CHAPTER 1

INTRODUCTION

At present, the production of energy mainly depends on limited resources of fossil fuels that were formed millions of years ago (Lazkano et al., 2017). The depletion of these fossil fuels is larger than its formation by natural processes (Capell et al., 2014). However, the major amount of energy is utilized in the form of electrical energy nowadays (EIA, 2019). According to the United States of America's energy information administration, this electrical energy is primarily harnessed from various sources like coal (25 %), natural gas/oils (37 %) and wind/solar energy (11 %) (EIA, 2019). Other routes include nuclear power of about 13 % and hydropower of about 7 % of the total electrical energy produced (EIA, 2019). The power generation statistics as reported by ministry of power, government of India, shows that coal has the largest share of 54.3 % in electricity generation followed by renewable energy sources (22 %), hydropower (12.7 %), gas (7 %), nuclear (1.9 %), lignite (1.7 %) and oil (0.2 %) (CEA, 2019). The combustion of coal and other fossil fuels release a large number of pollutants to our environments, e.g., CO_2, SOx, NOx, etc (Munawer 2018). Nuclear plants are very hazardous to health and environment if there is any accident (Thomas 2017). Solar electrical energy via solar photovoltaic cell (SPV) is expensive and problem of getting solar radiation round the year due to climate change. Availability of steady wind velocity is the major problem of wind energy. Thus, there is an immediate energy threat to our coming generations. To combat this problem, there is a need of an alternative energy source that is sustainable, pollution free, low cost, easily accessible and does not depend on the use of fossil fuels (Saez – Martinez et al., 2016). This need has led to an increasing trend in research and development on new energy devices such as fuel cells (Pramanik et al., 2007, Baik et al., 2018, Li et al., 2016 and Haneda et al., 2017). The fuel cells have gained considerable attention as a clean energy conversion device for powering portable equipments and automobiles (Pramanik et al., 2008). In addition, fuel cells are efficient, durable, silent system as it has no moving parts and no pollution or less pollution e.g., fuel cells operated with H_2 and O_2 produce electricity, and only water as byproduct. Thus, it is needless to say that fuel cells hold a bright future for energy production due to its advancement in science and technology with a large number of economical and environmental benefits (Andújar and Segura 2009 and Kirubakaran et al., 2009).

The fuel cells are electrochemical device that directly convert the chemical energy of supplied fuel into electrical energy and heat by redox reaction in the presence of electrocatalyst (Alleau and Barbier 2001). A typical schematic of alkaline direct alcohol fuel cell is shown in Fig (1). Fuel cells consist of an electrolyte medium sandwiched between anode and cathode. The fuels mostly hydrogen or hydrogen rich molecules is delivered to the anode side, and the oxidant is delivered to the cathode side. The electrons generated at the anode due to electrooxidation of fuels are transferred to the cathode through the external circuit, and hence the electricity is generated. Ions generated as a result of electrooxidation or reduction reaction are transported from one electrode to the other electrode through the ionically conducting electrolyte. In a typical alkaline fuel cell hydroxide (OH^-) ions move from cathode to the anode side. The fuel and oxidant streams do not mix with each other at any point in the fuel cell.

