Chapter 1 Introduction and Literature Survey

1.1 Introduction

The world's energy demands are continually evolving due to factors such as geopolitical tensions, economic shifts, and changes in energy use [1]. The world's energy demands are continually evolving due to factors such as geopolitical tensions, economic shifts, and changes in energy use. The International Energy Agency's World Energy Outlook provides an in-depth analysis of the global energy system. As of 2023, the world's energy consumption is growing, with demand increasing as economies develop and populations rise. The industrial revolutions have significantly shaped our world, driving technological advancements and economic growth. However, they have also increased natural gas consumption and other fossil fuels, contributing to the current energy crisis [2]. Moreover, despite their abundance, fossil fuels are finite resources. As we continue to consume them at an alarming rate, we edge closer to depletion. This looming energy crisis threatens not only our energy security but also our economic stability [3-5]. Due to its abundance and versatility, natural gas has become a significant player in meeting this demand. However, our reliance on natural gas and other fossil fuels has led to many problems. The combustion of these fuels results in the emission of carbon dioxide (CO_2), a greenhouse gas. This gas captures heat within the atmosphere, contributing to the phenomenon known as global warming., which results in climate change, characterized by melting ice caps, rising global temperatures, and extreme weather events [3, 5]. To address these challenges, there is an urgent need for sustainable solutions. Owing this reason, there has been significant progress in converting clean, renewable and sustainable energy such as wind, which is an abundant, widely distributed resource, especially in coastal and open areas. However, intermittent energy production dependent on wind speed and consistency brings limitations. Hydropower is reliable, has a low operating cost, and is dispatchable energy generation with long lifespans for hydropower plants but limited availability of suitable sites for large-scale hydropower projects. Biomass energy utilizes agricultural residues, organic waste materials and contribute to waste management, but competes with food production emissions of air pollutants and greenhouse gases during combustion, especially from inefficient or uncontrolled systems. Geothermal power generation is reliable and has a baseload life span and high-capacity factors, but it is limited to regions with accessible geothermal resources, such as tectonic plate boundaries and volcanic areas. Nuclear power-based energy generation provides high energy density and low greenhouse gas emissions during operation but brings concerns about nuclear accidents, radioactive waste disposal, and proliferation risks [6-8]. To resolve issues related to energy demand, the researcher needs to design efficacious, economical, clean, and eco-friendly electrochemical energy storage and conversion systems. In this regard, green hydrogen gas (H_2), which has a very high calorific value and almost no emissions of hazardous gases, has been promoted as one of the most promising sustainable and clean energy sources for ecological systems. Natural gas steam reforming is the primary method used in the industrial sector to produce H_2, but these processes release CO_2 into the atmosphere, compromising the environmental benefits of using H_2 as a fuel. Therefore, achieving sustainable commercial and industrial hydrogen production is a big challenge. Hydrogen production via electrolysis generates 99.9% pure hydrogen with zero emission of CO_2 gas compared to any other production method [9]. This technique has attracted much interest due to cost-effectiveness, environmental friendliness, high efficiency and, more importantly, zero percent CO_2 emission.

Generally, precious catalysts like Pt and RuO_2 are considered as the best electrocatalysts for hydrogen and oxygen evolution for water splitting, respectively, due to their low overpotential and fast kinetics, but the high cost and scarcity hinder the use of these catalysts. Therefore, non-precious catalysts are required, which must overcome the problem of high overpotential (η) in the electrochemical process [10]. Promising electrocatalysts are needed to reduce overpotential values to increase the efficiency and rate of reaction. Cost-effective and sustainable electrocatalysts such as metal oxides, metal dichalcogenides and carbon-based nanostructures are good choice for water splitting performance. In particular, good electrocatalytic activity requires the presence of rich active sites and a suitable surface structure. However, pristine carbon nanostructures do not act as promising electrocatalysts for water splitting, but they can work as excellent electrocatalysts after surface modification like functionalization and heterostructure formation. The choice of the electrocatalyst depends upon vital parameters such as high specific surface area, good porosity, high electronic conductivity, substantial electroactive sites, structural diversity and chemical stability for higher catalytic efficiencies. Electrocatalysts for electrolyzers can be classified based on the type of electrolyzer. Here are the three main types of electrolyzers and the corresponding classes of electrocatalysts: Traditional electrocatalysts for alkaline water electrolyzer are nickel and its derivatives, such as nickel-alloys and raney nickel. However, due to their high catalytic activities and abundance, research has rapidly progressed onto other classes of materials, such as oxides, hydroxides, phosphides, and chalcogenide-based nanostructured materials. Proton exchange membrane electrolyzers utilize a variety of platinum-based catalysts, which include everything from platinum black to carbon-supported platinum catalysts. Electrocatalysts made from Pt black are costly and needed in large amount due to limited surface area to achieve satisfactory performance. On the other hand, Pt decorated on carbon (Pt/C) electrocatalyst with larger active surface areas, are currently preferred in electrolyzers. Recently, platinum-transition metal alloys loaded on carbon (Pt-X/C), have shown two to four-fold increment in the performance of polymer exchange membrane electrolyzers. In solid oxide electrocatalyst based electrolyzer, asymmetric materials for cathode and anode are employed. Traditionally, nickel-doped yttria-stabilized zirconia has been used as a cathode and lanthanum strontium manganate is the most commonly used anode. However, there are several reports on the degradation of the catalyst materials and also the oxidation of nickel-to-nickel oxide. Various alternative combinations of materials are currently under investigation by different research groups [11, 12]. The choice of the electrocatalyst depends upon vital parameters such as good porosity, high specific surface area, high electronic conductivity, low electronegativity, low band gap, substantial electroactive sites, chemical stability, structural diversity, and better band alignment with water redox levels for higher electrocatalytic efficiencies.

