Chapter 1

Introduction and Literature review

1.1 Introduction

Fossil fuel consumption has raised serious concerns about contamination to the environment. Furthermore, the world's energy needs cannot be met by the fossil fuel reserves. Thus, there is a critical need for sustainable, eco-friendly energy sources. The expansion of the world economy, ongoing reliance on fossil fuels, and the rise of environmental concerns have sparked extensive study into the development of clean, renewable energy carriers and sources (R. Cao et al 2012, B. Wurster et al 2016 and X. Zou et al 2015).One of the cleanest forms of energy that can be reliably created is hydrogen through the process of water electrolysis. The oxygen evolution reaction (OER), which occurs on the anode side, has a considerable overpotential, which currently limits the overall efficiency of water electrolysis. Since it offers a source of clean and renewable energy, water splitting into hydrogen and oxygen has received a lot of attention in recent years (Y. Jiao et al 2015, J. Luo et al 2014, Z. Liu et al 2017 and M. Y. Song et al 2016). Similar to any other reaction, the activation energy barrier is associated with the reaction rate via a process known as the "linear free energy relationship"; the introduction of a catalyst can lower this barrier. In industry, IrO_2 and RuO_2 have been utilised to reduce the anode's overpotential. However, the widespread use of water electrolyzers has been impeded by their expensive cost and, more significantly, their limited availability. Due to many proton-coupled electron transfer stages, the oxygen evolution reaction (OER), despite being a slow reaction, is crucial to the water splitting process (J. P. McEvoy et al 2006, Y. Liang et al 2013, T. R. Cook et al 2013, X. Wang et al 2018, B. K. Kim et al 2018 and

K. Mamtani et al 2018). To increase the efficiency of the OER (Oxygen Evolution Reaction) process, researchers have sought to develop advanced catalysts, optimize reaction conditions, and improve electrode design. The need for sustainable energy and the obstacles still facing water electrolysis's ability to produce green hydrogen drive the hunt for extremely active OER catalysts. The benchmarking parameters for gauging OER catalyst performance are assessed in this chapter. As a result, producing oxygen and hydrogen as clean fuel sources by water splitting, which emits no carbon, is viewed as a sustainable solution to the problem of the energy crisis (C. Xiao et al 2016, J. Huang et al 2018, J. Chow et al 2003). However, the oxygen evolution reaction (OER), a bottleneck half-reaction involving multiple steps of proton-coupled electron transfer at the anode, demanded a substantial overpotential to overcome the slow kinetics and prevented the practical application of water splitting technology (F. Sun et al 2017, F. Sun et al 2017 and Y. Liu et al 2014). To reduce the overpotential and quicken the kinetics of the OER, effective catalysts should be designed and created. Modern precious metal-based compounds, such as RuO_2 or IrO_2, are the benchmark catalysts for OER, but because of their scarcity on earth, they are exceedingly expensive (P. Chen et al 2016 and T. Tang et al 2017). Therefore, tremendous effort has been put into creating effective and unique electro catalysts. Transition metal-based (3d) alternatives that are inexpensive and abundant on Earth have received a lot of interest in recent years (B. Zhang et al 2016). Apart from the well-developed metal oxides and (oxy) hydroxides catalysts (X. Y. Yu et al 2017), metal selenide (Y. Liu et al 2014), nitride (Y. Zhang et al 2016), phosphide (Y. Li et al 2017), boride (P. Chen et al 2017) and chalcogenide materials have also attracted large research attention for designing excellent OER electrocatalysts. Due to the synergetic impact between several metal species, bimetal-based materials have demonstrated increased electrocatalytic activity when compared to materials based on a

single metal (L. Han et al 2016). There are several materials that might be used as OER catalysts, but transition metal oxides and hydroxides stand out. We've analysed their structural characteristics and application as OER catalysts. The basic physics and chemistry of the materials underlying the catalytic process are also discussed. More details have been revealed about the mechanics underlying the OER on the surfaces of several catalysts. It has been stated how important it is to investigate how the catalyst interacts with the water around it. The significance of oxygen evaluation reactions lies in their versatile roles across different domains. In catalysis, these reactions serve as key steps in numerous transformations, enabling the synthesis of complex molecules with high efficiency and selectivity. For example, oxidative coupling reactions catalyzed by transition metal complexes have revolutionized the field of organic synthesis by providing access to a wide range of valuable compounds. In energy conversion technologies, such as fuel cells and electrolyzers, oxygen evaluation reactions are crucial for facilitating the efficient conversion of chemical energy into electrical energy and vice versa. Understanding the kinetics and mechanisms of these reactions is paramount for optimizing the performance and durability of energy devices.

The background and motivation for the synthesis of Co-Pd nanocomposite and its application in the oxygen evolution reaction (OER) stem from the pressing need for sustainable energy solutions. As the world transitions towards a low-carbon economy, the development of efficient and cost-effective catalysts for key electrochemical processes, such as water electrolysis and fuel cells, becomes paramount. The OER, in particular, is a crucial step in water splitting to produce oxygen, which serves as a clean energy carrier. Traditional catalysts for OER, such as noble metals like platinum and iridium, suffer from high cost and limited availability, hindering their widespread adoption. Additionally, these catalysts often exhibit sluggish kinetics and susceptibility to

corrosion, necessitating the exploration of alternative materials with enhanced catalytic performance. The combination of cobalt (Co), palladium (Pd), and silicon (Si) in a nanocomposite structure presents an intriguing opportunity to address these challenges. Each constituent element contributes unique properties: cobalt is known for its catalytic activity towards OER, palladium enhances catalytic stability, and silicon provides structural support and facilitates electron transfer. Despite their importance, oxygen evaluation reactions present numerous challenges, including issues related to selectivity, efficiency, and environmental impact. Developing efficient catalysts, understanding complex reaction mechanisms, and designing sustainable processes are among the key research objectives in this field. Moreover, with the increasing global demand for clean energy and environmentally friendly technologies, there is a growing need to explore alternative approaches and innovative solutions to address these challenges.

1.2 Synthesis of Palladium nanoparticles and the role of stabilizers

Palladium nanoparticles are highly active catalyst materials for practical applications like Hydrogen evolution reaction, organometallic reaction (Astruc et al 2007), electrochemical sensing etc. Palladium nanoparticles have been widely studied for their synthesis using various chemical and electrochemical methods via electrostatic and steric stabilization and for their immense catalytic potential (Qi et al 2014). Particle diameter is of immense importance for catalytic processes, as homogeneous colloidal dispersion of precious noble metals are used as efficient nanocatalyst in various reaction (Quiros et al 2002; Chen et al 2011). Synthesis of palladium nanoparticles involves reducing a palladium precursor in the presence of a stabilizing agent. Stabilizers play a crucial role in controlling the size, shape, and stability of the resulting nanoparticles. They prevent agglomeration and provide colloidal stability, allowing for better control over the nanoparticle properties. Here is an overview of the synthesis methods and the role of

stabilizers in palladium nanoparticle synthesis, along with some references for further reading. During the recent years, methods like wet chemical synthesis has emerged as a highly versatile and powerful tool for size and shape-controlled synthesis (Xiong et al.,2005; Niu et al.,2010; A nanikov et al.,2007). Nanoparticles are kinetically stabilized through various protection chemical stabilization techniques. The effective procedures for stabilization include, electrostatic or steric interaction or even both of them can be applied simultaneously (i.e, electrosteric forces) (Wu et al., 2006). Moat common stabilizers used till now are organic ligands, surfactants, polymers and dendrimers (Corain et al.,2004;Tu and Liu.,2000).