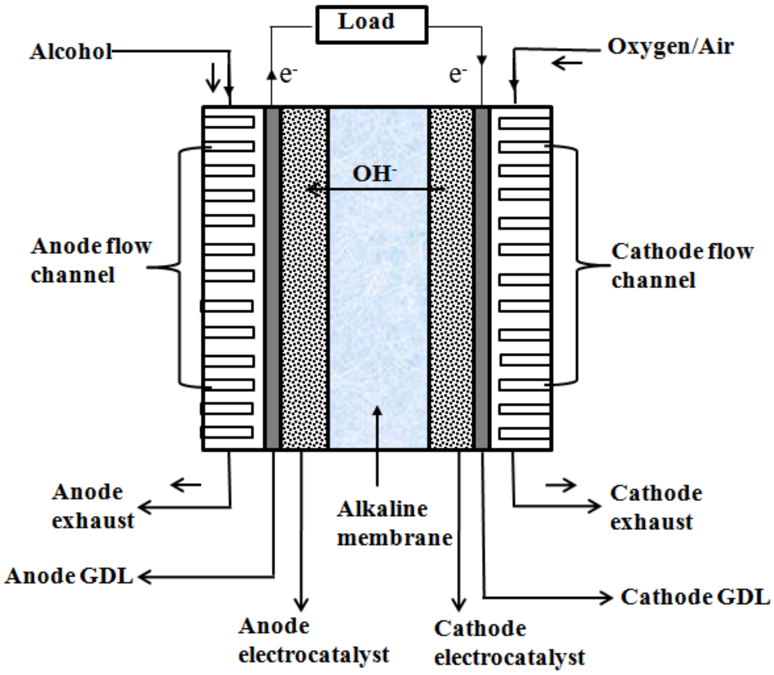

Figure 1 Schematic of alkaline direct alcohol fuel cell.

Although, fuel cells are oldest energy conversion technologies, the exact origin is obscure. The first working prototype of a fuel cell was developed by a Welsh, scientist, Sir William Robert Grove, a judge and an amateur scientist (Larmine and Dicks 2003). The first known demonstration of the fuel cell was conducted in 1839. Since then the researchers are working on various types of fuel cells to come up with a feasible solution which is low cost, high efficiency, and reliable (Larmine and Dicks 2003 and Pramanik et al., 2008).

The fuel cells are primarily classified according to electrolyte material used in cell and fuels used at anode. Alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) are named based on electrolyte used. Direct alcohol fuel cells (DAFC) are named based on the fuel used. The SOFC and MCFC are operated at very high temperature range (600 ^{o}C- 1000 ^{o}C) and rest of the fuel cells are operated from low

(60 ^{o}C) to medium (230 ^{o}C) temperature range (Peighambardoust et al., 2010). High temperature fuel cells are very difficult to fabricate and operate. The SOFC and MCFC fabrication require high temperature resistant materials having their desired properties to perform efficiently at this very high temperature. However, low temperature fuel cells are easy to fabricate and operate. Thus, they do not have any problem for material selection (Mekhilef et al., 2012). In this context, low temperature fuel cells based on solid electrolyte membrane technology are found very promising energy generation devices (Pramanik et al., 2007). Among all the low temperature fuel cells the direct alcohol fuel cell (DAFC) has drawn much attention due to its several positive aspects like low emission of pollutants, high energy density, and easy handling and transportation since it uses liquid fuel (Lamy et al., 2004 and De Luca et al., 2006).

There are some low aliphatic alcohols like methanol and ethanol which are widely used in proton exchange membrane (PEM) based DAFC (Pramanik et al., 2007, Li and Faghri 2013 and Kamarudin et al., 2013). The PEM is synthesized from Nafion® dispersion which is acidic in nature and have many advantages like high conductivity due to high acidity, no corrosion problem as it is a solid membrane consisting of polytetrafluoroethane (PTFE) backbone, no leakage problem and low ohmic resistance as it is very thin (Garaev et al., 2013 and Kayumov et al., 2015). However, main problem of Nafion® electrolyte is dehydration when operated beyond temperature (T) > 80 ^{o}C and thus, membrane conductivity goes down, consequently fuel cell performance decreases (Rosli et al., 2017). However, alkaline medium favours the DAFC electrode kinetics in comparison to acidic medium. The alkaline electrolyte may be in the form of liquid or solid membrane type. The liquid alkaline electrolytes have leakage problem, high resistance and stability problem due to formation of carbonate when alkaline electrolytes react with ambient CO_2 (Equation (2.1)) (Ni et al., 2006 and Kordesch and Cifrain 2010).

$$OH^- + CO_2 \rightarrow HCO_3^- + H_2O \quad (1.1)$$

These problems make the DAFC technically non-viable based on liquid electrolyte. Thus, presently researchers are working on the synthesis of solid alkaline electrolyte which could solve all these problems of liquid alkaline electrolyte. Nevertheless, recent development in the area of alkaline membrane has given a new insight to work on alkaline direct alcohol fuel cell using lower aliphatic alcohols methanol and ethanol, respectively.