The energy storage systems provide a way to store excess energy produced during peak times for use when production is low. Advancements in energy storage technologies are making these sources more reliable and efficient [13]**.** There are several energy storage systems thermal, mechanical, electrochemical, solar etc. Thermal energy storage refers to the process of storing thermal energy by either heating or cooling a storage medium. The stored energy can be used later for heating applications, power generation, etc [14]**.** Mechanical energy storage includes systems like pumped hydro storage and flywheels, where energy is stored in a mechanical form [15]. Chemical energy storage involves storing energy in the chemical bonds of a substance, like in a battery**.** Solar energy storage involves storing energy from the sun [7]. Among various electrochemical energy storage systems, Lithium-ion batteries have been the go-to easy solution for energy storage due to their long cycle life and high energy density. However, lithium-ion batteries face several challenges, including safety concerns related to overheating and the limited availability of lithium resources. As a result, there is a growing interest in alternative energy storage solutions such as metal-air batteries. Among these, zinc-air batteries are particularly promising due to their higher energy density safety advantages, and zinc is more abundant and environmentally friendly than lithium-ion batteries. The two-dimensional (2D) transition metal dichalcogenides (TMDs) such as $MoSe_2$, MoS_2, WSe_2, WS_2 etc. have been used as electrocatalysts for hydrogen and oxygen generation, overall water splitting and zinc-air batteries because of their high acidic/basic stability, natural abundance and excellent electrochemical activity. These TMDs as catalysts can help to lower the energy required to split the water and enhance hydrogen production. In the present thesis, we have investigated the HER/OER activity, overall water splitting and Zn-air battery performance of molybdenum diselenide ($MoSe_2$) based nanomaterials. In the following sections, we will look in to structure and properties of $MoSe_2$ suitable for energy applications.

1.2 Molybdenum diselenide ($MoSe_2$)

Transition Metal Dichalcogenides (TMDs) represent a broad family of compounds with the general formula MX_2. Here, 'M' stands for transition metals like molybdenum, titanium, vanadium, chromium, and others from groups 4 to 10. 'X' represents chalcogens (S, Se, Te etc.) from group 16, such as sulfur (S), selenium (Se), and tellurium (Te). This results in over 40 unique TMDs combinations, as depicted in **Figure 1.1**.

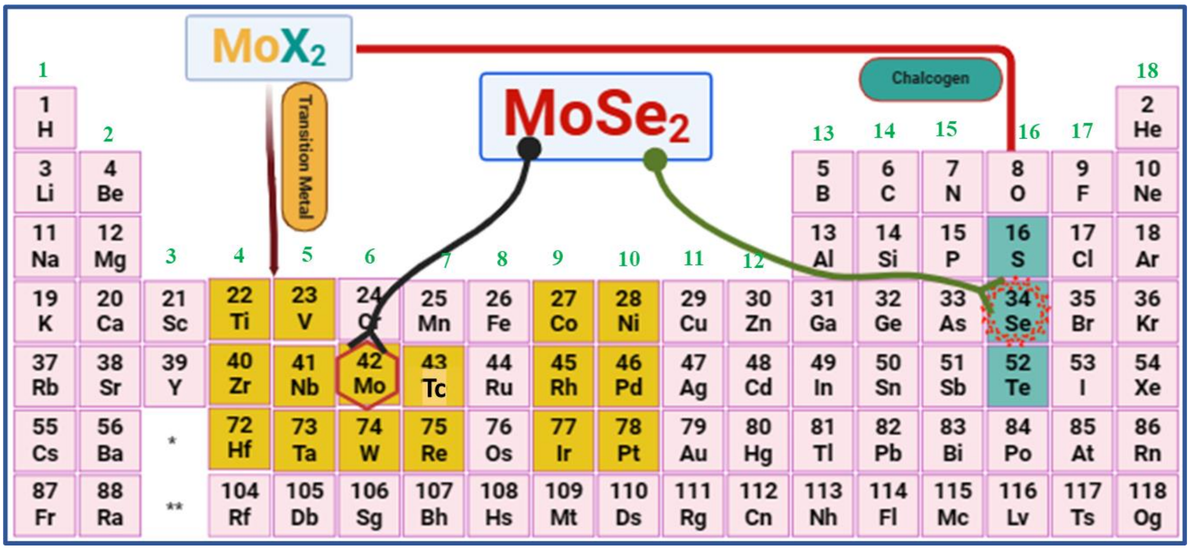

Figure1.1 *Periodic table showing transition metal and chalcogen elements.*

The 2D TMDs are sandwich-like structures composed of a transition metal layer enclosed by two chalcogen atom layers. Thus, monolayer of $MoSe_2$ consists of three atomic layers (1 of Mo and 2 of Se). In $MoSe_2$, molybdenum (Mo) carries a positive tetravalent charge, while selenium (Se) is negatively bivalent. Bulk $MoSe_2$ is created by stacking multiple $MoSe_2$

