CHAPTER - 1

INTRODUCTION

The energy demand has recently increased considerably due to increased population around the world. The energy demands in the various sectors like domestic, industrial and automobiles are fulfilled by traditional/conventional energy resources like energies such as crude oil, coal, natural gas, and so on (Choudhary and Pramanik 2020a; Singh and Pramanik 2012). Thus, consumption rate of conventional energy resources have gone up tremendously. However, the limited supply of conventional energy resources e.g., crude oil, coal and natural gas along with pollution problem are the main reason to think over alternative energy resources. The energy infrastructure is a vital component for a country's economy and economic growth. In general, two forms of energy, (i) thermal energy and (ii) electrical energy, are widely employed around the world. The creation of necessary electrical infrastructure is critical to the Indian economy in long-term prosperity. The energy demand is rising in together with economic activity. The energy demand of India is increased by roughly 4.1% over the last decade, and it is expected to climb by 6% per year over the next decade (CEA, 2022). To accommodate the rising demand for electricity, the power sector of India has expanded significantly. According to the central electricity authority (CEA, 2022), the government of India, coal is used in the highest amount for electricity generation (51 %), followed by natural gas (6 %), petroleum (0.0012 %), renewable energy (39 %), lignite (2 %) and nuclear energy (2 %). The total installed capacity of renewable electrical energy is made up of small hydro plants (3 %), bio-Power (7 %), wind (26 %), solar (34 %), and large hydro plants (30 %). As alternative the energy demand in the domestic and industrial sectors are met by conventional energy resources like, crude oil, coal, natural gas etc. However, the availability of fossil fuels (coal, natural gas, petroleum and nuclear energy) are limited, and they are also the main cause to air pollution by emitting harmful pollutant gases like CO_2, SOx, and NOx. The burning of fossil fuels are also responsible for global warming because emission of CO_2 and other gases (chlorofluorocarbons), which caused the heat-trapping in environment due to this earth temperature gradually increases with time. In nuclear energy production accidental leakage of radioactive rays is one of the main danger to human life, while transportation of nuclear fuel to a nuclear power plant can cause pollution to environment. It was found that nonrenewable energies are very costly and its use is also harmful for human health as well as environment. Renewable energy sources have a lot of advantages, but there are also certain drawbacks that need to be taken into account. The fluctuating supply of renewable energy is a serious disadvantage. When compared to wind power, which depends on wind speed, solar power depends on sunlight availability. It may be difficult to regularly match supply and demand because of this random nature. Batteries and various other energy storage technologies are being developed to address this problem, but they are currently very expensive and have capacity restrictions. Most renewable energy systems need considerable investments in land and resources. Large-scale wind and solar farms need a lot of land, which raises the cost of initial installation. Hydropower is one of several renewable energy sources that can have an impact on rivers and aquatic ecosystems. The initial cost of installing infrastructure for renewable energy sources can still be rather substantial. The main problem with biomass is its high moisture content, which complicates both pre-treatment and conversion procedures. When compared to traditional fossil fuels, renewable energy sources like wind and solar have substantially lower energy densities. Solar panels and wind turbines are two examples of renewable energy technologies that are produced through the extraction of raw materials and manufacturing procedures that may have an adverse effect on the environment.

