# CHAPTER I

# INTRODUCTION

## 1.1 Background

The technological revolution has led to an increase in population, where the world population has exceeded seven billion and is expected to continue to increase (Lee, 2011). With the increase in world population, this means that global energy consumption will also increase. Fossil fuels are still the main energy source to meet rapid industrialization and population growth. More than three-quarters of global energy production is generated by fossil fuels (i.e. oil, gas, and coal) and the remainder is provided by nuclear and other non-conventional or renewable energy sources (Delgado et al., 2013). The main problem with fossil fuels is that they are limited, non-renewable, and are the main source of $CO_2$ emissions into the atmosphere (Delgado et al., 2013). Non-renewable fossil fuels are increasingly depleting due to limited resources and concern for the environment, requiring exploration of alternative energy sources (Ng et al., 2021). Apart from that, the use of fossil fuels is one of the causes of global warming.

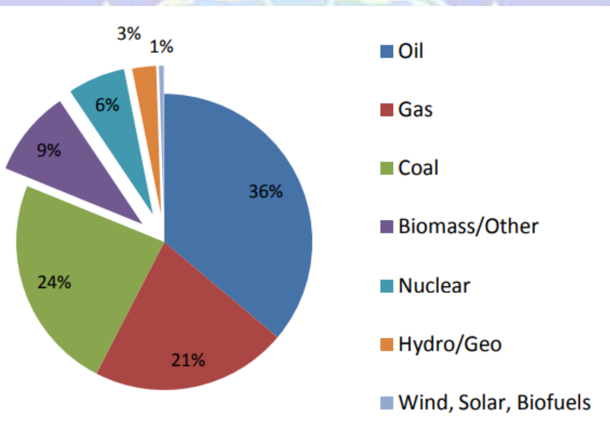

Figure 1. Classification of global energy

Therefore, it is crucial to analyze the trends in energy demand and develop strategies aimed to separate energy production from greenhouse gas emissions, using innovative materials and technological solutions essential for transitioning to eco-friendly energy systems (Gielen et al., 2016). Renewable energy sources, also known as alternative energy sources, tap into the Earth's natural systems, such as solar power, wind power, hydropower, and geothermal power (Cruden, 2005). Hydrogen, a widely available element found in the air, land, and water, offers a promising avenue as a clean and renewable energy source (Cruden, 2005). As a clean and renewable energy source, hydrogen (H2) holds promise for reducing greenhouse gas emissions, hydrogen is a fuel with enormous potential to meet the need for ecologically friendly energy sources. Moreover, hydrogen production from various energy sources, including renewables, underscores its versatility and potential as an energy carrier (Felseghi et al., 2019). Compared to other energy forms like electricity or heat, hydrogen offers the advantage of long-term storage capabilities, enhancing its appeal as an energy storage solution (Felseghi et al., 2019). Hydrogen is a chemical energy carrier capable of producing up to 39.39 kWh/kg of electricity, exceeding the energy density of most batteries (Manoharan et al., 2019). Hydrogen, being the most basic molecule, possesses the lowest energy density when measured by volume but boasts the highest energy density among all fuels when considering weight (Manoharan et al., 2019). It exists abundantly in the atmosphere in gaseous form and in liquid form within water, because of its remarkable energy content, hydrogen finds applications as a fuel in fuel cells and rocket propulsion systems (Manoharan et al., 2019). In contrast to fossil fuels, it does not produce harmful emissions, addressing a major drawback of traditional energy sources (Manoharan et al., 2019). Furthermore, the energy value of hydrogen exceeds that of petroleum by threefold, making it an attractive option for various industries and technologies (Manoharan et al., 2019).

Hydrogen holds significant potential for profitability across various sectors of the economy, serving as an industrial raw material, a fuel for automobiles, and an energy carrier in sustainable energy systems for generating electricity and heat through fuel cells (Felseghi et al., 2019). Leading car manufacturers like Honda, Toyota, and Hyundai have already embarked on producing fuel cell vehicles (FCVs) utilizing hydrogen as a primary fuel source (Manoharan et al., 2019). These FCVs are now available in markets across North America, Asia, and Europe, primarily attracting early adopters among consumers (Manoharan et al., 2019). These early adopters typically comprise highly educated individuals, affluent families, those with larger households, and individuals seeking lifestyle changes because of their interest in FCVs stems from a desire for innovative and environmentally friendly transportation solutions, reflecting a broader trend towards sustainable living (Manoharan et al., 2019).