monolayers on top of each other along the c-axis, with weak van der Waals forces facilitating the layering process [16, 17]. Every molybdenum (Mo) atom resides within the symmetry plane of a triangular prism, forming covalent bonds with six selenium atoms. Simultaneously, three molybdenum atoms commonly share each selenium atom in this configuration, as shown in **Figure 1.2**. The 2H phase (trigonal prismatic coordination) exhibits hexagonal symmetry, having two Se-Mo-Se layers per repeat unit. The 3R phase (trigonal prismatic coordination) features rhombohedral symmetry, having three Se-Mo-Se layers per repeat unit. In the 1T phase (octahedral coordination), the upper triangle is the inversion of the bottom triangle. The 1T and 3R phases are the metastable structures showing conducting characteristics. The 2H phase is a stable semiconducting structure with an indirect band gap of ~1.1 eV. The 1T phase significantly improves the charge transfer efficiency, making them suitable for energy applications like supercapacitors and batteries. At the same time, the 2H-phase serves applications in semiconductor-based electronic and optoelectronic devices along with energy-related applications [18-20].

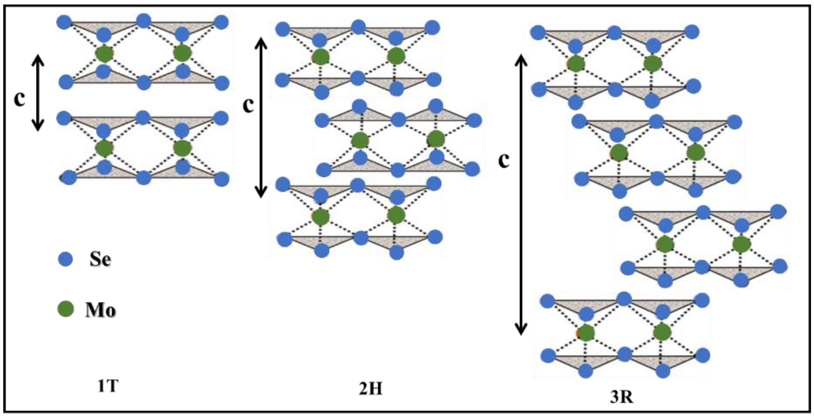

Figure 1.2 *Schematic diagram of* $MoSe_2$ *polytypes-1T, 2H, and 3R [17].*

1.3 Properties of $MoSe_2$

Electrical Property

The $MoSe_2$ boasts fascinating electrical properties that make it a promising candidate for next-generation electronics and optoelectronics devices.

In its bulk form, $MoSe_2$ is a semiconductor with an indirect bandgap. The bandgap of $MoSe_2$ can be tuned depending on the number of layers, transitioning to a direct bandgap of ~1.5 eV in single-layer $MoSe_2$, making it even more attractive for optoelectronic applications. The introduction of impurities (doping), can change $MoSe_2$ from an n-type (electron rich) to a p-type (hole rich) semiconductor, enabling the creation of p-n junctions crucial for electronic devices. $MoSe_2$ possesses high carrier mobility (121 $cm^2\ V^{-1}\ s^{-1}$), particularly in single-layer form [21]. This allows for efficient transport of charge carriers, making it desirable for high-speed electronic devices. The weak van der Waals forces between layers influence conductivity and can be exploited to create novel devices with specific functionalities. The surface of $MoSe_2$ plays a significant role in its electrical behavior. Defects and adsorbates (atoms or molecules attached to the surface) can trap charges and alter conductivity. Understanding and manipulating surface properties is crucial for optimizing $MoSe_2$ devices.

Mechanical property

Understanding mechanical properties of $MoSe_2$ is crucial for various applications, especially when it comes to designing robust and reliable devices. Fracture strength for 2H-$MoSe_2$ (hexagonal phase), is approximately 13.6 GPa for armchair chirality and 13.0 GPa for zigzag chirality at a temperature of 1 K. The Young's moduli in both armchair and zigzag directions exhibit similar values of approximately 100.9 GPa and 99.5 GPa, respectively [22].

Optical property

$MoSe_2$ exhibits nonlinear absorption across an ultrabroad spectrum, ranging from near-infrared (NIR) to mid-infrared (MIR) wavelengths. $MoSe_2$ has a bandgap that varies from approximately 1.1 eV (bulk material) to 1.58 eV (monolayer structure). This tunable bandgap makes $MoSe_2$ attractive for applications in catalysis, phototransistors, and optoelectronic devices.

Electrochemical property

The $MoSe_2$ is also considered as promising candidate for electrochemical energy storage due to its promising structural and electronic properties. $MoSe_2$ is being used in electrochemical energy storage/generation applications (metal air batteries, HER, OER, water splitting, ion batteries, supercapacitors and others) due to its small bandgap, low resistance, high surface activity and large interplanar distance. The $MoSe_2$ nanosheets containing different functional groups show enhanced wettability towards electrolyte. The curved and wrinkled surfaces with edges contribute to high defect density and enhanced electrochemical activity.

1.4 Synthesis methods of $MoSe_2$

Various methods have been developed for synthesizing few-layered $MoSe_2$ nanostructures, employing both top-down and bottom-up approaches, as shown schematically in the **Figure 1.3**.

