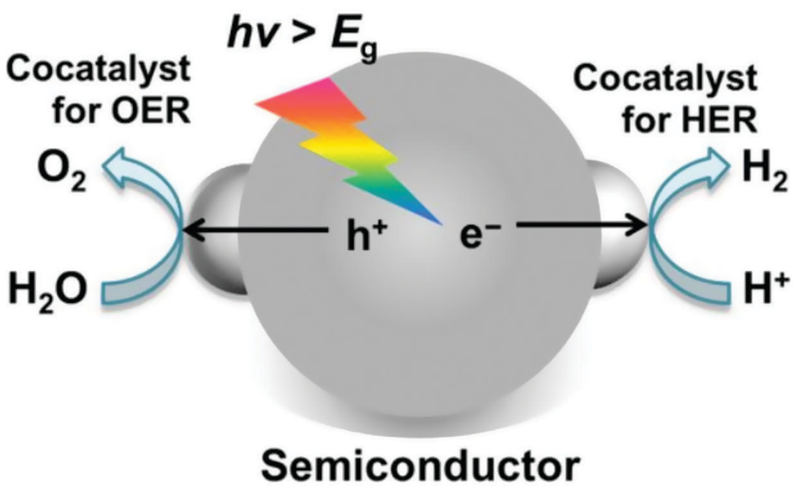

Figure 7. Pictorial representation chemical reaction of the water splitting. Reproduced with permission from reference (68). Copyright 2020 Elsevier.

Water-splitting has recently developed as a novel method for producing H_2 since it employs renewable and abundant natural energy sources, such as water and sunlight, to reduce CO_2 emissions and produce H_2 in its pure form compared to industrial production using fossil fuels. Water splitting is a chemical reaction that decomposes water into oxygen and hydrogen through natural breakdown (Figure 8). The H-O-H bond cleavage energy is obtained from several power sources such as electrical, thermal, and light. Water-splitting can be expressed in a chemical equation as follows

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \tag{37}$$

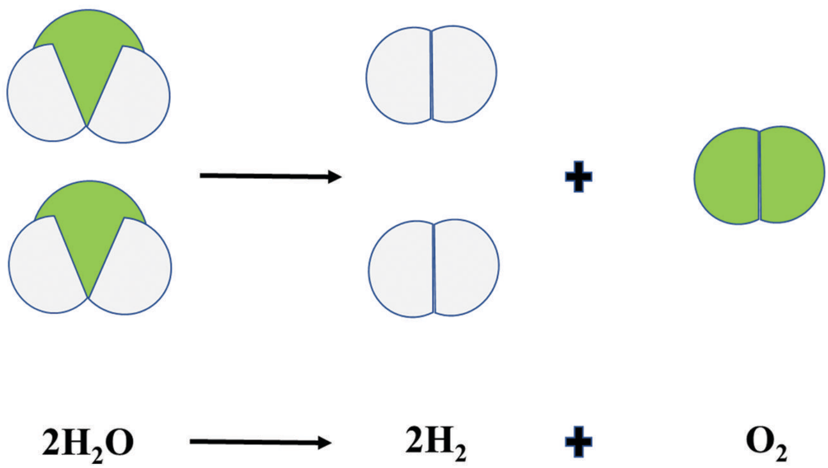

Figure 8. Pictorial representation chemical reaction of the water splitting.

Water splitting is accomplished by the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. The mechanics of these reactions are described in the section below.

Oxygen Evolution Reaction

Oxygen evolution reaction (OER) is one of the essential processes. It involves the transfer of four excitons and is why the PEC water splitting process moves more slowly. O*, HO*, and HOO* are the primary intermediates found in the OER. In OER reaction, M-O bonding interaction stabilizes reaction intermediates Hydrogen from photo electrocatalytic water splitting on the surface, which affects water splitting efficiency (*69*). The mechanism of the OER reaction in an acidic medium (Figure 9A) can be written as:

$$\text{Cathode reaction:} \quad 4H^+ + 4e^- \rightarrow 2H_2 \tag{38}$$

$$\text{Anodic reaction:} \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{39}$$

$$\text{Overall reaction:} \quad 2H_2O \rightarrow 2H_2 + O_2 \tag{40}$$

$$* + H_2O \rightarrow HO^* + H^+ + e^- \tag{41}$$

$$HO^* + HO^- \rightarrow O^* + H_2O + e^- \tag{42}$$

$$2O^* \rightarrow 2* + O_2 \tag{43}$$

$$O^* + H_2O \rightarrow HOO^* + H^+ + e^- \tag{44}$$

$$HOO^* + H_2O \rightarrow * + O_2 + H^+ + e^- \tag{45}$$

In alkaline medium (Figure 9):
Cathodic reaction:

$$4H_2O + 4e^- \rightarrow 2H_2 + HOO^* + 4OH^- \tag{46}$$

Anodic reaction:

$$4OH^- \rightarrow 2H_2 + 2H_2O + 4e^- \tag{47}$$

$$OH^- + * \rightarrow OH^- \tag{48}$$

$$HO^* + HO^- \rightarrow O^* + H_2O \tag{49}$$

$$2O^* \rightarrow 2 * + O_2 \tag{50}$$

$$O^* + H_2O \rightarrow HOO^* + e^- \tag{51}$$

$$HOO^* + HO^- \rightarrow * + H_2O \tag{52}$$

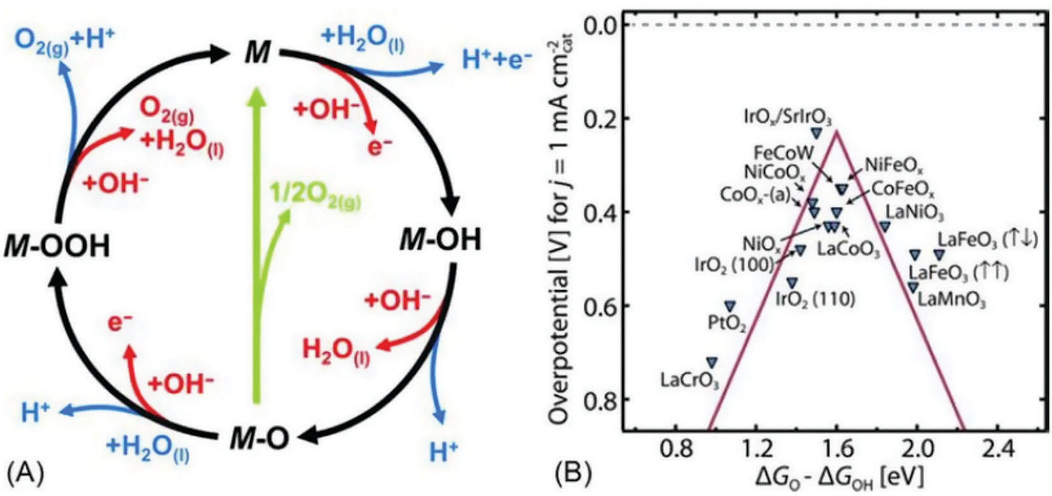

Figure 9. Pictorial representation chemical reaction of the water splitting. Reproduced with permission from reference (69). Copyright 2019 Elsevier.

Metal oxide catalysts such as perovskites, RuO_2, IrO_2, IrO_x / $SrIrO_3$, Ni-oxides, Co-oxides, Mn-oxides, and others like tertiary oxyhydroxides are the well-known electrocatalysts for the OER. Similar to HER, a volcano-type relationship (Figure 9B) can be arrived at for OER reaction using $(\Delta G_{O*} - \Delta G_{HO*})$ as a descriptor. The fundamental overpotential of the reaction could circumvent by stabilizing the $HOO*$ concerning $HO*$ intermediate on the catalyst surface.

Hydrogen Evolution Reaction

The process of producing hydrogen through water electrolysis is known as the hydrogen evolution reaction**.** Two semi-reactions in electrochemical water splitting are the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. The following equations represent HER on the cathode.

$$\text{Acidic solution:} \quad 2\,H^+ + 2e^- \rightarrow H_2 \tag{53}$$

$$\text{Neutral/Alkaline solution: } 2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^- \quad (54)$$

One electron migrates to the electrode's surface in acidic solutions and simultaneously decreases one proton, resulting in adsorbed hydrogen atom H_{ads} ($H^+ + e^- \rightarrow H_{ads}$). Because the proton content in the electrolyte is so low in neutral/alkaline solutions, H_{ads} can only be produced by reducing water molecules with the transmitted electron. ($H_2O + e- \rightarrow H_{ads} + OH^-$). Tafel reaction occurs when two adjacent H_{ads} combine to form one molecule of H2 on the electrode's surface.

Tafel reaction

$$H_{ads} + H_{ads} \rightarrow H_2 \quad (55)$$

HER moves more slowly in alkaline than in acidic media. This is because both the anode (OER) for electrolysers operating under acidic conditions and the cathode (HER) for electrolysers operating under alkaline conditions host the water dissociation half-cell reaction. Three key factors determine HER activity: i) the type of proton donors, such as water or hydronium; (ii) the energetics of the activated complex that produces H_2; and (iii) the availability of active sites for the reaction as expressed by $(1 - \Sigma\,\theta i)$, θ where is the amount of surface that is covered by adsorbed intermediates. A slow water dissociation process has been proposed to limit the HER kinetics in alkaline solutions. In contrast, the rapid dissociation of the hydronium ion in acid does not restrict HER in acidic media.

HER reaction pathways are easier to understand than OER because they only involve two electrons instead of OER's four. The catalyst surface typically doesn't experience significant changes, such as oxidation or restructuring, as seen in the potential range of OER, because of the reducing environment or low potential. Some catalysts under HER do experience changes brought on by H insertion and hydride formation.

Electrochemical Fluorination or Electro Fluorination

In industrial, organ fluorine compounds are essential. The fluorinating agents are used to determine the technique of preparation. The production of fluoro-organic chemicals by electrochemical fluorination is a standard industrial process. Two Electrochemical fluorination (EFC) synthesis methods have been commercialized and are widely used. They are Simon's process and the Phillips Petroleum process.

In Simon's chemical reaction process, Organic molecules are fluorinated at the anode of an electrochemical cell, commonly nickel, after being dissolved in anhydrous hydrogen fluoride (AHF). Fluorine substituted for all hydrogen atoms and saturated all carbon-carbon multiple bonds. Individual reactions can be described as follows

$$R_3C\text{–}H + HF \rightarrow R_3C\text{–}F + H_2 \quad (56)$$

Here R_3C–H is an Organic molecule, HF is hydrogen fluoride, R_3C–F is an Organ fluorine compound and $H_2$is a hydrogen gas.

The Phillips Petroleum process is similar to the Simons Process but is used to prepare volatile and chlorohydrocarbons. In the Phillips Petroleum chemical process, Electro fluorination is carried out in molten potassium fluoride in hydrogen fluoride at porous graphite anodes.