1.3 Properties of Palladium nanoparticles

Palladium nanoparticles possess unique properties due to their small size, high surface area, and quantum confinement effects. These properties make them highly attractive for various applications in catalysis, electronics, energy storage, and sensing. Here are some key properties of palladium nanoparticles along with references for further reading:

1.3.1 Catalytic Activity: Palladium nanoparticles exhibit excellent catalytic activity due to their high surface area and unique electronic properties. They are widely used as catalysts in various organic transformations, including hydrogenation, Heck coupling, Suzuki coupling, and carbon-carbon bond formation reactions. (Zhang et al., 2012;Corma et al 1997).

1.3.2 Hydrogen Storage: Palladium nanoparticles have a high capacity for hydrogen adsorption and desorption due to their large surface area and high reactivity. They are extensively studied for their potential application in hydrogen storage materials and fuel cells. (Chen et al 2002 and Hu et al 2017).

1.3.3 Electrical and Optical Properties: Palladium nanoparticles exhibit unique electrical and optical properties at the nanoscale. They can be used in electronics and optoelectronics applications, such as conductive inks, sensors, and plasmonic devices. (Chen et al 2003 and Gao et al 2015)

1.3.4 Catalytic properties: Palladium nanoparticles exhibit unique catalytic properties due to their high surface area, enhanced reactivity, and unique electronic structure. These properties make them highly desirable catalysts for a wide range of chemical reactions. Here are some key catalytic properties of palladium nanoparticles.

1.3.4.1 Surface Area: Palladium nanoparticles have a high surface area-to-volume ratio compared to bulk palladium, which allows for more active sites and increased contact with reactants. This high surface area enhances the catalytic activity and efficiency of palladium nanoparticles.

1.3.4.2 Reactivity: Palladium nanoparticles exhibit high reactivity due to their small size and high surface energy. The presence of unsaturated surface atoms and defects on the nanoparticle surface makes them more accessible to reactant molecules, leading to faster reaction rates.

1.3.4.3 Adsorption: Palladium nanoparticles possess strong adsorption capabilities, allowing them to bind reactant molecules onto their surfaces. This adsorption facilitates the activation of reactant molecules, making them more reactive and promoting catalytic reactions.

1.3.4.4 Size-Dependent Catalysis: The catalytic activity of palladium nanoparticles is size-dependent. Smaller nanoparticles exhibit higher catalytic activity compared to larger ones due to their larger fraction of surface atoms and increased surface energy. The size-controlled synthesis of palladium nanoparticles allows tuning of their catalytic properties.

1.3.4.5 Selectivity: Palladium nanoparticles often exhibit high selectivity towards specific reaction pathways. The controlled synthesis of palladium nanoparticles, along with the choice of reaction conditions and ligands, can influence their selectivity and enable precise control over the desired reaction products.

1.3.4.6 Stability: Palladium nanoparticles are known for their stability under harsh reaction conditions. They can withstand high temperatures, high pressures, and corrosive environments without significant deactivation or structural degradation, ensuring their long-term catalytic performance.

1.4 Synthesis and application of bimetallic analogues of palladium nanoparticles

Bimetallic analogues of palladium nanoparticles have gained significant attention in recent years due to their unique properties and potential applications in catalysis, sensing, energy storage, and more. These materials combine the advantages of both metals, offering enhanced catalytic activity, improved stability, and novel functionalities. Here is a brief synthesis and application overview of bimetallic analogues of palladium nanoparticles, along with some key references for further reading.

1.4.1 Synthesis of Bimetallic Analogues of Palladium Nanoparticles:

1.4.1.1 Co-Reduction Method: In this approach, metal precursors of palladium and another metal are co-reduced in the presence of a reducing agent, typically a mild reducing agent such as sodium borohydride (NaBH4). The choice of reaction conditions, such as temperature and pH, can influence the composition, size, and structure of the bimetallic nanoparticles. (Carretero-González et al 2018).

1.4.1.2 Galvanic Replacement Method: In this method, a sacrificial metal is used to react with a palladium precursor, resulting in the formation of bimetallic nanoparticles. The reaction occurs due to the difference in reduction potential between the two metals,

where the more reactive metal replaces palladium ions in the precursor.(X. Wang et al.,2018)

1.5 Applications of Bimetallic Analogues of Palladium Nanoparticles:

1.5.1 Catalysis: Bimetallic analogues of palladium nanoparticles exhibit enhanced catalytic activity and selectivity compared to their monometallic counterparts. Bimetallic palladium nanoparticles exhibit enhanced catalytic activity and selectivity compared to monometallic counterparts due to synergistic effects between the two metals. In heterogeneous catalysis, these nanoparticles are used in various reactions such as hydrogenation, dehydrogenation, Suzuki coupling, and Heck reactions.The addition of a second metal can modify the electronic structure and surface chemistry of palladium, leading to improved catalytic performance and stability.They are used as catalysts in various reactions, such as hydrogenation, oxidation, coupling reactions, and more. (J. Yang et al 2014).

1.5.2 Energy Storage: Bimetallic analogues of palladium nanoparticles have been explored for energy storage applications, particularly in electrochemical systems such as batteries and fuel cells. They can improve the performance, stability, and efficiency of energy storage devices. Bimetallic palladium nanoparticles are employed in energy storage and conversion devices, particularly in electrocatalysis for fuel cells, electrolyzers, and batteries. These nanoparticles serve as efficient catalysts for oxygen reduction, hydrogen evolution, and other electrochemical reactions, enabling the development of high-performance energy conversion systems. The composition, morphology, and surface structure of bimetallic nanoparticles play crucial roles in determining their catalytic activity, durability, and poisoning resistance in electrochemical environments. (C. Wang et al 2015).

1.5.3 Sensing: Bimetallic analogues of palladium nanoparticles have shown promising sensing capabilities due to their unique electronic and optical properties. They are utilized in various sensing platforms for the detection of gases, heavy metals, and biological molecules. Bimetallic palladium nanoparticles integrated with various substrates, such as graphene, carbon nanotubes, or metal oxides, have been employed in sensing and detection applications. These nanoparticles exhibit high sensitivity and selectivity towards target analytes, making them suitable for applications in gas sensors, biosensors, and environmental monitoring devices. The synergistic interactions between palladium and the second metal can modulate the sensing properties, improve the signal-to-noise ratio, and enhance the stability of the sensing platform. (C. Yu et al.,2018).

1.5.4 Environmental Remediation; Bimetallic palladium nanoparticles have shown promise in environmental remediation by facilitating the degradation of organic pollutants and the removal of heavy metals from contaminated water. These nanoparticles can be used in catalytic processes such as the reduction of nitroaromatic compounds, oxidative degradation of organic pollutants, and photocatalytic reactions under visible light irradiation. The incorporation of a second metal can enhance the catalytic activity, adsorption capacity, and recyclability of palladium nanoparticles, making them effective catalysts for water purification and wastewater treatment. (Wang et al 2016).

1.6 Metal based Nanoparticles and heterogeneous catalyst

Metal-based nanoparticles (NPs) have gained significant attention in various fields, particularly in catalysis, due to their unique properties arising from their small size and high surface area-to-volume ratio. Heterogeneous catalysis refers to catalytic processes where the catalyst exists in a different phase from the reactants. Metal-based nanoparticles serve as effective heterogeneous catalysts due to their tunable properties,

high catalytic activity, and selectivity. Here are some details about metal-based nanoparticles and heterogeneous catalysts

1.6.1 Synthesis of Metal-Based Nanoparticles

Metal-based nanoparticles can be synthesized through various methods such as chemical reduction, sol-gel processes, sonochemical methods, and green synthesis using plant extracts or microorganisms. These methods allow control over the size, shape, composition, and surface properties of the nanoparticles, which are crucial for their catalytic activity.