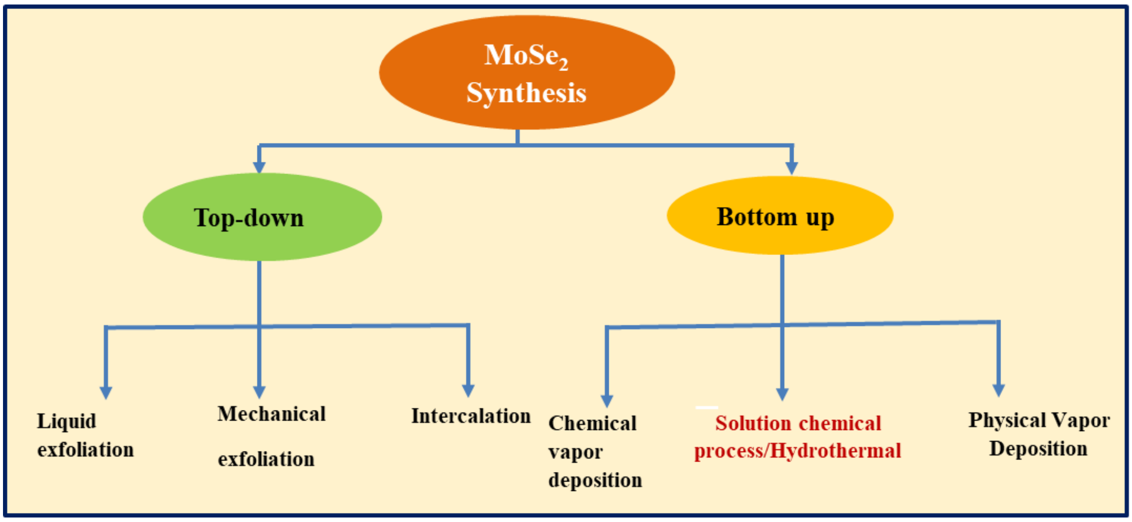

***Figure 1.3** Schematic representation of different synthesis methods for $MoSe_2$.*

The top-down route involves techniques like mechanical exfoliation, liquid-phase exfoliation, and chemical intercalations. Bottom-up methods such as CVD, PVD, and hydrothermal synthesis yield $MoSe_2$ films or flakes. Mechanical exfoliation produces thin, highly pure single- to few-layer $MoSe_2$ flakes suitable for fundamental electronics. However, challenges in size and thickness control, along with limitations for large-scale applications, remain drawbacks. Liquid exfoliation, a common top-down approach, disrupts cohesion between neighboring layers using direct sonication, dependent on solvent properties. The resulting materials exhibit random shapes, sizes, and layering. Liquid exfoliation surpasses mechanical exfoliation in terms of yield, although it may yield some defective flakes. This method becomes advantageous when large quantities of nanomaterials are needed, and defects do not significantly impact applications, especially in energy production and storage. It provides a cost-effective and straightforward approach for large-scale manufacturing of 2D $MoSe_2$ nanosheets. Another notable top-down technique involves lithium intercalation. By immersing a powder sample in lithium solution for intercalation and subsequently exposing it to water, resulting in the rapid separation of $MoSe_2$ layers [23]. The material produced through this exfoliation process exhibits distinct structural and electronic properties compared to its bulk counterpart. The chemical vapor deposition (CVD) method is robust for producing high-quality, large-area monolayers of 2D materials. Typically, this process involves high temperatures and solid/gas precursors of desired products. In the case of $MoSe_2$, CVD is being employed in various ways. Different precursors undergo chemical reactions in the vapor phase, leading to the deposition of the desired $MoSe_2$ product as a thin solid film [24]. The process typically starts with the evaporation of solid precursors, which are usually selenium (Se) and a molybdenum compound such as molybdenum trioxide (MoO_3) or molybdenum dioxide (MoO_2) or others. These precursors are placed in distinct zones within a quartz-tube furnace. The furnace is heated to a specific temperature that allows for controlled evaporation of the precursors. The evaporated materials then react and deposit on substrates like Si/SiO_2 to form layers of $MoSe_2$. The process can produce large-area, highly crystalline $MoSe_2$ atomic layers suitable for various applications, including photodetectors [25]. The CVD method also has disadvantages, such as high reaction temperature, high vacuum, and specific substrates. The synthesis of $MoSe_2$ via hydrothermal process is fascinating, and it has several advantages over other methods. It uses inexpensive precursors such as metal salts. Hydrothermal synthesis occurs at relatively low temperatures (around 200 °C) compared to other high-temperature methods like CVD, making it more energy-efficient. Hydrothermal synthesis is scalable, allowing for producing large quantities of $MoSe_2$, which is beneficial for commercial applications. It offers versatility regarding the morphology and size of the produced $MoSe_2$, which can be tailored by adjusting the synthesis parameters. The process is considered to have lower energy requirements and the use of water as a solvent, which is less harmful to the environment. Hydrothermal synthesis is relatively simple to operate and does not require sophisticated equipment, making it accessible for various research settings.

1.5 Applications of $MoSe_2$ nanostructure

Exceptional physical and chemical properties of $MoSe_2$ have shown great promise in a range of applications including transistors, photodetectors, solar cells, battery, logic devices, gas sensors, and photocatalysis. **Figure 1.4** provides a schematic representation of several important application areas for $MoSe_2$ nanostructures. The porous nature and high conductivity of $MoSe_2$ make it suitable for use as electrodes in electrochemical applications such as supercapacitors, batteries, and hydrogen production.