Hydro Dimerization of Acrylonitrile

Hydro dimerization is an organic reaction in which two alkenes combine to form a symmetrical hydrocarbon. When the reaction is carried out electrochemically, it is called electro dimerization. The organic compound acrylonitrile has the formula $CH_2 = CHCN$ Acrylonitrile ($CH_2{=}CHCN$) is a poisonous, colorless, pale-yellow liquid that is toxic to the eyes, skin, lungs, and nervous system. It has been linked to cancer. Exposure to acrylonitrile may cause harm to workers. Acrylonitrile is widely used in manufacturing rubber, resins, plastics, elastomers, synthetic fibers, and carbon for aircraft, defense, and aerospace applications.

Chlor-Alkali Process

Sodium hydroxide is formed when electricity is passed through an aqueous sodium chloride solution. The procedure is known as the chloralkaline alkali process. In this process, a sodium chloride aqueous solution is called "brine."

$$2NaCl\ (aq) + 2H_2O\ (electrolysis) \rightarrow 2NaOH\ (aq) + Cl_2(g) + H_2(g). \qquad (57)$$

In the Chlor-alkali alkali process, the anode produces chlorine gas, whereas the cathode produces hydrogen gas. The anode's chlorine evolution reaction (CER), the cathode's hydrogen evolution reaction (HER), and the electrolyte's NaOH production are all chlor-alkali processes. Chlorine has been utilized in a variety of applications, including the production of building products like polyvinyl chloride, organic synthesis, metallurgy, water treatment, and titanium dioxide production: membrane electrolytic cell technology. Currently, approximately 81% of global Chlor-alkali capacity.

Types of Metal-Based Electrocatalysts

Pt on a carbon support, Pt alloys, and transition metals are all examples of electrocatalysts utilized in fuel cell technology.

Noble-metal-based compounds are the most practicable electrocatalysts at this time in technology. The downsides of noble metal-based catalysts are the high cost, limited availability, susceptibility to pollutants, inadequate selectivity, poor durability, negative environmental consequences, and Pt dissolution. Effective, stable, and benchmark electrocatalysts are required to increase the electrochemical reaction of HER, ORR, and OER for energy applications. Different types of metal-based catalysts are shown in Figure 10.

Recent Advances in Electrocatalysts Based on Non-Noble Metals for Energy Applications

Fuel cells and transition metal-air batteries, which convert inefficient fossil fuels into clean and sustainable energy, are valuable technologies for storing and converting energy due to the depletion of fossil fuels, increasing energy demand, and mounting environmental concerns (*8*). In rechargeable metal-air batteries, both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) require catalysts; thus, integrating these energy technologies into our daily lives is a challenge (*19*). Historically, platinum-carbon catalysts (Pt/C) have been thought to be the best catalyst for ORR, but the material is subject to several drawbacks, like CO poisoning, time-dependent drift, and fuel crossover (*12*, *70*). Metal oxides (such as RuO_2, MnO_2, and perovskite oxides) have, on the other hand, been extensively investigated as OER electrocatalysts. Due to higher costs and shorter lifespans of noble metal and its oxide catalysts, fuel cells and transition metal-air batteries have not yet reached commercial maturity. Because of this, large-scale practical deployments of transition metal-air batteries and fuel cells will be impractical until expensive noble metal, and metal oxide electrocatalysts for OER/ORR can be replaced with more low-cost, durable and efficient materials.