Methanol is an attractive liquid fuel because it is relatively cheap, readily available, easily stored and handled and soluble in aqueous electrolyte. The energy density of methanol is about 6 KWh/Kg. Generally, methanol is synthesized from natural gas via its incomplete combustion, producing synthesis gas (CO + H_2) and further synthesis gas is catalytically converted to methanol. As reported in the literature, methanol electrooxidation is quite easier than ethanol due to its simple chemical structure with single carbon atom compared to ethanol which contain C-C bond (Ozoemena 2016). Methanol is the simplest and widely used aliphatic alcohol, in alkaline direct alcohol fuel cells and its electrooxidation has been studied intensively (Bagotzky et al., 1967). A number of studies have examined on the deprotonation mechanism of methanol fuel in fuel cell. Kwon and co-workers (Kwon et al., 2011) studied the electrolyte (KOH) concentration dependence for the deprotonation of a series of alcohols namely ethanol, methanol, isopropanol, isobutanol, glycerol, sorbitol, erythritol and ethylene glycol. Therein, they established that the electrolyte concentration directly affects the reaction kinetics of alcohol. It was suggested that, at high pH, the reactive species is the alkoxide anion, which explains that the activity for alcohol oxidation is higher at pH 13 than under acidic conditions, since the alkoxy species is more readily oxidized to the aldehyde. Although methanol is popular alcohol fuel in DAFC, it suffers from crossover problem, reducing the fuel cell efficiency.

Moreover, methanol is produced from non renewable sources, relatively toxic, volatile, inflammable and it is not a primary fuel (Heinzel et al., 1999, Song et al., 2005, and Hotza 2008).

However, ethanol is renewable in nature as it can be produced from sugar containing agricultural sources by fermentation (Hotza 2008 and Gnansounou 2010). It has a lower crossover rate across the membrane and affects cathode performance less severely than methanol (Andreadis et al., 2010, Zhou et al., 2004, Song et al., 2006 and Antolini 2007). The energy density of ethanol is about 7.44 KWh/Kg. Lai and co-authors (Lai et al., 2010) investigated the electrooxidation of ethanol on Pt and Au electrodes in electrolytes of varying pH and fuel concentration. It has been suggested that at lower solution pH the first step of electrooxidation is the cleavage of the O-H bond of ethanol on the electrocatalyst surface leading to adsorbed ethoxy species followed by electrooxidation to acetaldehyde and, eventually, further production of acetic acid via electrooxidation. It was proposed that at high pH ethoxy species in solution is the dominant reactant species for electrooxidation to acetaldehyde rather than ethanol. It is considered that the first step of the electrooxidation of ethanol to acetaldehyde requires the formation of an adsorbed ethoxy species, this would explain the increase of the ethanol electrooxidation rate at high pH values (>11). The formation of acetaldehyde is essentially a single step dehydrogenation process, as opposed to lower solution pH where it requires dehydrogenation in two steps. The authors suggested that the enhanced C-C bond breaking, combined with the $CH_{x,ad}$ (where x = 1, 2, 3…) and CO_{ad} can be electrooxidized at lower overpotentials in alkaline medium, compared to acidic medium (Lai et al., 2010). Although, methanol and ethanol are widely used they have their own merits and de-merits. Ethanol has C-C bond which is difficult to dissociate at room temperature using present Pt based electrocatalyst and thus 100 % electrooxidation to carbon dioxide is not possible by electrocatalysts in the temperature range of 25 °C to 90 °C (Lamy et al., 2001).