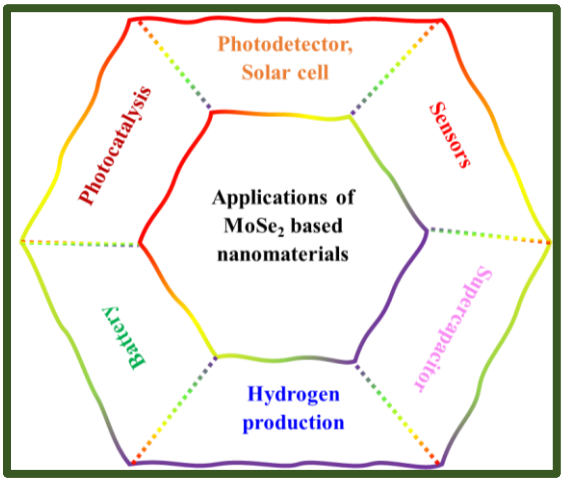

Figure 1.4 *Schematic diagram for different applications of* $MoSe_2$.

1.5.1 $MoSe_2$ for HER

As the world grapples with the urgent need to transition toward sustainable energy sources, hydrogen (H_2) emerges as a promising contender. Hydrogen is a crucial player in clean energy, with a higher gravimetric energy density of 39 kWh kg^{-1} of all chemical fuels, and it may greatly minimize carbon emissions and offer potential solutions to pressing environmental challenges. This means that a relatively small amount of hydrogen can store significant energy. Such high energy density makes hydrogen ideal for applications where weight and space constraints are critical, such as in transportation (e.g., fuel cell vehicles). Hydrogen combustion produces only water vapor as a byproduct, making it a zero-emission fuel when used in fuel cells. Electrochemical water splitting, or electrolysis, is a leading method for producing clean hydrogen. In this process, an electric current is passed through water (H_2O), causing it to split into hydrogen (H_2) and oxygen (O_2) gases, as shown in **equation 1.1-**

$$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2 \tag{1.1}$$

The cathode, anode and electrolyte are the primary parts of an electrochemical water-splitting cell, as shown in **Figure 1.5.**

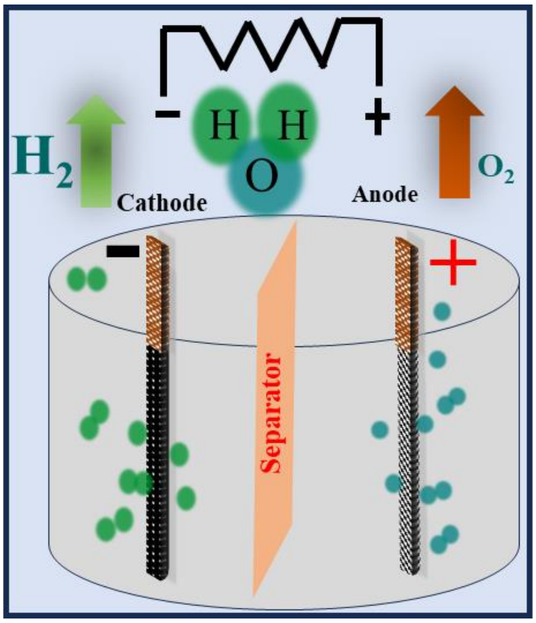

Figure 1.5 *Schematic of overall water splitting cell.*

Researchers focus on developing ideal catalysts that balance activity, stability, and affordability to enhance HER efficiency. An optimal HER catalyst should exhibit a Gibbs free energy close to zero during the reaction. This property ensures that hydrogen binding on the catalyst surface is neither too weak (leading to slow kinetics) nor too strong (hindering desorption). High catalytic activity is essential for efficient HER. Catalysts must withstand harsh electrochemical conditions without degradation. Stability ensures long-term performance and minimizes replacement costs. Cost-effective catalysts are crucial for large-scale hydrogen production. Platinum (Pt) is an excellent HER catalyst, but its scarcity and high cost limit widespread adoption. Researchers exploring earth-abundant elements (such as carbon, iron, nickel, cobalt, and molybdenum) or based materials are preferred over rare metals [26-28].