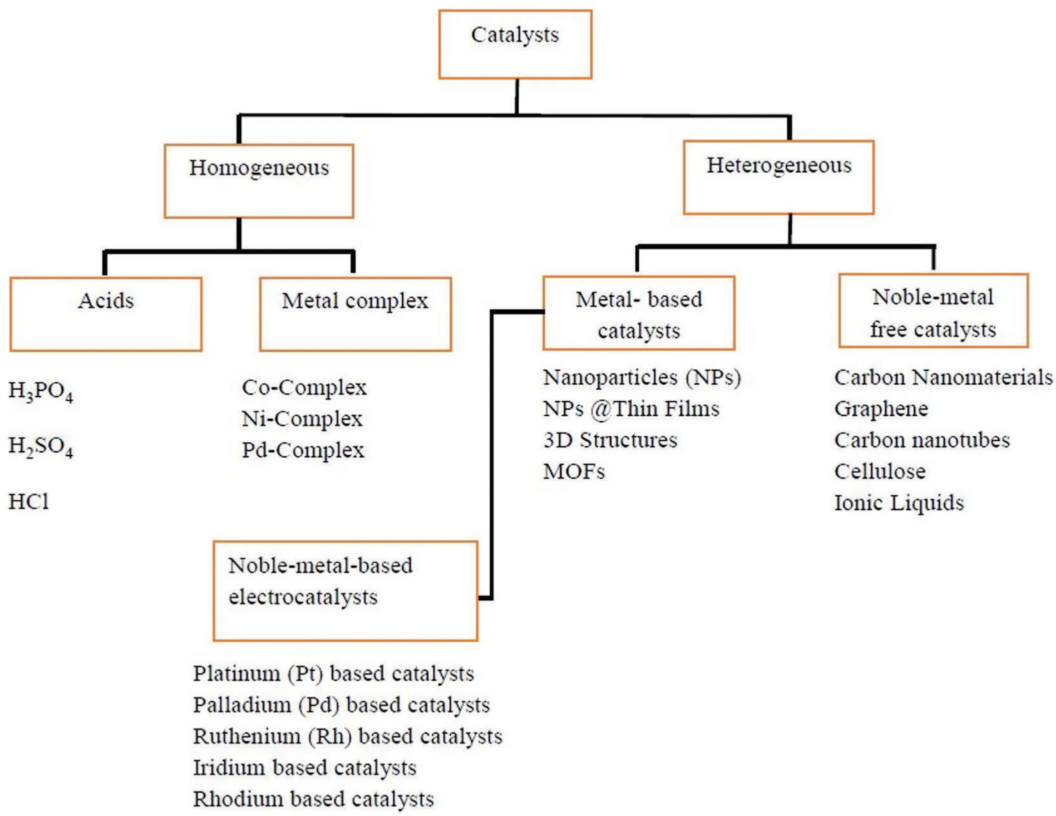

Figure 10. Flow chart of different types of metal-based electrocatalysts.

Electrocatalysts Based on Carbon for Energy Applications

Many research groups have developed a new class of low-cost, metal-free ORR/HER and OER catalysts based on carbon nanomaterials (for example, 1D CNT, 0D fullerenes, 3D graphite as well 2D graphene) which have been shown to act as economically efficient HER/ORR as well OER electrocatalysts in addition to the comprehensive research effort to develop non-noble metal catalysts to replace noble metal catalysts for Carbon-based-nanomaterials doped and co-doped with a variety of heteroatoms (e.g., I, B, N, S, P, Cl, and Br) have also been found to have considerable catalytic activity (*71–74*). Researchers have also shown that carbon-based nanomaterials can act as single active or functional metal-free catalysts in OER, ORR, HER, and even triiodide to iodide reductions that are important to transition metal-air batteries, fuel cells, water splitting to the generation of fuel, and dye-sensitive solar cells.

For high-performance electrolysis, nanocarbon nanoarchitectures with well-defined porous networks and large surface areas are particularly attractive. Research on metal-free carbon-based catalysts represents breakthroughs in this emerging field, removing bottlenecks in developing cheap-cost, carbon-based catalysts and adding new possibilities for generating and storing clean energy using cheap and long-lasting transition metal-air batteries and fuel cells (*75*). Utilization of metal-free carbon-based catalysts will almost certainly result in better lower emissions, fuel economy, and a reduction in dependence on petroleum. In the near future, this can significantly improve our daily lives. Carbon-based catalysts have recently been the subject of numerous theoretical and experimental studies resulting in this topic's development to a point where a critical assessment of its benefits and expectations for its future development is needed.

Recent Development in Carbon Nanomaterial-Based Electrocatalysts

The following are a few innovative ways that several research groups have devised to achieve a high catalytic activity in carbon nanomaterial-based electrocatalysts. We won't go into detail about these tactics here; instead, read (*76–82*) to learn more about current developments in carbon nanomaterial-based electrocatalysts for energy applications.

- Heteroatom-doped carbons (*83*)
- Heteroatom-doped CNTs (*83*, *84*)
- Heteroatom-doped graphene (*74*)
- Heteroatom-doped 3D carbon nanostructures (*85*)

Conclusion

Since electrocatalysis for HER was reported in 1920, the subject has sparked curiosity and found many forefronts applications, including industrial production, chemical sensors and green energy generation, which has brought hydrogen fuel cell automobiles out of a lab and into reality. Fuel cells have efficiently addressed clean energy requirements in transportation applications. Electrocatalysts play a vital role in HER, ORR and OER, which are essential for various applications like water splitting devices and fuel cells. An electrocatalyst is a catalyst that accelerates reaction kinetics by reducing activation energy without being consumed in the electrochemical processes. It may operate on electrode surfaces or is employed as an electrode surface in some situations. Selecting appropriate electrocatalysts and tailoring their characteristics demands evaluating their stability, selectivity and activity. Experiments have suggested that a catalyst's geometric/electronic structure and catalytic activity are highly correlated. This knowledge of the structure-activity relationship is essential in synthesizing new electrocatalytic highly efficient materials. DFT computational methods are employed in research to calculate the properties of atomic systems for the investigation of molecules, solids, heterogeneous reactions and electrocatalytic activities. Noble metals like Ir (iridium), Pd (palladium), Pt (platinum), and oxides of metals are used initially in electrocatalysis. However, to keep costs down, researchers invested in developing electrodes with metal-free and Pt-free catalysts to replace precious metals and their oxides while still retaining efficiency. This investigation has led to a breakthrough with the advent of materials like nanostructured materials, graphene and its composites and thin film-based electrocatalysts. However, the details of the reaction mechanism and relation between structural and electrical properties to its catalytic activity are not yet well understood and are the subject of active research. This chapter introduces the principles of catalysis in electrochemistry and the historical developments in electrochemistry and electrocatalysis that lead to the present-day understanding of the subject. It also briefly reviews fundamental ideas and theories essential to understanding and further investigating the mechanism of the electrocatalyst. It also explores various applications and discusses the present research trends in the field.