Additionally, certain parts of outdated or damaged equipment include dangerous compounds that need to be handled carefully and recycled, making disposal a task. It can be necessary to improve and modify current infrastructure significantly in order to integrate renewable energy into power systems. Due to the intermittent nature of renewable energy sources, a strong and adaptable grid system that can manage, the changes in supply and demand is necessary. These improvements might be time and money consuming. The overall amount of renewable energy from wind, water, and the sun will continue to rise, but due to their irregular availability, these sources are unsuitable for supplying the electrical energy base requirement. However, the main reason to consider alternative energy-producing technologies like fuel cells is the limited supply of conventional energy supplies, such as crude oil and coal, and the inconsistent availability of renewable energy. A fuel cell directly transforms the chemical energy of a fuel into electrical energy. Fuel cells are silent, portable and a source of clean energy. Hydrogen fuel-based fuel cell don't emit any harmful pollutants like SO_X and NO_X. As a result of their high theoretical efficiency and low level of pollution, fuel cells have been gaining attention (Pramanik and Rathoure 2017). The development of fuel cells as energy conversion devices began in the middle of the 19th century in 1839 (Bossel 2000; Larminie and Dicks 2003). Sir William Grove developed the fuel cells as an electrical energy conversion technology, however Christian Friedrich Schonbein actually found the basic idea (Carrette et al., 2001). The fuel cells are one of the oldest electrical energy conversion technologies known to man. As a result of the growing popularity of electricity at the beginning of the twentieth century, the conversion of chemical energy into electrical energy became more significant. The electrical energy conversion systems were first presented as small dispersed power generators, but subsequent advances resulted in megawatt-scale centralized plants. The need to enhance the flexibility of electricity generating, as well as the increase in population of world, have led to a growing interest in the creation of more powerful and more evenly distributed power generation during the previous decade. Fuel cells use pure hydrogen to generate electricity and only produce water as a byproduct, reducing our dependence on fossil fuels and preventing the release of any harmful gases. The free energy of a chemical process is turned into electrical energy through a fuel cells, which are galvanic cells. The cell voltage and a chemical reaction's change in Gibbs free energy. The cell voltage and the Gibbs free energy change of a chemical reaction are connected via Equation 1.1.

$$\Delta G = - nFE_0 \tag{1.1}$$

Where E_0 is the voltage of the cell for thermodynamic equilibrium in the absence of a current flow, n is the number of electrons involved in the reaction, F is the Faraday's charge constant.

A fuel cell consists of two electrodes sandwiched around an electrolyte. The oxidant oxygen passes over one electrode (cathode) and hydrogen or hydrogen rich molecule fuels over the other electrode (anode), generating electricity, water and heat as shown in Figure 1.1. The hydrogen gas ionizes at the anode of fuel cell, releasing electrons and producing H^+ ions (Equation 1.2). Water is formed when oxygen combines with electrons and H^+ ions from the electrolyte at the cathode (equation 1.3). It is clear that in order to continue these reactions (Equation 1.1 to Equation 1.2), the electrons created at the anode must travel to the cathode via an electrical circuit. The electrolyte must also permit the passage of H^+ ions from anode to cathode.

Anode Reaction:

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{1.2}$$

Cathode Reaction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{1.3}$$

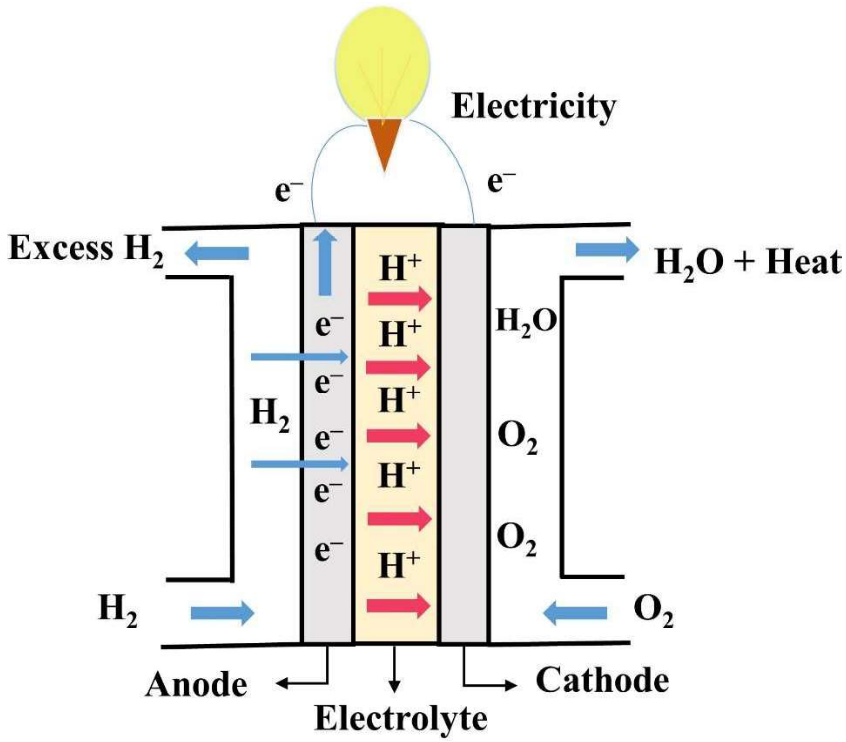

Figure 1.1 Hydrogen/oxygen fuel cell and its reactions based on the proton exchange membrane.