Literature Review on Electrocatalysts for HER

Noble metals like Pt and Ru exhibit exceptional HER activity in acidic/basic electrolytes. However, their scarcity and high cost hinder widespread adoption. Consequently, researchers have explored alternative electrocatalysts that are both cost-effective and abundant. Several classes of non-precious metal catalysts have garnered attention, Such as carbon-based nanostructures, transition metal oxides, transition metal phosphides, transition metal nitrides, TMDs, iron oxide (Fe_2O_3) and manganese oxide (MnO_2) have been investigated for HER. In order to obtain a metal-free, inexpensive HER catalyst, carbon-based nanomaterials, due to their low cost, diverse forms, and tuneable electronic structures, have emerged as promising HER catalysts. Mishra *et al.* demonstrated that multiwalled carbon nanotubes grown over iron nanocatalysts as HER electrocatalysts. It showed good electrochemical activity with overpotential (η_{10}) ~ 192 mV and Tafel slope ~ 105 mV dec $^{-1}$ in 0.5M H_2SO_4 for HER process [29]. Li *et al.* demonstrated different functionalized carbon nanotubes such as EDA-MWCNTs and ionic liquid (AMMI-Br) functionalized MWCNTs as metal-free inexpensive HER catalyst shows the Tafel slope of 116 and 125 mV dec^{-1}, respectively [30]. Li *et al.* have shown nanosheet heterostructure of dual phase $MoSe_2$ (1T/2H) on MXene as HER electrocatalyst. It achieves a low overpotential of 95 mV and a Tafel slope of 91 mV dec^{-1} for HER, suggesting effective hydrogen evolution capability. The high-conducting MXene nanosheets serve as substrates for $MoSe_2$ that promote charge transfer ability and prevent 1T/2H $MoSe_2$ from aggregating [31]. Singh *et al.* demonstrated the synthesis of $MoSe_2$/SnS nano heterostructures via colloidal growth mechanism for HER activity. During this in-situ synthesis procedure of $MoSe_2$/SnS nano heterostructures, the formation of MoO_{3-x} occurs at the interface between $MoSe_2$ and SnS, results in the activation of inactive basal planes of $MoSe_2$ nanosheets. The electrocatalyst exhibits significantly improved performance, with low overpotential and Tafel slope of 374 mV and 137 mV dec^{-1}, respectively. The enhancements in electrocatalytic activity are primarily attributed to the manipulation of electronic properties due to synergistic effect between $MoSe_2$ and the substrates [32]. In general, electrodes are prepared by using binders to hold the catalyst on the substrate of the electrode, however, they hinder the performance of the catalyst due to reduction in effective surface area and electrical conductivity of the electrode. Hence, the development of binder free electrodes is required for high performance electrolyzers [33]. Zhao *et al.* have discussed that enhancement of HER kinetics for alkaline water splitting using heteroatom-doped $MoSe_2$ Nanosheets. This study reveals improved Tafel slopes (81 mV dec^{-1}) and overpotential (η_{10} ~206 mV) [34]. Sajjad *et al.* reported that $MoSe_2$/graphene/NF composites showed excellent electrocatalytic activity for HER, with a low overpotential of 92 mV at a current density of 10 mA cm^{-2} and a Tafel slope of 42 mV dec^{-1} [35]. In the present thesis, we have demonstrated the high electrocatalytic performance of pristine $MoSe_2$ nanosheets, *in-situ* grown $MoSe_2$ over different substrates, and Ni-decorated $MoSe_2$ nanocomposites based electrodes for HER activity.

1.5.2 $MoSe_2$ for OER

The OER plays a pivotal role in various energy conversion and storage devices. Electrolyzer devices split water into hydrogen and oxygen using electrical energy. The OER occurs at the anode, where water molecules are oxidized to release oxygen gas. OER in metal–air batteries (such as zinc-air or lithium-air batteries), the OER takes place during the discharge process. Oxygen is generated at the cathode, combining with metal ions to form metal oxides. OER is essential for converting stored chemical energy back into electrical energy. The sluggish kinetics of the OER hinder its efficiency. Catalysts must accelerate the reaction while maintaining stability. In alkaline electrolytes, the overall reaction for OER is:

$$4OH^- \rightarrow O_2 + H_2O + 4e^- \quad (1.2)$$

Literature Review on Electrocatalysts for OER

Noble metals like RuO_2 and IrO_2 exhibit exceptional OER activity in the basic electrolytes. However, their scarcity and high cost hinder widespread adoption. Researchers continue to address challenges, seeking opportunities to improve catalyst efficiency. Perspectives include novel materials, surface modifications, and tailored nanostructures. Among various energy conversion processes, the OER stands out as a crucial step in water splitting, fuel cells, and metal-air batteries. Several classes of non-precious metal catalysts have garnered attention, such as carbon-based nanostructures, transition metal oxides, transition metal phosphides, transition metal nitrides, TMDs, and metal oxides have been investigated for OER [36-38]. Researchers around the world are developing new, less expensive electrocatalysts with faster kinetics, such as carbon, transition metal dichalcogenides (TMDs), and transition metal (Fe, Co, Ni, Mn) oxides nanostructures. Metal oxides such as Co_3O_4, MnO_2, $NiCo_2O_4$ and others are promising materials for OER due to their high electrocatalytic activity, low cost, non-toxicity, abundance and stability in a variety of environments, including high temperatures and harsh chemicals [39-44]. TMDs can be considered good electrocatalysts due to their fascinating properties like good conductivity and high surface area, which can show enhanced activity by site doping, control of growth morphology, and heterostructure formation. Shen *et al.* have synthesized Co-1–Ni-0.5/NC which showed the HER overpotential of 179 mV and Tafel slope of 110 mV dec^{-1} indicating superior electrocatalytic reactive kinetics [45]. Duan *et al.* has synthesized porous C_3N_4 nanolayers@N-Graphene films as highly efficient electrocatalyst electrodes for OER. It showed overpotential of 80 mV at current density of 10 mA cm^{-2} and Tafel slope of 49.1 mV dec^{-1} [46]. Thi *et al.* present a bifunctional electrocatalyst for OER, which is composed of single-atom co-decorated MoS_2 nanosheets assembled on titanium nitride nanorods. They have shown the overpotential ~340 mV and Tafel slope ~340 mV and 81.2 mV dec^{-1} for OER [47]. Upadhyay *et al.* reported that $MoSe_2$ with optimal Se content show a overpotential of 320 mV at current density of 10 mA cm^{-2} with a low Tafel slope of 45.3 mV dec^{-1} [48]. Zheng *et al.* reported that $MoSe_2$/NG-4 composite as an efficient catalyst for HER. The $MoSe_2$/NG-4 composite shows a low overpotential of 120 mV at 10 mA cm^{-2} and a Tafel slope of 69 mV dec^{-1} for HER. The excellent performance is attributed to the synergy between nitrogen doping, graphene's conductivity, and abundant active sites [49]. In the present thesis, we have demonstrated the high electrocatalytic performance of pristine $MoSe_2$ nanosheets, *in-situ* grown $MoSe_2$ over different substrate, bimetal oxides ($NiFe_2O_4$, $CoFe_2O_4$, $NiCo_2O_4$/NiO), Ni decorated $MoSe_2$ nanocomposites-based electrode for OER activity.