References

1. Wang, X.; Li, Z.; Qu, Y.; Yuan, T.; Wang, W.; Wu, Y.; Li, Y. Review of Metal Catalysts for Oxygen Reduction Reaction: From Nanoscale Engineering to Atomic Design. *Chem.* **2019**, *5* (6), 1486–1511.
2. Acres, G. J. K.; Frost, J. C.; Hards, G. A.; Potter, R. J.; Ralph, T. R.; Thompsett, D.; Burstein, G. T; Hutchings, G. J. Electrocatalysts for fuel cells. *Catal. Today.* **1997**, *38* (4), 393–400.
3. Wendt, H.; Spinacé, E. V.; Oliveira Neto, A.; Linardi, M. Electrocatalysis and electrocatalysts for low temperature fuel cells: fundamentals, state of the art, research and development. *Química Nova.* **2005**, *28*, 1066–1075.
4. Tian, H.; Cui, X.; Dong, H.; Meng, G.; Kong, F.; Chen, Y.; Peng, L.; Chen, C.; Chang, Z.; Shi, J. Engineering single MnN4 atomic active sites on polydopamine-modified helical carbon tubes towards efficient oxygen reduction. *Energy Storage Mater.* **2021**, *37*, 274–282.
5. Xie, S. L.; Gao, X. T.; Wu, H. H.; Zhou, F.; Zhou, J. Direct electrochemical defluorinative carboxylation of gem-difluoroalkenes with carbon dioxide. *Org. Lett.* **2020**, *22* (21), 8424–8429.
6. Panero, S. *Encyclopedia of Electrochemical Power Sources*; Elsevier: Amsterdam, 2009; pp 1-7.
7. Chen, J.; Xu, L.; Li, W.; Gou, X. α-Fe_2O_3 nanotubes in gas sensor and lithium-ion battery applications. *Adv. Mater.* **2005**, *17* (5), 582–586.
8. Kintner-Meyer, Y. Z. Z. J.; Lemmon, M. L. X. C. D. J. P; Liu, J. Electrochemical energy storage for green grid. *Chem. Rev.* **2011**, *111*, 3577–3613.
9. Sajid, H.; Heiki, E.; Nadezda, K.; Maido, M.; Mihkel, R.; Väino, S.; Gilberto, M.; Kaido, T. Pt particles electrochemically deposited on multiwalled carbon nanotubes for oxygen reduction reaction in acid media. *J. Electrochem. Soc.* **2017**, *164* (9), F1014–F1021.
10. Zhou, R.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Determination of the electron transfer number for the oxygen reduction reaction: from theory to experiment. *ACS Catal.* **2016**, *6* (7), 4720–4728.
11. Suo, Y.; Zhuang, L.; Lu, J. First-principles considerations in the design of Pd-Alloy catalysts for oxygen reduction. *Angew. Chem.* **2007**, *119* (16), 2920–2922.
12. Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G. Recent advances in carbon dioxide hydrogenation to methanol via heterogeneous catalysis. *Chem. Soc. Rev.* **2020**, *120* (15), 7984–8034.
13. Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y. L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution. *Nat. Commun.* **2013**, *4* (1), 1–7.
14. Kanan, M. W; Nocera, D. G. In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+}. *Science* **2008**, *321* (5892), 1072–1075.
15. Wu, H. B.; Xia, B. Y.; Yu, L.; Yu, X. Y; Lou, X. W. D. Porous molybdenum carbide nano-octahedrons are synthesized via confined carburization in metal-organic frameworks for efficient hydrogen production. *Nat. Commun.* **2015**, *6* (1), 6512.
16. Gao, M. R.; Liang, J. X.; Zheng, Y. R.; Xu, Y. F.; Jiang, J.; Gao, Q.; Li, J.; Yu, S. H. An efficient molybdenum disulfide/cobalt diselenide hybrid catalyst for electrochemical hydrogen generation. *Nat. Commun* **2015**, *6* (1), 1–7.

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ACS Symposium Series; American Chemical Society: Washington, DC, 2022.