The anode and cathode electrodes, as well as an electrolyte, are present in every fuel cell. Different electrolytes and electrodes are used in fuel cells, and different temperatures are used for different electrochemical processes. Because of this, each type of fuel cell (or fuel cell technology) has unique advantages and disadvantages, and making it better suited for particular markets and applications. The hydrogen fuel-based low temperature fuel cells gaining attention due to their flexibility to choose electrolyte material like Nafion® as proton exchange membrane (PEM), alkaline solution KOH and phosphoric acid, etc (Choi et al., 2021). The proton exchange membrane fuel cells (PEMFC) are mostly used as a source of energy for a wide range of commercial or industrial applications (Rodriguez et al., 2021; shroti and Daletou 2022). The low temperature fuel cell has high power at relatively low temperatures of 30-100 ^{o}C in comparison to other types without emitting any harmful emissions. High energy density and low operating temperature make the PEMFC more reliable for future energy requirements over fossil fuel-based energy devices. Moreover, fossil fuels storage is limited and they are gradually decreasing as the energy demand is increasing day by day. The hydrogen based PEMFC is considered as an alternative to fossil fuels for future energy generation (Rodriguez et al., 2021). The PEMFC is similar to any sort of battery in which anode, cathode and electrolyte/PEM form a sandwich having electrolyte in between anode and cathode (Termpornvithit et al., 2012). The fuel hydrogen is fed at the anode and oxidant oxygen/air at the cathode irrespective of the type of electrolyte used in various types of low temperature fuel cells.

However, fuel cells suffer from different types of losses/polarization viz activation losses, ohmic losses and concentration losses. Activation polarization is due to the slow electrochemical reactions at the electrode surface, where the species are oxidized or reduced in a fuel cell electrode reaction. Activation polarization is directly related to the rate at which the fuel or the oxidant is oxidized or reduced (Tayal et al., 2012). This loss in potential, switch over the fuel cell reaction reversible to irreversible and it predominates at the start of fuel cell. The origin of ohmic polarization comes from the resistance to the flow of ions in the electrolyte and flow of electrons through the electrodes and the external electrical circuit (Srinivasan 2006). The concentration losses occur over the entire range of current density. However, these losses become prominent at high limiting currents where it becomes difficult for gas reactant flow to reach the fuel cell reaction sites. Several factors are responsible for the concentration polarization. The main reason for concentration polarization is the resistance to the mass transfer from outer surface (bulk) of gas diffusion layer (GDL) to electrocatalyst sites and it predominates at high current density. Among, these three types of major polarization in fuel cells, activation loss is the important one. As, literature suggest that faster electrode kinetics of fuel cell improves current density which in return gives high power density at low activation loss. Thus, fabrication of fuel cell electrode and its micro structure is an important aspect. The performance of electrode could be enhanced by synthesizing a suitable bimetallic alloy electrocatalyst.

It is seen in literature that the cathode activation loss is higher than the anode activation loss for low temperature fuel cell in acidic medium. It is well known through various studies reported in the literature that anode electrooxidation of H_2 fuel in presence of Pt based electrocatalyst is faster in acidic medium/PEM in comparison to oxygen reduction at the cathode (Wang et al., 2008). Thus, slow reduction kinetics at cathode on single metal Pt-based electrocatalyst for PEMFC is one of the many challenges like proton conductivity problem at elevated temperature (T) > 80 ^{o}C, high activation loss and high cost of pure Pt-based electrocatalyst.