1.6.1.1 Types of Metal-Based Nanoparticles

Various metals and metal alloys can be used to prepare nanoparticles, including noble metals such as gold, silver, platinum, and palladium, as well as transition metals like iron, nickel, cobalt, and copper. Bimetallic or multimetallic nanoparticles, composed of two or more different metals, offer synergistic effects that can enhance catalytic performance.

1.6.1.2 Properties of Metal-Based Nanoparticles

High surface area: Metal nanoparticles possess a large surface area per unit mass, providing abundant active sites for catalytic reactions. Size and shape effects: The size and shape of nanoparticles influence their electronic structure, which in turn affects their catalytic activity and selectivity. Surface chemistry: The surface of metal nanoparticles can be functionalized with ligands or stabilizing agents to modify their surface properties and enhance catalytic performance.

1.7 Applications of Metal-Based Nanoparticles in Catalysis

Hydrogenation and dehydrogenation reactions: Metal nanoparticles catalyze the addition or removal of hydrogen atoms from organic compounds, important in industrial processes such as the production of fine chemicals and pharmaceuticals. Oxidation

reactions: Metal nanoparticles can catalyze oxidation reactions, including the oxidation of alcohols, hydrocarbons, and pollutants, with high efficiency and selectivity. Carbon-carbon bond formation: Metal nanoparticles serve as catalysts in various carbon-carbon bond-forming reactions, including Suzuki, Heck, and Sonogashira coupling reactions, vital in organic synthesis. Environmental remediation: Metal nanoparticles are used as catalysts for the degradation of environmental pollutants, such as organic dyes, pesticides, and pharmaceuticals, through advanced oxidation processes.

1.8 Heterogeneous Catalysis

In heterogeneous catalysis, the reactants and catalyst are present in different phases, typically the catalyst being solid and the reactants either gaseous or liquid. The solid catalyst provides active sites for the adsorption of reactant molecules, facilitating chemical reactions to occur. Heterogeneous catalysis offers advantages such as ease of separation of catalyst from reaction products, recyclability of the catalyst, and applicability to a wide range of reaction conditions.

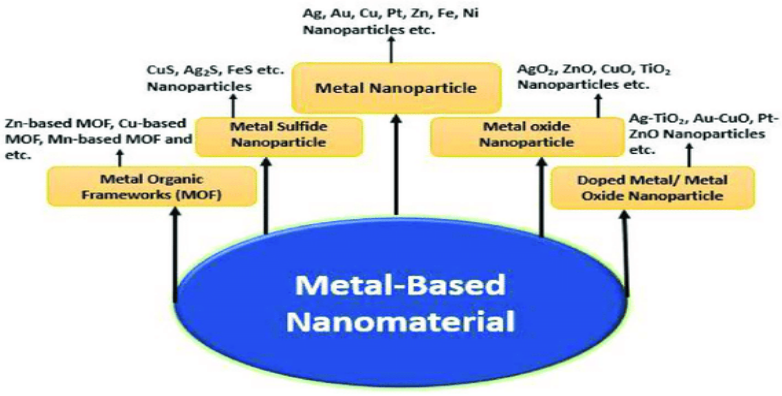

Figure 1.1 Various types of metal-based Nanomaterial

Metal-based nanoparticles serve as highly efficient heterogeneous catalysts due to their unique properties and are widely utilized in various catalytic processes with applications ranging from industrial chemical synthesis to environmental remediation. Understanding

the synthesis, properties, and applications of these nanoparticles is crucial for advancing catalysis research and developing sustainable chemical processes.

1.9 Electrochemical water splitting

Electrochemical water splitting is a process that involves the decomposition of water into hydrogen and oxygen using an electrical current. This process typically occurs in an electrolyzer, which consists of two electrodes (an anode and a cathode) immersed in an electrolyte solution, usually water containing an electrolyte such as potassium hydroxide (KOH) or sulfuric acid (H_2SO_4). Even in antiquity, references to the separation of water into its constituent elements, hydrogen (H_2) and oxygen (O_2), are found. This process, known as water-splitting, utilizes electrical energy to break down water (H_2O) molecules. Within this electrochemical reaction, two crucial half-processes occur: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).

The HER involves a mechanism wherein two protons and two electrons are combined, whereas the OER is characterized by a more complex process that uses four electrons and four protons. This intricate interplay of electrons and protons underpins the fundamental chemistry of water-splitting. Dating back over 200 years, the concept of water-splitting has fascinated scientists and thinkers across generations. Its historical significance underscores the enduring quest to unlock the secrets of water and harness its elemental components for various purposes (X. Li et al 2020). The Agastaya Samhita, an ancient text, describes a method to generate hydrogen (H_2) and oxygen (O_2) by splitting water molecules using a dry cell containing copper sulfate and zinc amalgam. This process yields a current of 23 mA at 1.138 volts. Remarkably, these observations date back to 1789, and in 1800, Nicholson and Carlisle were the first to apply this technique to industrial water electrolysis. Their experimental setup involved a sealed vertical tube filled with water (R. L. Arantegui et al 2018). In their experimental setup, Nicholson and

Carlisle inserted a platinum wire connected to the terminals of a voltaic pile into one end of a sealed tube filled with water. As the tips of the wire gradually approached each other, bubbles emerged from each tip, identified as oxygen and hydrogen, respectively. This observation led to the recognition of the electrolysis of water into its constituent gases. With the capacity to produce 10,000 Nm^3 of hydrogen per hour, large-scale hydrogen production operations commenced in 1939 using water electrolysis facilities. Despite the thermodynamic potential of 1.23 V required to split water into hydrogen and oxygen, achieving a current density of 1A cm^{-2} necessitates a cell voltage of 1.85-2.05 V. Consequently, the conversion efficiency is limited to 60-66.5%, with an electricity loss of 33.5-40% (K. Zhang et al 2016). Electrochemical water-splitting technology holds promise for generating green hydrogen gas (S. Anantharaj et al 2018). This hydrogen, devoid of pollution emissions, stands as an ultra-efficient energy carrier suitable for diverse applications. However, the sluggish kinetics and elevated overpotential associated with the oxygen evolution reaction (OER) significantly impact the efficiency of water electrolysis. Metal-air batteries, water splitting, and fuel cells emerge as straightforward, highly efficient, and sustainable methods for both energy production and storage via electrochemical reactions. The fundamental reactions underlying the reversible process in each of these systems are the water oxidation reaction (WOR), commonly known as OER, HER, and ORR (M. Tahira et al 2017).

1.9.1 Water- splitting at different pH and thermodynamic feasibility

1.9.1.1 Water-splitting at pH=7 (pure water)

Pure water, due to its insufficient self-ionization, exhibits poor electrical conductivity, approximately one millionth that of seawater. Consequently, the electrolysis of pure water becomes a time-consuming endeavor, requiring additional energy in the form of

overpotential to overcome various activation barriers. Without this supplementary energy, the process progresses sporadically or may even fail to occur.

At pH =7 and 25°C, electrolysis of pure water takes place as shown below (Eq. 1.1-1.3):

Half reaction at the cathode: $2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-$ $E^0 = -0.42\ V$ Eq. 1.1

Half reaction at the anode: $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ + 4e^-$ $E^0 = +0.82\ V$ Eq. 1.2

Overall reaction: $2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g)$ $E^0 = -1.24\ V$ Eq. 1.3

Given that the overall reaction possesses a negative cell potential, rendering it thermodynamically unfavorable, it can only proceed with an external voltage of approximately 2.4 V. Furthermore, an additional voltage, typically around 0.6 V, is required at each electrode to sustain the reaction due to the low ion concentration and electron transfer interfaces. To enhance the effectiveness of electrolysis, electrocatalysts and a suitable electrolyte, such as salt, acid, or base, can be employed.