17. Zhao, Y.; Nakamura, R.; Kamiya, K.; Nakanishi, S.; Hashimoto, K. Nitrogen-doped carbon nanomaterials as non-metal electrocatalysts for water oxidation. *Nat. Commun.* **2013**, *4* (1), 1–7.
18. Li, Y.; Zhou, W.; Wang, H.; Xie, L.; Liang, Y.; Wei, F.; Idrobo, J. C.; Pennycook, S. J; Dai, H. *Nat. Nanotechnol* **2012**, *7*, 394.
19. Kumar, A.; Bhattacharyya, S. Porous NiFe-oxide nanocubes as bifunctional electrocatalysts for efficient water-splitting. *ACS Appl. Mater. Interfaces.* **2017**, *9* (48), 41906–41915.
20. Qu, L.; Liu, Y.; Baek, J. B; Dai, L. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. *ACS. Nano.* **2010**, *4* (3), 1321–1326.
21. Zeng, X.; Shui, J.; Liu, X.; Liu, Q.; Li, Y.; Shang, J.; Zheng, L.; Yu, R. Single-atom to single-atom grafting of Pt1 onto Fe—N4 center: Pt1@ Fe —N— C multifunctional electrocatalyst with significantly enhanced properties. *Adv. Energy Mater.* **2018**, *8* (1), 1701345.
22. Jiang, X.; Kuklin, A. V.; Baev, A.; Ge, Y.; Ågren, H.; Zhang, H.; Prasad, P. N. Two-dimensional MXenes: From morphological to optical, electric, magnetic properties and applications. *Phys. Rep.* **2020**, *848*, 1–58.
23. Roduner, E. Selected fundamentals of catalysis and electrocatalysis in energy conversion reactions—a tutorial. *Catal. Today.* **2018**, *309*, 263–268.
24. McCreery, R. L. Advanced carbon electrode materials for molecular electrochemistry. *Chem. Rev.* **2008**, *108* (7), 2646–2687.
25. Sinar Mashuri, S. I.; Ibrahim, M. L.; Kasim, M. F.; Mastuli, M. S.; Rashid, U.; Abdullah, A. H.; Islam, A.; Asikin Mijan, N.; Tan, Y. H.; Mansir, N.; Mohd Kaus, N. H; Yun Hin, T.-Y. Photocatalysis for organic wastewater treatment: From the basis to current challenges for society. *Catalysts.* **2020**, *10*, 1260.
26. Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Design of electrocatalysts for oxygen-and hydrogen-involving energy conversion reactions. *Chem. Soc. Rev.* **2015**, *44* (8), 2060–2086.
27. Ma, T. Y.; Dai, S.; Jaroniec, M.; Qiao, S. Z. Metal–organic framework derived hybrid Co_3O_4-carbon porous nanowire arrays as reversible oxygen evolution electrodes. *J. Am. Chem. Soc.* **2014**, *136* (39), 13925–13931.
28. El-Sawy, A. M.; Mosa, I. M.; Su, D.; Guild, C. J.; Khalid, S.; Joesten, R.; Rusling, J. F; Suib, S. L. Controlling the active sites of sulfur-doped carbon nanotube–graphene nanolobes for highly efficient oxygen evolution and reduction catalysis. *Adv. Energy Mater.* **2016**, *6* (5), 1501966.
29. Fa, S.; Yamamoto, M.; Nishihara, H.; Sakamoto, R.; Kamiya, K.; Nishina, Y.; Ogoshi, T. Carbon-rich materials with three-dimensional ordering at the angstrom level. *Chemical Science.* **2020**, *11* (23), 5866–5873.
30. Lu, X.; Yim, W. L.; Suryanto, B. H; Zhao, C. Electrocatalytic oxygen evolution at surface-oxidized multiwall carbon nanotubes. *J. Am. Chem. Soc.* **2015**, *137* (8), 2901–2907.
31. Xu, P.; Zhang, X.; Wang, X.; Li, J.; Liu, G.; Kuang, Y.; Xu, J.; Zheng, X.; Ren, L.; Wang, G.; Zhang, Y. Genome sequence and genetic diversity of the common carp, Cyprinus carpio. *Nat. Genet.* **2014**, *46* (11), 1212–1219.
32. Koza, J. A.; He, Z.; Miller, A. S; Switzer, J. A. Electrodeposition of Crystalline Co_3O_4– A Catalyst for the Oxygen Evolution Reaction. *Chem. Nanomater.* **2012**, *24* (18), 3567–3573.

33. Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nat. Mater.* **2011**, *10* (10), 780–786.
34. Yang, J.; Cooper, J. K.; Toma, F. M.; Walczak, K. A.; Favaro, M.; Beeman, J. W.; Hess, L. H.; Wang, C.; Zhu, C.; Gul, S.; Yano, J. A multifunctional biphasic water splitting catalyst tailored for integration with high-performance semiconductor photoanodes. *Nat. Mater.* **2017**, *16* (3), 335–341.
35. Chen, H.; Ouyang, S.; Zhao, M.; Li, Y.; Ye, J. Synergistic activity of Co and Fe in amorphous Co x–Fe–B catalyst for efficient oxygen evolution reaction. *ACS Appl. Mater. Interfaces.* **2017**, *9* (46), 40333–40343.
36. Long, X.; Li, J.; Xiao, S.; Yan, K.; Wang, Z.; Chen, H.; Yang, S. A strongly coupled graphene and FeNi double hydroxide hybrid as an excellent electrocatalyst for the oxygen evolution reaction. *Angewandte Chemie.* **2014**, *126* (29), 7714–7718.
37. Fominykh, K.; Chernev, P.; Zaharieva, I.; Sicklinger, J.; Stefanic, G.; Döblinger, M.; Müller, A.; Pokharel, A.; Böcklein, S.; Scheu, C.; Bein, T. Iron-doped nickel oxide nanocrystals as highly efficient electrocatalysts for alkaline water splitting. *ACS Nano.* **2015**, *9* (5), 5180–5188.
38. Zhang, G.; Feng, Y. S.; Lu, W. T.; He, D.; Wang, C. Y.; Li, Y. K.; Wang, X. Y; Cao, F. F. Enhanced catalysis of electrochemical overall water splitting in alkaline media by Fe doping in Ni_3S_2 nanosheet arrays. *ACS Catal.* **2018**, *8* (6), 5431–5441.
39. Su, H.; Wang, X. T.; Hu, J. X.; Ouyang, T.; Xiao, K.; Liu, Z. Q. Co–Mn spinel supported self-catalysis induced N-doped carbon nanotubes with high efficiency electron transport channels for zinc–air batteries. *J. Mater. Chem. A.* **2019**, *7* (39), 22307–22313.
40. Menezes, P. W.; Indra, A.; Bergmann, A.; Chernev, P.; Walter, C.; Dau, H.; Strasser, P.; Driess, M. Uncovering the prominent role of metal ions in octahedral versus tetrahedral sites of cobalt–zinc oxide catalysts for efficient oxidation of water. *J. Mater. Chem. A.* **2016**, *4* (25), 10014–10022.
41. Zhao, Y.; Jia, X.; Chen, G.; Shang, L.; Waterhouse, G. I.; Wu, L. Z.; Tung, C. H.; O'Hare, D.; Zhang, T. Ultrafine NiO nanosheets stabilized by TiO_2 from monolayer NiTi-LDH precursors: an active water oxidation electrocatalyst. *J. Am. Chem. Soc.* **2016**, *138* (20), 6517–6524.
42. Nardi, K. L.; Yang, N.; Dickens, C. F.; Strickler, A. L; Bent, S. F. Creating highly active atomic layer deposited NiO electrocatalysts for the oxygen evolution reaction. *Adv. Energy Mater.* **2015**, *5* (17), 1500412.
43. Morales, D. V.; Astudillo, C. N.; Lattach, Y.; Urbano, B. F.; Pereira, E.; Rivas, B. L.; Arnaud, J.; Putaux, J. L.; Sirach, S.; Cobo, S.; Moutet, J. C. Nickel oxide–polypyrrole nanocomposite electrode materials for electrocatalytic water oxidation. *Catal. Sci. Technol.* **2018**, *8* (16), 4030–4043.
44. Cao, X.; Cui, L.; Wang, X.; Yang, W.; Liu, J. Nickel-Borate/Reduced Graphene Oxide Nanohybrid: A Robust and Efficient Electrocatalyst for Oxygen Evolution Reaction in Alkaline, Near Neutral Media. *ChemCatChem.* **2018**, *10* (13), 2826–2832.
45. Yu, F.; Zhou, H.; Huang, Y.; Sun, J.; Qin, F.; Bao, J.; Goddard, W. A.; Chen, S.; Ren, Z. High-performance bifunctional porous non-noble metal phosphide catalyst for overall water splitting. *Nat. Commun.* **2018**, *9* (1), 1–9.