1.5.3 $MoSe_2$ for aqueous alkaline electrolyzer

Hydrogen is hailed as a promising energy carrier for a sustainable future. When produced using renewable energy sources, it becomes a clean and versatile option. Currently, less than 4% of hydrogen production relies on electrolysis processes, with most of derived from fossil fuels via steam reforming. Aqueous alkaline electrolysis offers a pathway to produce hydrogen sustainably, reducing dependence on fossil fuels. Alkaline water electrolysis is crucial for large-scale hydrogen production. It provides a cost-effective and well-proven method for generating substantial volumes of low-carbon hydrogen. In aqueous alkaline electrolysis, water molecules are dissociated into hydrogen ions (H^+) and hydroxide ions (OH^-) at the cathode and anode, respectively.

Literature Review on aqueous alkaline electrolyzer

Electrocatalysts play a pivotal role in accelerating these reactions by lowering the activation energy required for the electrochemical processes. Bifunctional electrocatalysts are materials that can simultaneously catalyze both the HER and the OER during water electrolysis. The ideal bifunctional electrocatalyst should exhibit high activity, stability, and selectivity for both reactions while minimizing energy losses. Bifunctional electrocatalysts simplify the electrolyzer fabrication process, leading to more efficient hydrogen generation. Single material for both HER and OER (bifunctional catalysts) reduces the need for separate components, making the overall system more cost-effective. Researchers are exploring non-precious metal-based bifunctional catalysts to replace expensive electrocatalysts like Pt, RuO_2 and IrO_2. Nickel-based electrocatalysts are commonly used as non-noble metal electrocatalysts in alkaline water electrolysis. Nickel is abundant and cost-effective compared to noble metals like Pt. Despite being non-noble, Ni demonstrates decent catalytic activity for the HER and OER. Polymer based exchange membrane is another important component in alkaline electrolyzers. They separate the anode and cathode compartments while allowing OH^- ions to pass. Multiple investigations on TMDs based electrodes for overall electrochemical water splitting have been demonstrated in recent years [52-57]. Majumdar *et al.* have discussed a study on the development of a heterostructure catalyst for efficient overall water splitting. They introduce a heterostructure composed of molybdenum $MoSe_2$ and $NiCo_2Se_4$, exhibiting excellent catalytic performance (overpotential ~89 mV and Tafel slope ~ 65 mV dec^{-1}) for the HER. Further, Single atom iridium decoration over $MoSe_2$@$NiCo_2Se_4$ heterostructure enhances OER activity after electrochemical surface reconstruction. They have also investigated the electrolyzer performance using the $MoSe_2$@$NiCo_2Se_4$ as cathode and its Ir decorated counterpart as anode, showing the overpotential of 280 mV at a current density of 10 mA cm^{-2} [58]. Inta *et al.* discussed the performance of electrolyzer using a $Ni_{0.85}Se/MoSe_2$ interfacial structure as cathode for HER and $Ni_{0.75}Se$ as anode for OER. It shows a current density of 10 mA cm^{-2} at a cell potential of 1.7 V and high durability, indicating effective overall water splitting [59]. In the present thesis, we have demonstrated the performance of the electrolyzer using pristine $MoSe_2$ nanosheets, *in-situ* grown $MoSe_2$ over different substrate and Ni decorated $MoSe_2$ nanocomposites as electrodes.

1.5.4 $MoSe_2$ for zinc-air battery

Metal-air batteries have the potential to overcome the limitations of Li-ion batteries due to their economical and non-flammable nature. Among metal-air batteries, Zn-air batteries have theoretical energy density of 1353 Wh kg^{-1} and show experimental results around 1000 Wh kg^{-1} of energy density [60-63]. A zinc-air battery is a type of metal-air electrochemical cell powered by the oxidation of zinc with oxygen from the air. The reactions produce a theoretical voltage of 1.65 Volts, which is reduced to 1.35-1.4 V in available cells. These batteries have high energy densities and are relatively inexpensive to produce. The overall efficiency of the Zn-air battery is mainly determined by two critical reactions: oxygen reduction reaction (ORR) and OER. The ORR occurs at the air cathode during battery discharging, whereas OER occurs at the air cathode during battery charging. Platinum and Ruthenium-based electrocatalysts are preferred for ORR and OER, respectively, but have the limitation of high cost.