1.9.1.2 Water-splitting in the presence of acid (pH lower than 7)

In the presence of an acid, additional hydrogen ions (H^+) are generated, which undergo reduction at the negative electrode, while water is oxidized at the positive electrode.

The reactions proceed as follows in the presence of acid at 25°C (Eq. 1.4-1.6):

Half reaction at cathode: $2H^+ + e^- \rightarrow H_2(g)$ $E^0 = +0.0\ V$ Eq. 1.4

Half reaction at anode: $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ + 4e^-$ $E^0 = +1.23V$ Eq. 1.5

Overall reaction: $2H_2O\ (l) \rightarrow O_2\ (g) + 2H_2\ (g)$ $E^0 = -1.23\ V$ Eq. 1.6

While the electrode potential (E^o) for the overall reaction is indeed negative, indicating a thermodynamically unfavorable process, in comparison to pure water, the reaction occurs at a significantly lower potential.

1.9.1.3 Water-splitting in the presence of a base (pH higher than 7)

In the presence of a base, additional hydroxyl ions (OH^-) are generated. These hydroxyl ions oxidize at the anode, releasing electrons to form oxygen (O_2), while water molecules at the cathode are reduced to form hydrogen gas (H_2).

The reactions proceed as follows in the presence of a base at 25°C (Eq. 1.7-1.9):

Half reaction at cathode: $2H_2O\ (l) + 2e- \rightarrow H_2\ (g) + 2OH^-$ $E^0 = -0.83V$ Eq. 1.7

Half reaction at anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ $E^0 = +0.4V$ Eq. 1.8

Overall reaction: $2H_2O\ (l) \rightarrow O_2\ (g) + 2H_2$ $E^0 = -1.23V$ Eq. 1.9

The electrode potential for the overall reaction remains the same as in the acid medium.

1.10 Oxygen evolution reaction (OER)

Technologies for energy conversion and storage (ECS) such as fuel cells, water electrolyzers, and metal-air batteries are essential for the global transition away from fossil fuels. With the aid of these technologies, we are able to generate and store renewable energy in chemical forms while also further transforming it into electricity when it is needed (A. Grimaud et al 2013 and P. Rao et al 2021). OER, which is regarded as a reliable mechanism for producing pure oxygen quickly, is essential for these ECS devices because it serves as a carrier by providing electrons in the electrochemical cycles that convert chemical fuels into power (M. Tahira et al 2017). In a water electrolyzer, chemical fuels are produced through the process of water-splitting, followed by the oxygen evolution reaction (OER) at the anode (Y. Pan et al 2020). Conversely, in metal-air batteries (MAB), the OER takes place on the cathode, and the performance of MAB during charging and discharging is directly impacted by the activity and stability of the OER(J. Zhang et al 2019 and W. Sun et al 2021). In fuel cells, the presence of the oxygen evolution reaction (OER) is crucial for enabling long-term energy storage and its

eventual transformation back into electrical energy (Y. N. Regmi et al 2020). Therefore, enhancing the efficiency of the OER is essential for projecting a closed-cycle clean energy structure by effectively converting and storing renewable energy.

1.10.1 OER in water splitting

In water splitting, the oxygen evolution reaction (OER) or water oxidation reaction is the primary obstacle that impedes energy conversion efficiency due to its slow kinetics (M. Rana et al 2018). This reaction occurs at the anode, where the formation of the O=O (O_2) bond takes place through four consecutive proton-coupled electron transfer steps (J. Rossmeisl et al 2007, N. Snir et al 2019 and Q. Liang et al 2021). The multistep nature of the oxygen evolution reaction (OER) results in the generation of several reaction intermediates, leading to significant reaction overpotential and sluggish kinetics. The OER reaction is highly dependent on pH, and the equilibrium half-cell potential (Ea^0) for this reaction at 1 atm and 298 K (25°C), expressed in terms of the standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE), is defined as follows (Eq. 1.10-1.12).

$At\ pH$ =0; $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Ea^0 =1.23 V Eq. 1.10

$At\ pH$ =7; $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Ea^0 =0.817 V Eq. 1.11

$At\ pH$ =14; $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ Ea^0 =0.404 V Eq. 1.12

At pH=0, the hydrogen evolution reaction (HER) occurs at 0.0 V, while the oxygen evolution reaction (OER) occurs at a higher potential of 1.23 V. Therefore, to achieve the potential difference of 1.23 V versus the standard hydrogen electrode (SHE), an external current is necessary to facilitate the OER. According to the Nernst equation, there is an approximate 59 mV shift in the reaction potential per unit pH (M. Gong et al 2015).

Consequently, to maintain a working potential of 1.23 V, a reversible hydrogen electrode (RHE) is used as a reference electrode. This prevents pH effects on the applied voltage, ensuring accurate control of the electrochemical reactions.

1.11 Mechanism of OER

In general, the oxygen evolution reaction (OER) mechanism can be described using two main approaches: the adsorbate evolution mechanism (AEM) and the lattice-oxygen-mediated mechanism (LOM) (J. Li et al 2022 and E. Fabbri et al 2018).

1.11.1 Adsorbate evolution mechanism (AEM)

According to the AEM, the process of oxygen evolution reaction (OER)in both acidic and alkaline conditions. In acidic conditions, OER involves the oxidation of water molecules, resulting in the production of oxygen gas (O_2), along with the generation of protons (H^+) and electrons (e^-). This process typically involves four elementary steps with four electron/proton transfer steps. On the other hand, in alkaline conditions, OER proceeds differently. Here, oxygen is produced through the oxidation of hydroxyl groups (OH^-) into water (H_2O), accompanied by the transfer of four electrons. Both processes are essential in understanding how oxygen is evolved during water electrolysis, which is crucial in various applications such as water splitting for hydrogen production or in certain types of electrochemical cells.

1.11.1.1 In an Acidic medium

At p=1 bar and T= 298.15 K the overall water oxidation reaction (J. Rossmeisl et al 2007, N. Snir et al 2019 and Q. Liang et al 2021)

$$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ + 4e^-;\quad \Delta G_0 = 4.92\ eV \qquad \text{(Eq. 1.13)}$$

Takes place in four steps (J. Rossmeisl et al 2007, N. Snir et al 2019 and Q. Liang et al 2021) (Eq. 1.14-1.17)-

$Step\ 1$: $H_2O\ (l) + M \rightarrow M{-}OH + H^+ + e^-$ Eq. 1.14

$Step\ 2$: $M{-}OH \rightarrow M{-}O + H^+ + e^-$ Eq. 1.15

$Step\ 3$: $H_2\ (l) + M{-}O \rightarrow M{-}OOH + H^+ + e^-$ Eq. 1.16

$Step\ 4$: $M{-}OOH \rightarrow M + O_2 + H^+ + e^-$ Eq. 1.17

1.11.1.2 In an alkaline medium

At p=1 bar and T= 298.15 K, the OER reaction (N. Snir et al 2019)

$4OH^- \rightarrow O_2\ (g) + 2H_2O\ (l) + 4e^-$ Eq. 1.18

Takes place in four elementary steps as follows (N. Snir et al 2019 and Q. Liang et al 2021 and Y. Zuo et al 2019) (Eq. 1.19-1.22) –

$Step\ 1$: $M + OH^- \rightarrow M{-}OH + e^-$ Eq. 1.19

$Step\ 2$: $M{-}OH + OH^- \rightarrow M{-}O + H_2\ (l) + e^-$ Eq. 1.20

$Step\ 3$: $M{-}O + OH^- \rightarrow M{-}OOH + e^-$ Eq. 1.21

$Step\ 4$: $M{-}OOH + OH^- \rightarrow M + O_2\ (g) + H_2O\ (l) + e^-$ Eq. 1.22

Where M indicates the catalyst's active site (*), and M-OH, M-O, and M-OOH display the adsorbed species on the catalyst's active site. The letters "g" and "l" stand for the species' gas and liquid phases.