46. Gorlin, Y.; Lassalle-Kaiser, B.; Benck, J. D.; Gul, S.; Webb, S. M.; Yachandra, V. K.; Yano, J.; Jaramillo, T. F. In situ X-ray absorption spectroscopy investigation of a bifunctional manganese oxide catalyst with high activity for electrochemical water oxidation and oxygen reduction. *J. Am. Chem. Soc.* **2013**, *135* (23), 8525–8534.
47. Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S. Y; Suib, S. L. Structure–property relationship of bifunctional MnO_2 nanostructures: highly efficient, ultra-stable electrochemical water oxidation and oxygen reduction reaction catalysts identified in alkaline media. *J. Am. Chem. Soc.* **2014**, *136* (32), 11452–11464.
48. Indra, A.; Menezes, P. W.; Sahraie, N. R.; Bergmann, A.; Das, C.; Tallarida, M.; Schmeißer;, D.; Strasser, P.; Driess, M. Unification of catalytic water oxidation and oxygen reduction reactions: amorphous beat crystalline cobalt iron oxides. *J. Am. Chem. Soc.* **2014**, *136* (50), 17530–17536.
49. Ma, W.; Ma, R.; Wu, J.; Sun, P.; Liu, X.; Zhou, K.; Sasaki, T. Development of efficient electrocatalysts via molecular hybridization of NiMn layered double hydroxide nanosheets and graphene. *Nanoscale* **2016**, *8* (19), 10425–10432.
50. Li, M.; Xiong, Y.; Liu, X.; Bo, X.; Zhang, Y.; Han, C.; Guo, L. Facile synthesis of electrospun MFe_2O_4 (M= Co, Ni, Cu, Mn) spinel nanofibers with excellent electrocatalytic properties for oxygen evolution and hydrogen peroxide reduction. *Nanoscale* **2015**, *7* (19), 8920–8930.
51. Maheshwari, S.; Li, Y.; Agrawal, N.; Janik, M. J. Density functional theory models for electrocatalytic reactions. *Adv. Catal.* **2018**, *63*, 117–167.
52. Li, M.; Feng, C.; Zhang, Z.; Shen, Z.; Sugiura, N. Electrochemical reduction of nitrate using various anodes and a Cu/Zn cathode. *Electrochem. Commun.* **2009**, *11* (10), 1853–1856.
53. Fernandes, M. D.; Andrade, S. D. P.; Bistritzki, V. N.; Fonseca, R. M.; Zacarias, L. G.; Gonçalves, H. N. C.; De Castro, A. F.; Domingues, R. Z; Matencio, T. SOFC-APU systems for aircraft: A review. *Int. J. Hydrogen Energy* . **2018**, *43* (33), 16311–16333.
54. Cottrell, F. G. Residual current in galvanic polarization, regarded as a diffusion problem. *Z. Phys. Chem.* **1903**, *42*, 385–431.
55. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-sensitized solar cells. *Chem. Rev* . **2010**, *110* (11), 6595–6663.
56. Franklin, T. C. Some mechanisms of action of additives in electrodeposition processes. *Surf. Coat. Technol.* **1987**, *30* (4), 415–428.
57. Arrhenius, S. Electrolytic dissociation. *Am. Chem. J.* **1912**, *34* (4), 353–364.
58. Frumkin, A.; Polianovskaya, N.; Bagotskaya, I.; Grigoryev, N. Electrocatalysis and electrode surface properties. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *33* (2), 319–328.
59. Horiuti, J.; Polanyi, M. A. Catalysed reaction of hydrogen with water. *Nature.* **1933**, *132* (3343), 819.
60. Krstajić, N.; Trasatti, S. Cathodic Behavior of RuO_2-Doped Ni/Co_3O_4 Electrodes in Alkaline Solutions: Surface Characterization. *J. Electrochem. Soc.* **1995**, *142* (8), 2675.
61. Janssen, L. J. J. Hydrogen fuel cells for cars and buses. *J. Appl. Electrochem.* **2007**, *37* (11), 1383–1387.
62. Liu, X.; Li, S.; Liu, Y.; Cao, Y. Formic acid: A versatile renewable reagent for green and sustainable chemical synthesis. *Chin. J. Catal.* **2015**, *36* (9), 1461–1475.