The oxygen reduction at the cathode of a PEMFC proceeds through either 2 step 4 electron mechanism (Equation 1.4 to Equation 1.7) or a single step 4 electron mechanism as is given below Equation (1.8).

$$O_2 + Pt \rightarrow Pt - O_2 \quad (1.4)$$

$$Pt - O_2 + H^+ + e^- \rightarrow Pt - HO_2 \quad (1.5)$$

$$Pt - HO_2 + Pt \rightarrow Pt - OH + Pt - O \quad (1.6)$$

$$Pt - OH + Pt - O + 3H^+ + 3e^- \rightarrow 2Pt + 2H_2O \quad (1.7)$$

Or

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1.8)$$

The ORR mechanism via 2 steps 4 electron path indicates that chemisorption of oxygen takes place in the first step (Equation 1.5) which further proceeds and at the end, only water molecule is produced as a byproduct on the cathode (Equation 1.7) (Bard et al., 2022; Arico et al., 2001; Xiong et al., 2018). Apart from slow reduction kinetics at the cathode of a PEMFC, activation loss also contributes to voltage loss when current is drawn from the cell ($i > 0$). Thus, developing an efficient cathode electrocatalyst could positively improve cell performance in term of voltage and current density. Till date noble metal Pt-based electrocatalyst is widely used at fuel cell cathode for ORR (Pramanik et al., 2017). Presently, researchers are working tremendously to develop a highly efficient bimetallic cathode electrocatalyst that could reduce the consumption of expensive platinum (Pt), reduce activation loss/overpotential, and improves current density to a few fold higher than the existing one. All these improvements intern would give higher power output from a single PEMFC or stack at a low cost.

The cost of a fuel cell depends on the individual cell components like anode electrocatalyst, cathode electrocatalyst, membrane electrolyte, gas diffusion layers, and current collectors/flow channels. Thus, reduction of cathode electrocatalyst cost by adding other non-noble metals Co, Ni, Cr, and W to Pt when developing bimetallic electrocatalysts for oxygen reduction reaction (ORR) at PEMFC cathode, would undoubtedly reduce the total fabrication cost of the fuel cell. Most of the published literature shows that noble metals like Pt, Pd, and Ru are considered as suitable electrocatalyst for ORR at the cathode side of a low temperature fuel cells (Rodriguez et al., 2021; Shroti and Daletou 2022; Termpornvithit et al; Balbuena et al., 2012; Chaisubanan et al., 2015). The cathodic properties of noble metals mainly depend upon their crystallite size, shape, and electronic configuration. The catalytic activity of Pt is the best among all noble metals which are often used in ORR of a low temperature PEMFC. The electrocatalytic performance of Pt based nano-crystals strictly depends upon their morphology due to the exposed surface which has distinct crystallite planes according to their size and shapes (Guo et al., 2013; Chen et al., 2009; Peng and Yang 2009). Antolini et al., (2005) reported that the activity of electrocatalysts supported by Pt alloy is increased when Pt-Pt bond distance got decreased. Paffett et al., (1988) reported the dissolution of more oxidizable Pt alloying and its change in surface structure improve the activity of Pt based ORR electrocatalysts. Thus, many such works on the synthesis of bimetallic alloy electrocatalysts like Pi-Co, Pt-Ni, Pt-Cr, have been reported in the open literature. Peng et al., (2009) explained that the addition of a transition metal to Pt not only enhanced kinetics but also provided the electrocatalyst with the proper crystallite phase and composition, allowing for optimal atomic arrangements.