One of the main problems facing hydrogen energy developers is the high cost of producing and storing hydrogen (Le et al., 2023). As a result, the current price of hydrogen fuel is still very high and less competitive than current conventional fuel (Le et al., 2023). Currently the focus of researchers is effective, efficient and environmentally friendly hydrogen production (Le et al., 2023). So it can produce hydrogen in large quantities and at low production costs (Le et al., 2023).

Electrochemical water splitting is increasingly recognized as a promising pathway for sustainable and eco-friendly hydrogen ($H_2$) production (Li et al., 2020). By utilizing various green energy systems to harvest and convert energy from the environment, water splitting offers an efficient way to minimize external power consumption. Among the environmentally friendly energy systems employed, water electrolysis with two electrodes stands out (Li et al., 2020). In the process of hydrogen production via electrochemical water splitting, there are several essential components play crucial roles, including the electrolyte, cathode, anode, and catalyst (Felseghi et al., 2019). This components work together to facilitate the activation and transformation of energy-related small molecules under ambient conditions. Electrochemical energy conversion systems offer a reliable solution for driving reactions like the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), these reactions are vital steps in the process of electrochemical water splitting, ultimately leading to the production of clean and sustainable hydrogen fuel (Wang et al., 2020).

Hydrogen and oxygen are fundamental elements that combine to produce water, the bond between hydrogen and oxygen is highly stable and requires a substantial input of energy to break (Cruden, 2005). However, once this bond is severed, hydrogen becomes a highly flammable gas. When hydrogen is burned, it recombines with oxygen in the air, producing water (Cruden, 2005). From a thermodynamic perspective, water splitting is an upward reaction and not spontaneous. It necessitates external energy input to drive the process because the reverse reaction occurs readily (Tee et al., 2017). Efficient water splitting requires materials capable of catalyzing both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) (Zou et al., 2018). In a standard electrochemical water splitting setup, these reactions occur separately: the OER takes place at the anode, while the HER occurs at the cathode (Zhou & Fan, 2020). However, the widespread implementation of commercial electrochemical water splitting for large-scale hydrogen production encounters significant challenges (Zhou & Fan, 2020).

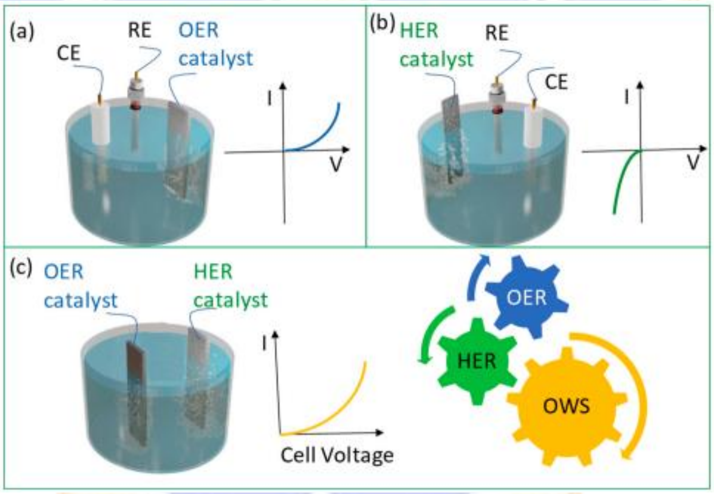

Figure 2. Electrochemical setup and the corresponding I-V polarization curve for (a) Oxygen Evolution Reaction, (b) Hydrogen Evolution Reaction, and (c) Corresponding full cell.

In addition, the process of splitting hydrogen and oxygen atoms requires more energy than can be obtained from burning hydrogen itself, so it requires an energy source that is abundant and does not damage the environment which can break down water molecules (Cruden, 2005). The ideal bifunctional electrocatalyst for water splitting should be cost-effective, highly active, and employ an economical preparation method, while also provide long-term stability for both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) in the electrolyte (Li et al., 2020).