The initial step involves the adsorption of water (in an acidic medium) or hydroxide ions (in a basic medium) on the active site of the electrocatalyst, typically a metal coordinated with oxygen. This leads to the formation of an adsorbed OH species (M-OH) through the

first electron transfer (step 1). Subsequently, a second electron transfer oxidizes the M-OH to M-O (step 2). The M-OOH intermediate is then formed in subsequent steps by the adsorption of an additional water molecule (in an acidic medium) or hydroxide ions (in a basic medium) on the catalyst's active site. This intermediate is then oxidized further to release oxygen gas, regenerating the original, undamaged active site of the catalyst.

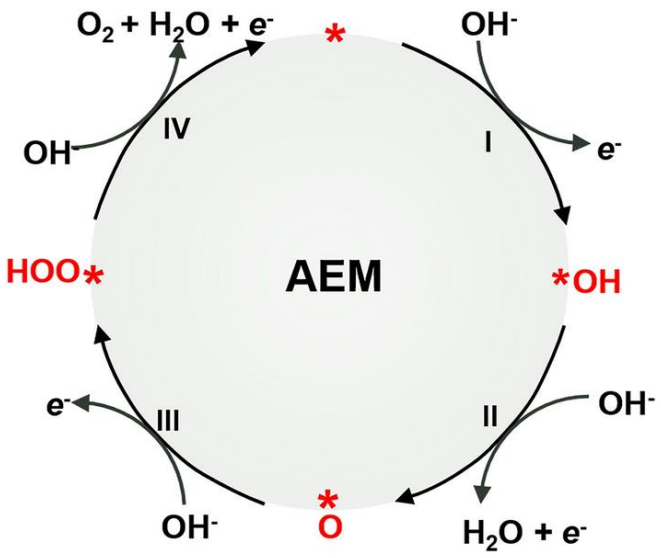

Figure 1.2 OER reaction mechanism based on AEM theory. Here * shows the active site (M) of the transition metal cation and I,II,III and IV corresponds to the four elementary steps involved in the reaction (J. Li et al 2022).

The reaction-free energies (ΔG) for these steps can be analyzed using a theoretical study, such as density functional theory (DFT). Ideally, any one of these four reaction steps could be utilized to evaluate the catalytic activity for the oxygen evolution reaction (OER) of a particular electrocatalyst. For a perfect OER electrocatalyst, the reaction-free energies of the four steps should be comparable even without an external bias. However, achieving this balance typically requires the application of an external bias due to the interdependence of the adsorption binding energies of M-OH ($EM{-}OH$), M-O ($EM{-}O$), and M-OOH ($EM{-}OOH$). The relationship between these binding energies is

characterized by the fact that the slope of $EM{-}OOH/EM{-}OH$ is approximately 1, with an intercept of 3.2 eV (I. C. Man et al 2011). On the other hand, since M-O is doubly bonded to the surface while M-OH and M-OOH are single bonded, both $EM{-}OOH/EM{-}O$ and $EM{-}OH/EM{-}O$ exhibit slopes close to 0.5 (J. Rossmeisl et al 2005). This correlation of binding energy is prevalent on the surfaces of metals and metal oxides such as rutile, spinels, and perovskites, among others. The binding energy remains consistent regardless of the binding strength or location on the surface. The formation of M-OOH and M-OH species controls the strength of the binding between oxygen and the catalyst surface. Strongly bonded surfaces tend to form M-OOH species, while weakly bonded surfaces tend to form M-OH species (I. C. Man et al 2011). As a consequence, a volcano-like relationship emerges between the electrocatalytic performance and the adsorption energy of oxygen (Y. Jiao et al 2015). At the volcano's peak, catalysts achieve a stable equilibrium of binding energies, leading to enhanced OER performance. This model, which has gained widespread recognition as a global descriptor, allows for the accurate description and estimation of the OER performance of various electrocatalysts. Optimizing and hypothesizing catalytic activity can be achieved by moving the difference between $\Delta GM{-}O$ and $\Delta GM{-}OH$ ($\Delta GM{-}O - \Delta GM{-}OH$) closer to the top of the volcano plot (Z. F. Huang et al).

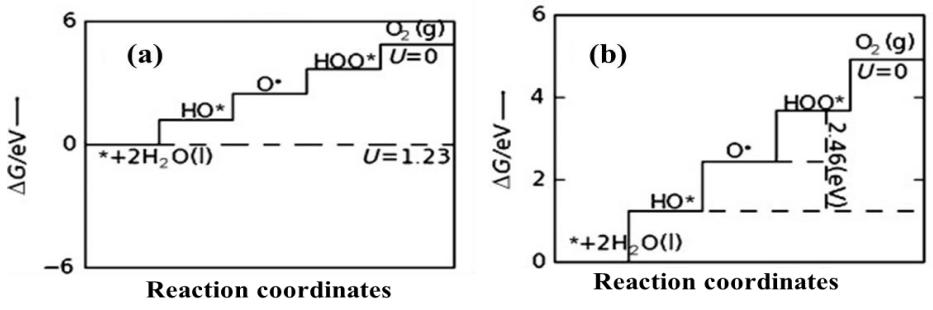

Figure 1.3 Standard free energy plot for the ideal catalyst (a) at zero potential (U=0), equilibrium potential for OER (U=1.23) and (b) at the potential, U = 2.46 V (I. C. Man et al 2011).

1.11.2 Lattice-oxygen-mediated mechanism (LOM)

In this mechanism, the electrocatalyst contains lattice oxygen, which is utilized to produce O_2 gas. In the first step, a water molecule adsorbs onto the active sites of the electrocatalyst (M or *), forming M-OH through the generation of an H^+ and e^- pair. In the second step, this M-OH is converted to M-O, similar to the acidic mechanism (AEM). In the third step, the electrocatalyst's lattice oxygen atom interacts with M-O to release an oxygen molecule (O_2) and create an oxygen vacancy (V_o). In the fourth step, a clean M site is regenerated by removing the adsorbed H^+ from M-OH. This step also involves the adsorption and dissociation of additional H_2O to produce adsorbed H^+ and M-OH. According to the lattice oxygen mechanism (LOM), the electronic structure of the catalyst is governed by the bond strength of the oxygen-metal bond, which in turn regulates the OER mechanism.

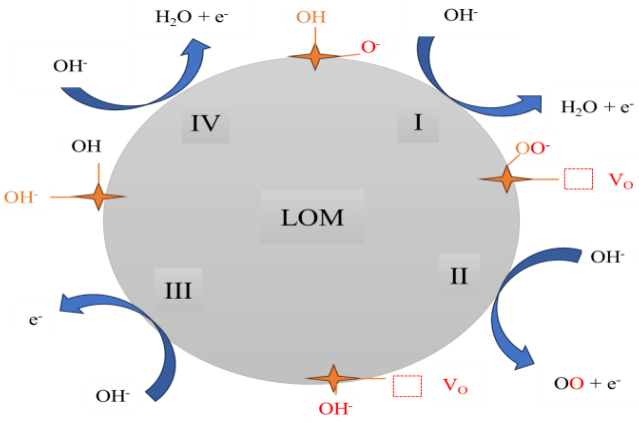

Figure 1.4 Construction of OER cycle path accordingly LOM theory. Here, * represents the active site of the catalyst (transition metal cation) and I, II, III and IV are elementary steps(E. Fabbri et al 2018).