Literature review on Zn-air battery

Researchers around the world are developing new, less expensive electrocatalysts with faster kinetics, such as carbon, transition metal dichalcogenides (TMDs), and transition metal (Fe, Co, Ni, Mn) oxides nanostructures. Metal oxides such as Co_3O_4, MnO_2, $NiCo_2O_4$ and others are promising materials for Zn-air batteries due to their high electrocatalytic activity, low cost, non-toxicity, abundance and stability in a variety of environments, including high temperatures and harsh chemicals [39-44]. However, these materials suffer from low conductivity and poor oxygen mobility, which can limit their performance. TMDs can be considered to be good electrocatalysts due to their fascinating properties like good conductivity and high surface area, which can show enhanced activity by site doping, control of growth morphology, and heterostructure formation. To date, TMDs as electrocatalysts have not been sufficiently explored in air cathode for Zn-air batteries. Among the TMDs family, few studies have been reported on MoS_2 based electrocatalysts for rechargeable Zn-air batteries [64-66]. The MoS_2@Fe-N-C NSs shows 360 mV overpotential (η_{10}) for OER and its Zn-air battery shows specific capacity of 442 mAh $g^{-1}{}_{Zn}$ [64]. The Zn-air battery with heterolayered MoS_2/Graphene nanosheets shows specific energy density of 130 W h kg^{-1}, while $Co(Zn_{0.5})$@MoS_2/CC based Zn-air battery exhibits power density of 72.4 mW cm^{-2} [65, 67]. Ling *et al.* demonstrated Co_3O_4/WS_2 (η_{10}~ 330 mV) based Zn-air battery shows specific capacity of 830 mAh $g^{-1}{}_{Zn}$ [67, 68]. Liu *et al.* developed a facile strategy to directly grow cobalt nanoparticles embedded in N-doped carbon nanotube arrays (Co@NCNTAs) on carbon cloth substrates and showed high specific capacity of 368 mAh g^{-1} for flexible solid-state Zn-air battery at a current density of 2 mA cm^{-2} and power density of 38.6 mW cm^{-2} [69]. Wang *et al.* reported a tri-doped graphene with N, S, and P for better electrocatalytic oxygen reactions. The tri-doped graphene, as a cathode catalyst, provides a power density up to 225 mW cm^{-2} as well as good long-term charge-discharge durability for rechargeable Zn-air battery [70]. Challa *et al.* demonstrated MoS_2/graphene hybrid nanoplatelets as Zn-air battery cathode using bovine serum albumin (BSA) as an exfoliant for MoS_2 sheets to synthesize hybrid sample. They demonstrated flexible, and bioabsorbable/biodegradable Zn-air batteries with high open-circuit voltage of 1.4 V and energy density of 130 W h kg^{-1} [71]. As a durable electrocatalyst,

MoS_2@FeN-C nanosphere interfaced with single Fe atoms was investigated for wearable Zn-air battery, exhibiting remarkable deformation stability, high special capacity (442 mA h $g^{-1}{}_{Zn}$) and excellent power density (78 mW cm^{-2}) [72]. In spite of these efforts, the real potential of Zn-air batteries is yet to be explored so that theoretically expected energy density can be achieved. In the present thesis, we have demonstrated the performance of the Zinc-air battery using pristine $MoSe_2$ nanosheets and different metal oxides ($CoFe_2O_4$, $NiFe_2O_4$ and $NiCo_2O_4$/NiO) and their hybrid nanostructure with $MoSe_2$ as air cathode.

1.6 Scope and objectives of the present work

Given the increasing environmental concerns, there is a significant push within the scientific community to create sustainable and renewable energy devices to cater the escalating global energy needs. Hydrogen generation and Zinc-air batteries are potential solutions for energy generation and storage. $MoSe_2$ is a material of interest due to its unique properties, such as layered structure, high conductivity, large surface area, flexibility, and stability in acidic or basic environments. These properties make $MoSe_2$ nanostructures suitable for energy generation and storage applications. Pristine $MoSe_2$, hybrid nanostructure with different metal oxides ($CoFe_2O_4$-$MoSe_2$, $NiFe_2O_4$-$MoSe_2$ and $NiCo_2O_4$/NiO-$MoSe_2$) and Ni decorated $MoSe_2$ nanocomposites have highly active edge site, adjustable morphology, abundance, and cost-effectiveness, are suitable for HER and OER, electrodes for electrolyzer and zinc-air battery. The primary objectives of the current thesis work include-

- Successful synthesis and characterization of pristine $MoSe_2$, *in-situ* growth of $MoSe_2$ over different conducting substrate (Ni foam and conducting carbon paper), different metal oxides ($CoFe_2O_4$-$MoSe_2$, $NiFe_2O_4$-$MoSe_2$ and $NiCo_2O_4$/NiO-$MoSe_2$) and their hybrid nanostructure with $MoSe_2$ ($CoFe_2O_4$-$MoSe_2$, $NiFe_2O_4$-$MoSe_2$ and $NiCo_2O_4$/NiO-$MoSe_2$) using hydrothermal technique.

- Examination of the electrocatalytic behavior of prepared pristine $MoSe_2$, $MoSe_2$-Ni foam, $MoSe_2$-CCP and Ni-$MoSe_2$ nanocomposites for HER.
- Examination of the electrocatalytic behavior of prepared pristine $MoSe_2$, $MoSe_2$-Ni foam, $MoSe_2$-CCP and Ni-$MoSe_2$ nanocomposites, different metal oxides and their hybrid nanostructures ($CoFe_2O_4$-$MoSe_2$, $NiFe_2O_4$-$MoSe_2$ and $NiCo_2O_4$/NiO-$MoSe_2$) for OER.
- Indigenous design of electrolyzer and zinc-air cells.
- Performance study of electrolyzer using pristine $MoSe_2$, $MoSe_2$-Ni foam, $MoSe_2$-CCP and Ni-$MoSe_2$ nanocomposites.
- Performance study of zinc-air battery using prepared pristine $MoSe_2$, different metal oxides and their hybrid nanostructures ($CoFe_2O_4$-$MoSe_2$, $NiFe_2O_4$-$MoSe_2$ and $NiCo_2O_4$/NiO-$MoSe_2$) as air cathode.