The development of highly efficient and cost-effective catalyst electrodes for water splitting reactions is crucial, given that noble metals currently possess the highest intrinsic activity for both hydrogen evolution reactions (HER) and oxygen evolution reactions (OER) (Zou et al., 2018). However, the use of precious metals as electrocatalysts is associated with high costs and limited availability. Therefore, there is a pressing need for non-precious electrocatalyst materials for HER and OER, particularly those based on transition metals such as molybdenum, tungsten, cobalt, nickel, and iron (Zou et al., 2018). Among these transition metals, iron offers significant advantages over noble metals and even other transition metals. Firstly, iron is one of the most abundant metals on Earth, ensuring a stable and ample supply. Second, iron is comparatively more affordable than noble metals, making it a cost-effective option for large-scale applications. Third, iron is relatively less toxic, and iron-based catalysts are known to effectively facilitate several essential biological processes in nature (Zou et al., 2018). These attributes highlight iron-based catalysts as promising candidates for control water splitting reactions, offering both economic and environmental benefits.

Transition metal compounds are promising alternative catalysts for alkaline water electrolysis, due to their excellent performance, cost efficiency, structural diversity and when synthesized they act as binder-free electrodes (Zhang et al., 2019). Sulfide-based compounds show promise in water splitting due to their high electronic conductivity (Zhang et al., 2019). Iron-based sulfides, including FeS, $FeS_2$, and $Fe_3S_4$, have great applications in electrochemistry and catalytics (Pan et al., 2019). Based on this, it is considered to develop active Fe-based electrocatalytic materials, especially Fe-S-based catalysts for general water splitting and using nickel foam as a substrate.  Nickel foam (NF) is a cheap commercial material with high electronic and ionic conductivity, making it an excellent electrode material

(Ding et al., 2018). The maximum amount of interaction between the electrolyte material and the electrode is achieved by its three-dimensional open porous structure (Gadisa et al., 2021)..

One method that can be used to develop Fe-S based catalysts is Hydrothermal. Hydrothermal synthesis method for the preparation of 2DMs offers several advantages such as low cost, easy experimental set up, and high yield (Senapati & Maiti, 2020). The hydrothermal method utilizes wet-chemical techniques to crystallize materials into nanostructures (Dahiya et al., 2018). This approach involves coating particles through hydrothermal synthesis, aiming to enhance their characteristics or introduce new functionalities to the substrate particle (Dahiya et al., 2018). In addition to offering precise control over material characteristics and stoichiometry, hydrothermal synthesis provides several significant advantages. These advantages include (Suvaci & Özel, 2021): (1) Operating at low synthesis temperatures: Hydrothermal synthesis can be conducted at relatively low temperatures, reducing energy consumption and minimizing thermal stress on materials. (2) Facilitating fast and flexible continuous or batch processing: Hydrothermal synthesis allows for efficient and adaptable processing methods, whether in continuous or batch operations, enabling flexibility in production. (3) The scalability of hydrothermal synthesis makes it suitable for industrial-scale production, ensuring mass production of materials with consistent quality. (4) Leading to cleaner and more environmentally friendly processing routes. (5) Eliminates the need for energy-intensive processes such as high-temperature calcination and milling, reducing overall energy consumption. On the other hand, liquid-based methods excel in enhancing control over the thermodynamics and kinetics involved in nucleation and growth processes (Suvaci & Özel, 2021). By adjusting parameters such as temperature, reactant concentration, duration of crystal growth, and the incorporation of additives, these methods allow for the growth of particles with diverse morphologies (Suvaci & Özel, 2021).