As methanol is easily oxidized and ethanol is renewable in nature, thus, utilizing the benefits of both the fuels, with special emphasis on ethanol is highly desirable. So far only a few studies have been reported on the performance evaluation of ethanol and methanol mixture. Wongyao et al., 2011 showed that the performance of mixed fuel is decreased even at low amounts of ethanol (2.5 vol %) mixture. Leo et al., 2013 also reported decrease in performance of mixture compared to pure methanol. Both the studies were carried out in an acidic environment using commercial Nafion® membranes. To the best of our knowledge no such detailed study using mixture of methanol and ethanol as fuel has been conducted in alkaline environment. As already mentioned, the development of alkaline membrane in the area of fuel cell has given momentum to work on DAFC due to several advantages of solid alkaline membrane (page no. 4). The use of solid alkaline membrane as an electrolyte offers many benefits: (i) it improves water management, (ii) reduces crossover problem, (iii) enhances oxygen reduction kinetics in alkaline medium at a low temperature and (iv) provides low resistance to ion transport across the membrane (Couture et al., 2011). The electrolyte membrane synthesized from polyvinyl alcohol, a polyhydroxy polymer, has evoked special interest among scientist due to its large availability, easy manufacturing, low cost and environment friendly properties (Wu et al., 2010 and Xu et al., 2013). It has good film forming ability, hydrophilic properties, chemical stability, and a large density of chemical functions, which favours easy crosslinking by chemical, thermal and physical treatment methods (Merle et al., 2012, Fu et al., 2010 and Mokhtar 2016). The chemical stability of a PVA based membrane is recognized as a key factor that affects fuel cell performances, especially in an alkaline medium and high KOH concentration. Crosslinking is one important parameter for stable membrane formation. The membrane would swell too much and eventually dissolve in water without proper crosslinking. The crosslinking makes a three-dimensional mesh network structure, which holds the polymer in place and provides a framework for doping with KOH. Mainly chemical and physical crosslinking methods are used, as reported in the literature. Chemical crosslinking is done with chemicals like glutaraldehyde, acetaldehyde, formaldehyde, methanol, etc. The freeze-thaw method is used in physical crosslinking. The chemical method increases complexity and cost, and most of the chemicals are harmful. On the other hand, physical crosslinking is cheap, simple, and some research work has reported good results (Zugic et al., 2013). Although, physical crosslinking of membrane synthesis have certain benefits, the chemical crosslinking has been preferred over physical crosslinking as it gives better membrane quality in terms of chemical and thermal stability. The hydroxyl ion conductivity is also better when KOH is doped in the membrane structure (Maiti et al., 2012). Thus, in the present study PVA has been considered as a basic polymeric material for the synthesis of alkaline membrane followed by KOH doping. It should be noted that membrane electrolyte is the heart of the any fuel cell and thus, special emphasis was given in the present study to manufacture alkaline membranes following the routes (i) physical crosslinking and (ii) chemical crosslinking, respectively.

Although, there are many researches ongoing they are not being published to protect the intellectual property rights. Thus, in this thesis work a thorough study on the synthesis and characterization of low cost polyvinyl alcohol (PVA) based alkaline membrane using physical and chemical crosslinking methods have been performed followed by development of membrane electrode assembly (MEA) for the use in alkaline DAFC. The performance of the synthesized PVA based alkaline membrane were checked using methanol or ethanol or their mixture as fuel on platinum based bimetallic carbon supported electrocatalyst in a single cell DAFC. The half cell studies were also performed in detail to substantiate the optimum results of different parameters obtained in single cell DAFC. The optimum conditions of different parameters e.g. concentration of alcohols, electrocatalyst loading and electrolyte concentration were investigated in order to achieve highest performance using the prepared electrodes in terms of current density with low overpotential. The thesis chapters are described below in brief.

General introduction about the energy scenario, basic principle of the fuel cell, methanol and ethanol as fuel along with their benefits and alkaline membrane electrolyte are discussed in detail in **Chapter 1**. **Chapter 2** presents the literature reviews and specific objectives of the thesis. **Chapter 3** describes the material used throughout the experiment and experimental details related to the development of alkaline membrane, e.g synthesis of membrane, treatment and optimization of membrane parameters, fabrication of anode, cathode, and membrane electrode assembly, fabrication of single cell set up, cyclic voltammetry for half cell analysis, and cell performance. **Chapter 4** presents the result and discussion based on the physicochemical characterization of membrane viz., water uptake, KOH uptake, ion exchange capacity, ionic conductivity, membrane morphology, crystal structure, thermal properties, functional groups analysis, electrodes morphology, half cell analysis, polarization and power density curves are discussed. The experimental results of the single cell are also discussed in detail. Finally, **Chapter 5** summarizes the essential conclusions and discussions of the thesis, and some important recommendation for the further work in this area is also showed. The appendices and the references are provided at the end of the thesis.