The OER mechanism can shift from the Adsorbate Evolution Mechanism (AEM) to the Lattice Oxygen Mechanism (LOM) depending on the energy levels of the metal's d-band and the oxygen's p-band in the metal oxide. When the energy level of the metal's d-band is higher than that of the oxygen's p-band, electrons transfer from the d-band to the p-

band. Additionally, the metal site serves as an active center for adsorption, facilitating water oxidation via AEM. On the other hand, when the energy levels are reversed, ligand holes can be created as electrons move from the ligand's p-band to the metal's d-band. Additionally, by arranging their structural elements to require less energy, these ligand holes promote the evolution of oxygenated species [$(O_2)n$]. Consequently, this allows the OER mechanism to switch from AEM to LOM. This transition in the mechanism can be observed on the reversible hydrogen electrode scale for pH-dependent processes (N. C. Sagaya Selvam et al 2020 and X. Rong et al 2016).

1.12 Importance of OER in other fields

1.12.1 Metal-air batteries

Lithium-ion batteries (LIBs) have been widely used as an energy source for a long time, but their limited energy density (theoretically 400 Wh kg-1) restricts their suitability as the energy source for the next generation (T. B. Reddy et al 1984 and L. Li et al 2017). In this context, metal-air batteries have emerged as a promising candidate to meet the growing demand for high energy density. They offer inexpensive, environmentally friendly power sources for portable electronics and electric vehicles and hold significant potential for large-scale electricity storage. Unlike traditional batteries, which have a closed system, metal-air batteries feature an open cell structure that allows oxygen from the surrounding environment to be used as an active cathode material (L. Li et al 2017). As a result, the battery's weight is reduced, enhancing the energy density of metal-air batteries. These batteries primarily consist of three components: a porous cathode, an electrolyte, and a metal anode, commonly utilizing metals such as lithium (Li), sodium (Na), and zinc (Zn) (L. Li et al 2017 and R. Cao et al 2012). All metal-air batteries undergo oxygen reduction reactions and oxygen evolution reactions, irrespective of the

anode material. The nature of the electrolyte used dictates how these reactions will proceed. During the ORR in an aqueous lithium-air battery, Li_2O_2 or LiO_2 is formed on the catalyst's surface. These compounds are insoluble and accumulate in the pores of the air cathode (Y. C. Lu et al 2010).

The overall reaction can be described as the catalyst, which is insoluble, being attracted to the pores of the air cathode (Y. C. Lu et al 2010).

$$2\,Li\,(s) + O_2\,(g) \rightarrow Li_2O_2(s) \qquad E^0=2.96\,V \quad \text{Eq. 1.23}$$

$$4\,Li\,(s) + O_2\,(g) \rightarrow 2Li_2O\,(s) \qquad E^0=2.91\,V \quad \text{Eq. 1.24}$$

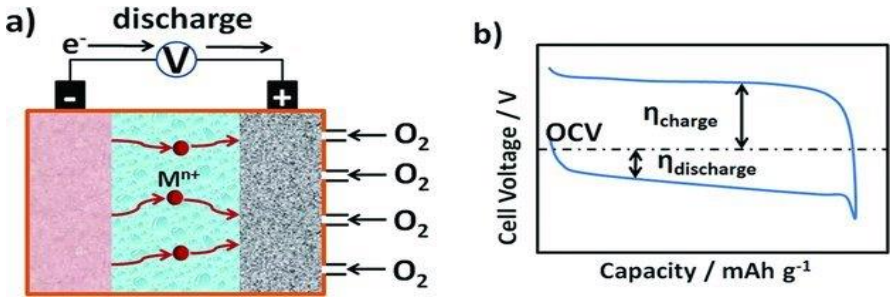

Figure 1.5 Schematic showing the image of a metal-air battery; the metal act as a anode and porous air electrode act as a cathode and, (b) charge discharge curve for metal air battery(R. Cao et al 2012).

In contrast, the alkaline aqueous electrolyte employed in Li-air batteries leads to the generation of LiOH during the ORR. LiOH is soluble in the electrolyte and does not block the pores of the air cathode during discharge (R. Cao et al 2012). The reaction can be sketched as-

$$Li\,(s) + O_2(g) + 2H_2O(l) \rightarrow 4LiOH\,(s) \qquad E^0=3.2\,V \qquad \text{Eq.1.25}$$

Similar to an aqueous Li-air battery, the discharging process in the Zn-air battery transforms oxygen into hydroxyl ions or superoxide ions. Simultaneously, zinc ions from the anode are discharged, interacting with hydroxyl ions to produce zincate ions [$Zn(OH)_4^{2-}$]. Additionally, the decomposition of zincate ions leads to the formation of zinc oxide (ZnO) (R. Cao et al 2012).

The reaction might be expressed as-

$$2Zn\,(s) + O_2\,(g) \rightarrow 2\,ZnO\,(s) \qquad E^0 = +1.65\,V \qquad \text{Eq.1.26}$$

Zn-air batteries are known for their affordability, practicality, and high energy density. However, among all types of metal-air batteries, lithium-air batteries hold the potential to offer the highest theoretical density when exposed to high potentials. Despite these advantages, both Zn-air and Li-air batteries still face several drawbacks, such as low power density, vulnerability to airborne contaminants, and electrolyte evaporation due to their open cathode designs. The main performance metrics for any metal-air battery include charge-discharge rate, capacity retention, energy efficiency, and cycle life. These metrics are predominantly influenced by two processes: oxygen reduction and oxygen evolution. These reactions occur during the discharge and charge cycles of the metal-air battery. The typical discharge-charge curve of a metal-air battery (MAB) is illustrated in Figure 1.5(b). The power output and efficiency throughout a complete cycle of metal-air batteries are significantly affected by the overpotentials of both processes: oxygen reduction reaction (ORR) during discharge (ηdischarge) and oxygen evolution reaction (OER) during charge (ηcharge). In the air electrode of metal-air batteries, several processes are involved in the oxygen reduction reaction (ORR). Initially, O_2 diffuses to the catalyst surface from the surrounding atmosphere. Subsequently, oxygen molecules accept electrons from the anode, weakening the O=O bond, and hydroxyl ions are

released as a by-product from the catalyst surface into the electrolyte (in non-aqueous Li-air batteries, a solid product is formed). Conversely, during the oxygen evolution reaction (OER) when a metal-air battery is being charged, the process reverses. The performance of the air electrode in a metal-air battery is influenced by the activity and morphology of the catalyst, as well as the structural design of the air cathode. Considerable efforts have been dedicated to the development of highly active ORR catalysts in recent years (Y. C. Lu et al 2010 and A. Debart et al 2007). However, numerous real-world issues and underlying problems still require clarification. Several studies indicate that incorporating catalytically active materials into the air electrode can substantially decrease the overpotentials for both processes (A. Debart et al 2007, S. Kumar et al 2022 and S. Kumar et al 2022). Hence, comprehending the detailed mechanisms of ORR and OER is crucial for successfully designing efficient catalyst materials for both processes. Noble transition metals and their alloys, while exhibiting excellent electrocatalytic performance for ORR and OER, are prohibitively expensive for large-scale applications. Thus, there is a need to develop catalysts that are affordable and practical for metal-air batteries.