In previous research, iron-based sulfidation was studied as a catalyst for water splitting. In research conducted by Hui Li and colleagues (2022) entitled Chrysanthemum-like $FeS/Ni_3S_2$ heterostructure nanoarray as a robust bifunctional electrocatalyst for overall water splitting, successfully fabricated a chrysanthemum-like FeS/Ni3S2@NF heterogeneous structure using a straightforward one-step hydrothermal method. They induced etching on the surface of nickel foam by employing thioacetamide. The resulting composite electrocatalyst exhibited outstanding performance in electrocatalytic water splitting (Li et al., 2021). Under 1.0 M KOH alkali solution, the composite electrocatalyst demonstrated low overpotentials of 192 mV and 130 mV to achieve current densities of 10 $mA/cm^2$ and 10 $mA/cm^2$, respectively (Li et al., 2021). Moreover, a dual electrode device fabricated using the FeS/Ni3S2@NF nanoflower array catalyst achieved a current density of $mA/cm^2$with a voltage of only 1.51 V, showcasing excellent stability over 50 hours of operation (Li et al., 2021). Apart from that, in research conducted by Eric A. Runge and colleagues (2023) entitled Sulfidation of nano-magnetite to pyrite: Implications for interpreting paleoenvironmental proxies and biosignature records in hydrothermal sulfide deposits, synthetic nano-magnetite was subjected to incubation in anoxic artificial seawater with a sulfide:Fe ratio of 4:1, at varying pH levels (7, 10), and temperatures ranging from 20 to 80 degrees Celsius. After 46 days, nanomagnetite was only observed at 20 degrees Celsius and pH around 10 and at pH around 10 with temperatures equal to or greater than 20 degrees Celsius, mackinawite and greigite containing Fe(III) were formed. At pH around 7 and 80 degrees Celsius, magnetite underwent conversion to pyrite within just 19 days, a process accelerated by the presence of polysulfides generated from sulfide-mediated reduction of Fe(III), particularly in the presence of $S_0$ (Runge et al., 2023). These findings indicate a potential bias favoring nano-magnetite in sulfide hydrothermal environments and suggest that the interpretation of pyrite-related paleoenvironmental indicators and microbial biosignatures related to Fe and

S cycling in hydrothermal deposits may be influenced by interactions between diagenetic fluids and minerals (Runge et al., 2023).

In this research, sulfidation of iron based nanomaterials was carried out using a multipurpose hydrothermal method that is simple, easy to operate and fast to directly synthesize iron sulfide - iron hydroxide composite materials on nickel foam ($Fe_xS_y$ /$Fe(OH)_2$ @NF) by varying the concentration of Sodium Sulfide Nonahydrate. Then material analysis was carried out to determine the morphology of ($Fe_xS_y$ /$Fe(OH)_2$ @NF) and electrochemical tests to determine the electrocatalytic activity of ($Fe_xS_y$ /$Fe(OH)_2$ @NF) as a catalyst for water splitting.

## 1.2 Problem Limitation

The limitation is important because it underscores the synthesis methods and characterization techniques used in this study. In this research using hydrothermal method and characterization techniques including XRD and FE SEM will provide comprehensive insight into the properties of the $Fe_xS_y$ nanoparticles produced. Apart from that, there are electrochemical tests to determine the characteristics of $Fe_xS_y$ produced as a catalyst in water splitting. All these limitations support the achievement of effective and relevant research objectives.

## 1.3 Problem Formulation

Based on the background presented, the following problem formulation can be summarized as follows.

1.3.1 How is the synthesis of nanomaterials $Fe_xS_y$ using hydrothermal method?

1.3.2 How is the characterization of $Fe_xS_y$ nanomaterials as a catalyst for water splitting in general?

1.3.3 How is the performance of the electrocatalytic activity of $Fe_xS_y$ as a water splitting catalyst in general?

## 1.4 Hypothesis

The sulfidation process of iron-based nanomaterials through a hydrothermal method, varying the concentration of Sodium Sulfide Nonahydrate, will result in ($Fe_xS_y$ /$Fe(OH)_2$ @NF) composite materials exhibiting enhanced electrocatalytic activity for water splitting.

## 1.5 Aims of Research

Based on the problem formulations outlined, the objectives to be achieved in this research are as follows.

1.5.1 To understand the synthesis of nanomaterials $Fe_xS_y$ using hydrothermal method

1.5.2 To investigate the characterization of $Fe_xS_y$ nanomaterials as a catalyst for water splitting in general

## 1.6 Significance of study

Through this research, the author hopes to provide benefits both theoretically and practically, which are described as follows.

1.6.1 Theoretically, this research has significant potential to cover various aspects of nanoparticle characterization, especially $Fe_xS_y$ particles. Using hydrothermal method opens up new opportunities in the exploration of nanoscale materials with broad applications in various fields of science and industry. In the context of further research development, the findings from this research can become a basis for further research which may involve increasing synthesis efficiency as well as varying other factors such as temperature or pressure to obtain better results.

1.6.2 From a practical perspective, the results of this research have the potential to have a direct impact on technological and industrial developments. The use of $Fe_xS_y$ particles can be used in water splitting, namely Hydrogen evolution reaction (HER) and Oxygen evolution reaction (OER). This has the potential to develop renewable energy which can overcome the energy crisis, replace fossil fuels and global warming.