63. Fu, C.; Liu, C.; Li, T.; Zhang, X.; Wang, F.; Yang, J.; Jiang, Y.; Cui, P.; Li, H. DFT calculations: A powerful tool for better understanding of electrocatalytic oxygen reduction reactions on Pt-based metallic catalysts. *Comput. Mater. Sci.* **2019**, *170*, 109202.
64. Guo, M.; Ji, M.; Cui, W. Theoretical investigation of HER/OER/ORR catalytic activity of single atom-decorated graphyne by DFT and comparative DOS analyses. *Appl. Surf. Sci.* **2022**, *592*, 153237.
65. Laursen, A. B.; Varela, A. S.; Dionigi, F.; Fanchiu, H.; Miller, C.; Trinhammer, O. L.; Rossmeisl, J.; Dahl, S. Electrochemical hydrogen evolution: Sabatier's principle and the volcano plot. *J. Chem. Educ.* **2012**, *89* (12), 1595–1599.
66. Kakaei, K.; Esrafili, M. D; Ehsani, A. Graphene and anticorrosive properties. *Interface Sci. Technol.* **2019**, *27*, 303–337.
67. Sivanantham, A.; Lee, H.; Hwang, S. W.; Ahn, B.; Cho, I. S. Preparation, electrical and electrochemical characterizations of CuCoNiFeMn high-entropy-alloy for overall water splitting at neutral-pH. *J. Mater. Chem. A.* **2021**, *9* (31), 16841–16851.
68. Kanazawa, T.; Maeda, K. Photochemical synthesis of nanoscale multicomponent metal species and their application to photocatalytic and electrochemical water splitting. *Nanostruct. Photocatal.* **2020**, 19–38.
69. Narayanan, H.; Viswanathan, B.; Krishnamurthy, K. R and Nair, H. Hydrogen from photo-electrocatalytic water splitting. *Solar Hydrogen Production*. Academic Press. 2019, 419-486.
70. Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Design of electrocatalysts for oxygen-and hydrogen-involving energy conversion reactions. *Chem. Soc. Rev.* **2015**, *44* (8), 2060–2086.
71. Hu, C.; Xiao, Y.; Zou, Y.; Dai, L. Carbon-based metal-free electrocatalysis for energy conversion, energy storage, and environmental protection. *Electrochem. Energy Rev.* **2018**, *1* (1), 84–112.
72. Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98* (2), 1372–1377.
73. Zheng, Y.; Jiao, Y.; Ge, L.; Jaroniec, M.; Qiao, S. Z. Two-step boron and nitrogen doping in graphene for enhanced synergistic catalysis. *Angewandte Chemie.* **2013**, *125* (11), 3192–3198.
74. Wang, S.; Zhang, L.; Xia, Z.; Roy, A.; Chang, D. W.; Baek, J. B; Dai, L. BCN graphene as efficient metal-free electrocatalyst for the oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2012**, *51* (17), 4209–4212.
75. Su, D. S.; Perathoner, S.; Centi, G. Nanocarbons for the development of advanced catalysts. *Chem. Rev.* **2013**, *113* (8), 5782–5816.
76. Kumar, S.; Nehra, M.; Kedia, D.; Dilbaghi, N.; Tankeshwar, K.; Kim, K. H. Carbon nanotubes: A potential material for energy conversion and storage. *Prog. Energy Combust. Sci.* **2018**, *64*, 219–253.
77. Zhou, W.; Jia, J.; Lu, J.; Yang, L.; Hou, D.; Li, G.; Chen, S. Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction. *Nano Energy.* **2016**, *28*, 29–43.
78. Macchi, S.; Denmark, I.; Le, T.; Forson, M.; Bashiru, M.; Jalihal, A.; Siraj, N. Recent Advancements in the Synthesis and Application of Carbon-Based Catalysts in the ORR. *Electrochem.* **2021**, *3* (1), 1–27.
79. Yulong, Y.; Xinsheng, P. Recent advances in carbon-based dots for electroanalysis. *Analyst.* **2016**, *141* (9), 2619–2628.

80. Zhao, S.; Wang, D. W.; Amal, R.; Dai, L. Carbon-based metal-free catalysts for key reactions involved in energy conversion and storage. *Advanced Materials.* **2019**, *31* (9), 1801526.
81. Meng, Y.; Huang, X.; Lin, H.; Zhang, P.; Gao, Q.; Li, W. Carbon-based nanomaterials as sustainable noble-metal-free electrocatalysts. *Front. Chem.* **2019**, 7, 759.
82. Rangraz, Y.; Heravi, M. M. Recent advances in metal-free heteroatom-doped carbon heterogonous catalysts. *RSC Adv.* **2021**, *11* (38), 23725–23778.
83. Li, J. C.; Hou, P. X; Liu, C. Heteroatom-doped carbon nanotube and graphene-based electrocatalysts for oxygen reduction reaction. *Small.* **2017**, *13* (45), 1702002.
84. Paul, R.; Du, F.; Dai, L.; Ding, Y.; Wang, Z. L.; Wei, F.; Roy, A. 3D heteroatom-doped carbon nanomaterials as multifunctional metal-free catalysts for integrated energy devices. *Adv. Mater.* **2019**, *31* (13), 1805598.
85. Zhang, J.; Xia, Z.; Dai, L. Carbon-based electrocatalysts for advanced energy conversion and storage. *Sci. Adv.* **2015**, *1* (7), 1500564.