1.12.2 Fuel cell

A fuel cell, an electrochemical cell, offers a platform for generating green and clean energy without harming the environment. It transforms the chemical energy of a fuel, such as H_2, and an oxidizing agent, like O_2, into electricity via two redox reactions. Similarly, batteries also convert chemical energy into electrical energy. In contrast to most batteries, fuel cells continuously have access to fuel, with oxygen being utilized to sustain the chemical reaction. Conversely, batteries rely on the chemical energy stored within their components. The inception of the first fuel cell dates back to Sir William Grove's discovery in 1838, while Thomas Bacon's hydrogen-oxygen fuel cell, also

known as an alkaline fuel cell, was developed in 1932, more than a century later (K. Artyushkovaa et al 2019). During the NASA Apollo mission, the alkaline fuel cell, often called the Bacon fuel cell, was utilized to provide both water and electricity to the crew.

The components of a fuel cell include the anode, cathode, and electrolyte, facilitating the transfer of hydrogen ions (H^+) or hydroxyl ions (OH^-) between the two sides. At the anode, H_2 undergoes oxidation through the hydrogen oxidation reaction (HOR), while at the cathode, O_2 is reduced via the oxygen reduction reaction (ORR).

Reaction at the cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ Eq. 1.27

Reaction at the anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$ Eq. 1.28

Overall cell reaction: $2H_2 + O_2 \rightarrow 2H_2O$ Eq. 1.29

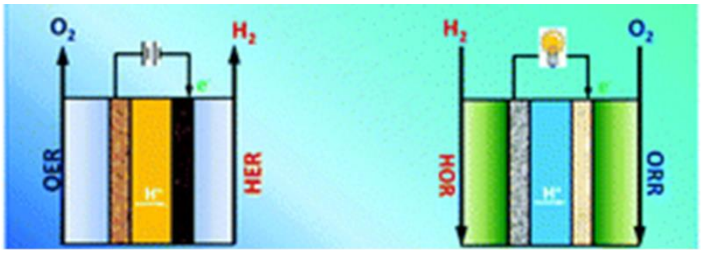

Figure 1.6 (a) Diagrammatic illustration of the electrolytic cell and fuel cell and, (b) polarization curves related to the hydrogen involving reactions (presented as red curves) and oxygen involving reactions (shown in blue curves), respectively (Y. Jiao et al 2015).

Various types of fuel cells are produced based on the electrolyte and fuels utilized, including molten carbonate fuel cells, solid oxide fuel cells, alkaline fuel cells, polymeric electrolyte membrane (PEM) fuel cells, and phosphoric acid fuel cells. Among these, solid oxide fuel cells are noted for their high efficiency (theoretical efficiency around 85%) and relatively cost-effectiveness. However, their application is limited by their high

operating temperatures, typically between 800 to 1000 °C (K. Artyushkovaa et al 2019). To ensure continuous power supply, intermittent energy storage and conversion are sought with reduced cost and increased energy density. Reversible fuel cells (RFCs), a novel concept addressing this need, integrate a fuel cell with an electrolyzer akin to a rechargeable battery. Reversible fuel cells boast a larger theoretical specific energy of 3660 Wh/kg, with a specific energy ranging from 400 to 1000 Wh/kg, nearly five times higher than batteries. Reversible fuel cells can be operated using either the fuel cell approach or the electrolyzer approach. In the fuel cell mode of RFCs, chemical energy from a fuel (H_2) and an oxidant (O_2) is efficiently and sustainably converted into electrical energy and water. Conversely, the electrolyzer mode stores electricity by splitting water into H_2 and O_2 (Y. Jiao et al 2015). When generating power and storing it in chemicals using electricity,the fuel cell and electrolyzer modes are analogous to the discharging and charging phases of a battery, respectively. The oxygen electrode plays a crucial role, acting as the cathode in a fuel cell and the anode in an electrolyzer. This electrode must be both stable and active because it facilitates the oxygen reduction reaction in the fuel cell and the oxygen evolution reaction in the electrolyzer. Since various applications require transitioning the oxygen electrode from functioning as the cathode for the ORR in a fuel cell to the anode for the OER in an electrolyzer, it is essential to develop dual-purpose catalysts that are simultaneously active for both reactions (Y. Gorlin et al 2010). Theoretical studies indicate that no single active site is capable of catalyzing both ORR and OER simultaneously (M. Busch et al 2016), which presents a significant challenge in the electro-catalysis field. For example, while Pt-based catalysts are considered state-of-the-art for ORR, they are not a viable option for OER in the high potential window due to the accumulation of Pt oxides on the surface, which reduces the catalyst's activity. Ir and Ru oxides are the most effective and stable catalysts

for OER because of their high activity, stability, and superior electrical and ionic conductivities. However, their ineffectiveness for ORR prevents them from being used as bifunctional catalysts (E. Antolini et al 2014).

1.13 Evaluating parameters for OER activity

The catalyst is an imperative and first prior component for the good performance of any reaction, but the selection of appropriate electrolyte and specific kinetic parameters for instance, overpotential, Tafel slope, electrochemically active surface (ECSA) etc., have significant importance in understanding and interpreting the mechanism of any reaction. A detailed description of these parameters is listed in the subsequent subdivisions.

1.13.1 Electrode and electrolyte

The working electrode and electrolyte are crucial for ensuring good reaction performance. The reaction rate is significantly influenced by the structure, conductivity, and wettability of the working electrode or substrate. There are two types of electrode supports based on surface structure and electrolyte movement: flat surfaces and 3D electrodes. Flat surface electrodes, such as glassy carbon (GC), Cu/Ti foil, and indium-doped tin oxide (ITO) substrates, allow one-sided diffusion of electrolytes. In contrast, 3D substrates like carbon cloth (CC), carbon paper (CP), and Ni foam provide multiple pathways for electrolyte access from all sides of the catalyst. Electrolytes play a crucial role in influencing the performance of electrode materials, with the catalyst's activity showing varying responses in different electrolytes. Alkaline mediums provide better support for OER, whereas achieving satisfactory performance in neutral electrolytes poses a challenge, and in acidic mediums, the performance is notably poor. Research efforts are primarily focused on identifying stable electrocatalysts suitable for alkaline environments. While carbon-based materials, transition metal oxides or oxy-hydroxides,

hybrids, spinels, perovskites, and metal organic frameworks (MOFs) demonstrate high stability as electrode materials in alkaline mediums, their stability is compromised in acidic conditions due to their elevated oxidation potential. Thus, there's considerable interest in finding an Oxygen Evolution Reaction (OER) electrocatalyst capable of functioning across a broad pH spectrum from 0 to 14.

1.13.2 Onset/ Overpotential (η)

Determining the exact onset potential for gauging the Oxygen Evolution Reaction (OER) performance of catalysts can be challenging. Hence, evaluating the potential at a defined current density is commonly utilized to assess catalyst performance. In a comprehensive manner, a specific current density of 10 $mAcm^{-2}$ is commonly employed, and the potential value at this current density is referred to as the overpotential (η). Overpotential is defined as the variance between the electrode potential (E) and the equilibrium potential (Eeq) of the electrode reaction, typically set at 1.23 volts versus the reversible hydrogen electrode (RHE). Equation 1 illustrates the Nernst equation, as follows:

$$E = E^0 + \frac{RT}{nF}\left(\frac{C_O}{C_R}\right) \qquad \text{Eq. 1.30}$$

Given E as the real applied potential, $E0$ as the standard electrode potential, R as the gas constant (8.314 J $K^{-1}mol^{-1}$), T as the absolute temperature, n as the number of electrons transferred in a battery reaction, C_O and C_R as the concentrations of the oxidized and reduced species respectively, and F as the Faraday constant (96485.33 $sAmol^{-1}$), respectively.