Although various efforts have been made to synthesize suitable Pt based bimetallic electrocatalysts, the effect of various types of solvents has never been studied earlier for catalyst synthesis in any research works. It should be noted that solvent also plays a key role in synthesizing highly active electrocatalysts by acting as an agent in the preparation of highly active core-shell electrocatalysts and controlling the size of synthesized particles and shape as well. The reaction equilibrium, reaction kinetics, and products all could be significantly altered by the interactions of solvents with reactants, intermediates, and products. The interaction of solvents with nanoparticles or their decomposition products can function as structural modulators. The solvent effects are influenced by the solvent's polarity, dielectric constants, and viscosity (Demazeau 2010). The compatibility of dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), ethylene glycol (EG) and water (W) with common reactants has led to their frequent usage as solvents. The main purpose of present study is to find out the best solvent for synthesis of most active and efficient cathode electrocatalysts which could enhance the performance of a PEMFC. Thus, the commonly used solvents as referred in the various literatures were selected as solvents in the present study. It should be noted that there is no such research work on comparative study on solvents for electrocatalyst synthesis. Most of the research work used single solvent like EG or DMSO or DMF or water as solvent for the electrocatalyst synthesis in their study (Khan et al., 2022; Chen et al., 2017a; Chaudhary and Pramanik 2022). It is very difficult to compare the effect of solvents in electrocatalysts synthesis by comparing the performance of electrocatalyst reported in various reported published literature, as the synthesis method or metals types or electrocatalysts supports always differ from each other in the reported research works. Thus, undoubtedly this present research work will enable to understand the effect of various solvents in bimetallic Pt-M cathode electrocatalyst synthesis for same catalyst support, metal composition with same concentration in all the four synthesized electrocatalysts. Moreover, the merits and demerits of the proposed solvents are also important factors before it is used for catalysts synthesis. It is seen from the thorough literature survey that EG has several important properties over other solvents such like DMSO and DMF and water. It is fact that EG is less expensive and less harmful than other organic solvents. The EG has also been used extensively as a solvent and reducing agent, since it contains hydroxyl groups with reducing properties (Lai et al., 2015b). The several important properties of EG facilitates the formation of electrocatalysts of better quality. The other three solvents DMSO, DMF and water have some merit and demerits. The DMSO is often utilised as a solvent in the production of numerous organic and inorganic compounds (Tashrifi et al., 2020) However, a major problem of DMSO is strong pungent odour which causes nausea. Similarly, the DMF is an organic solvent with a broad solubility range for both organic and inorganic molecules and may be used as an alternative solvent (Lai et al., 2015b). The demerits of DMF is fishy or ammonia like odour, hazardous in nature, long-term exposure may damage the liver, kidneys and causes headache, dizziness. Water (W) as solvent provides many benefits e.g., with increase in temperature - (i) ion product increases (ii) viscosity decreases, high polarity, natural resource so easily available therefore cheap in cost (Lai et al., 2015b and Demazeau 2010). The demerits of water is high critical point, lower yield of water insoluble bio-oil. In contrary, EG has no any harmful effect on human health for handing, no odour problem and not even hazardous in nature. Thus, EG could be preferred as solvent over DMSO, DMF, and W, respectively. To recommend ethylene glycol (EG) as best solvent, a thorough studies is required, however, no such detailed studies on the synthesis of cathode electrocatalysts using various types of solvents and thorough characterization of the synthesized electrocatalysts followed by testing in half-cell and single cell PEMFC have been reported to date. In this perspective, bimetallic Pt-M/C_{AB} (M = Co, Ni) electrocatalysts were synthesized in the laboratory using various types of solvents for effective ORR in hydrogen based PEMFC. Four different types of solvents namely dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), ethylene glycol (EG) and water (W) were used for the synthesis of three different types of bimetallic cathode electrocatalysts e.g., Pt-Co/C_{AB}-DMSO, Pt-Co/C_{AB}-DMF, Pt-Co/C_{AB}-EG and Pt-Co/C_{AB}-W via solvothermal process maintaining the synthesizing temperature very close to their boiling temperature. Among all four solvents, ethylene glycol (EG) based solvothermal process produced highly efficient active cathode electrocatalyst Pt-Co/C_{AB}-EG which exhibited the best performance for ORR in half-cell and single PEMFC.

In the chapter 1, the present energy generation scenario and its disadvantages with alternative sources to meet the current requirements using PEMFC technology are comprehensively examined. Chapter 2 discussed a thorough literature review including membrane electrolyte, electrode materials, different characterization techniques of cathode electrocatalyst, performance of a single PEMFC with different type of cathode electrocatalysts, and in the end thesis objectives on the basis of detailed literature review. Chapter 3 provides information on the materials used in the experiment as well as experimental details to perform proton exchange membrane fuel cell based on hydrogen fuel, the synthesis of cathode electrocatalyst, the physical and electrochemical characterization of synthesized electrocatalyst, the fabrication of electrodes, and single cell performance. In Chapter 4, the response surface methodology was discussed to optimized operating parameters of the PEMFC to obtain maximum power density. The results and discussion in Chapter 5 are based on the physical characterization of the synthesized cathode electrocatalyst using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM), while electrochemical characterization was carried out using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Using polarization and power density curves, the outcomes of single PEMFC investigations are discussed. Using RSM, process parameters are optimized, and the outcomes are thoroughly examined with experimental results at optimum and random condition of process parameters, and stability test also discussed in the end of this chapter. Finally, Chapter 6 provides a summary of the thesis with key findings and conclusion as well as some significant suggestions for additional research in this field. At the end of thesis references and appendices are presented.