Overpotential is expressed as follows:

$$\eta = E - E_{eq} \qquad \text{Eq. 1.31}$$

Typically, overpotential is measured in millivolts (mV). For instance, if a catalyst achieves a current density of 10 $mAcm^{-2}$ at 1.53 V vs. RHE, the overpotential is 300 mV. A lower overpotential indicates better catalytic activity. Catalysts with overpotentials in the range of 300-400 mV are considered exceptional for the oxygen evolution reaction (OER).

1.13.3 Exchange current density (i_0) and Tafel slope (b)

Exchange current density and Tafel slope are two essential parameters for assessing the electrochemical performance of a catalyst. The exchange current density indicates the intrinsic efficiency of the catalyst, reflecting the rate of electron transfer between the electrode and the electrolyte. The Tafel slope provides insight into the reaction kinetics and mechanism (M. E. Orazem et al 2008). Typically, an electrochemical reaction consists of two half-reactions occurring at the cathode and anode, respectively. The reaction at the cathode is known as the cathodic reaction, while the reaction at the anode is known as the anodic reaction. Consequently, the total current (j) is the sum of the anodic current (i_a) and the cathodic current (i_c), expressed as:

$$j = j_a + j_c \qquad \text{Eq. 1.32}$$

At equilibrium, when $E=E$eq, the overpotential (η) is zero. In this state, the absolute values of the anodic and cathodic currents are equal, resulting in a net current of zero and no net electrolysis. The exchange current density (i_0) is defined as the current at zero overpotential and in the absence of net electrolysis. It is calculated as the ratio of the exchange current (j_0, which is the magnitude of the intercepts when the reaction is at equilibrium) to the geometric area of the electrode (s), as follows:

$$i_0 = \frac{J_0}{s} \qquad \text{Eq. 1.33)}$$

A higher i_0 value indicates a more efficient electrocatalyst. Although its magnitude cannot be directly measured, it can be calculated using the Tafel equation. The Butler-Volmer equation, also known as the Erdey-Gruz-Volmer equation, describes the relationship between the current density and the voltage difference between the electrode and the electrolyte, encompassing both cathodic and anodic reactions.

1.13.4 Electroactive surface area (ECSA)

Catalytic activity of the catalyst is typically expressed in terms of current density, normalized by the geometric area of the electrode. Alternatively, the current can be normalized by the surface area of the catalyst material. For non-porous materials, surface area is measured using microscopic techniques such as atomic force microscopy. For materials with high surface areas, gas adsorption techniques, such as nitrogen or hydrogen adsorption, are employed. Although these techniques are crucial for assessing the surface area of various materials, they cannot distinguish between electrically conductive and non-conductive components, nor can they identify surface areas that are accessible or inaccessible to the electrolyte (C. Wei et al 2019 and S. Trasami et al 1992). Therefore, the electrochemically active surface area (ECSA) is considered an appropriate tool for correlating the different structural properties of catalysts with their electrochemical behavior.

The ECSA of the catalyst can be calculated using the relationship between the double-layer capacitance (C_{dl}) and the specific capacitance (C_s) as shown below (S. Trasami et al 1992

$$ECSA = \frac{C_{dl}}{C_s} \qquad \text{Eq. 1.34}$$

Cdl can be measured using either cyclic voltammetry (CV) for direct current (DC) or electrochemical impedance spectroscopy (EIS) for alternating current (AC). Using

the EIS method, the value of C_{dl} can be determined using the equation (A. J. Bard et al 1980).

$$C_{dl}=Y_0[R_s^{-1}+R_{ct}^{-1}]^{n-1} \quad \text{Eq. 1.35}$$

Where R_s is the solution resistance, and R_{ct} is the charge transfer resistance parallel to the constant phase element (CPE). Y_0 (in mS·s) and n (dimensionless) are the coefficient and exponent of the CPE, respectively. To determine C_{dl} from CV, first select a non-faradaic region where no redox reactions occur. Run CV at various scan rates to obtain a rectangular-shaped CV plot. The value of C_{dl} is found from the slope (divided by 2) of the linear relationship between the difference in anodic and cathodic current densities and the scan rates. A higher C_{dl} value indicates a larger ECSA. Comparing the catalytic activity of various catalyst materials under different conditions is challenging due to the differing electrochemical reactions of each material. However, evaluating the performance of a series of similar catalyst materials under identical conditions is easier and more reliable.

1.13.5 Stability

In electrochemistry, exceptional stability is just as important as superior activity when evaluating the quality of catalysts. For catalysts to be viable on a large scale, stability is a crucial aspect. To assess the stability of electrocatalysts, three common measurements are typically used: cyclic voltammetry (CV), chronoamperometry (current versus time at a fixed potential), and chronopotentiometry (potential versus time at a constant current density). Using CV, typically 500 to 1000 continuous cycles are run. Afterward, the shift in the overpotential at a specific current density is measured by comparing the linear sweep voltammetry (LSV) results before and after these cycles. For the other two methods, stability is assessed by conducting the

experiment over an extended period at either a fixed potential (chronoamperometry) or a constant current density (chronopotentiometry).

1.14 Scope of the work and objective of the thesis

In envisioning a fossil fuel-free future, renewable energy technologies have become imperative. Water splitting, rechargeable metal-air batteries, and fuel cells are essential for producing and storing renewable energy, as well as for its conversion into other forms of energy. Within these devices, the Oxygen Evolution Reaction (OER) plays a crucial role in generating pure oxygen. However, the slow kinetics of OER present a significant challenge, hindering the widespread application of these devices at a large scale. In water-splitting, compared to the Hydrogen Evolution Reaction (HER), the Oxygen Evolution Reaction (OER) is a more intricate process. It requires a significant overpotential to achieve the same current density, indicating a substantial kinetic barrier for OER. While noble metal oxides such as IrO2 and RuO2 are recognized as benchmark OER catalysts, numerous other materials have been employed for OER. However, there remains a vast unexplored space in this field. Spinel materials, comprising bimetallic and trimetallic oxides, along with metal-organic frameworks, a category of porous crystalline materials, have recently garnered significant attention for their potential in the Oxygen Evolution Reaction (OER). Their straightforward synthesis methods offer a promising avenue for discovering alternatives to expensive electrocatalysts for OER. Given these insights and the forefront applications of OER in renewable energy, this thesis is dedicated to addressing the following objectives:

- Creating heterogeneous catalysis-based electrocatalysts to investigate the Oxygen Evolution Reaction (OER). In particular, a straightforward hydrothermal process is used to create cobalt-palladium, which is used in a variety of applications.

- Another component of the thesis is the hydrothermal synthesis of noble metal nanocatalysts for heterogeneous catalysis. Cobalt, palladium, and organotrialkoxysilane-mediated production of Co@Pdnps were created utilising Co-NTA nanowires as a precursor. The catalyst is then used as an active ingredient to change carbon cloths (CC) in order to improve the Oxygen Evolution
- The thesis also describes how a low overpotential, little catalyst loading on the carbon fabric, and a modest Tafel slope were achieved by the Co@Pdnps-based nanostructured silica-derived thin film, which created a very high current density. These substances have been specially designed to be used in the Oxygen Evolution Reaction (OER).
- Since the electrocatalytic process takes place on intricate composite structures, a precise and in-depth reinvestigation of the reaction mechanism is necessary for redox processes utilizing carbon-based polymer composites.
- In order to continually supply and meet energy demands, renewable energy sources must be combined with electrochemical conversion and energy storage.
- To satisfy the demands of industrial applications with performance as high as noble metals, research efforts should be focused on conjugated polymer composites to enhance the redox processes.