PREFACE

In the present times, energy demand is mainly fulfilled by vast resources of fossil fuels that were formed millions of years ago. The depletion of these fossil fuels is larger than its formation by natural processes. Thus, there is an immediate energy threat to our coming generations. To combat this problem there is an urgent need for an alternative energy source that is sustainable and pollution free, and does not depend on the use of fossil fuels. Fuel cell is the energy conversion device that can solve all these problem. Low temperature fuel cells based on solid electrolyte membrane technology are found very promising energy generation devices. Among them, the direct alcohol fuel cell (DAFC) has drawn much attention. The positive aspects of a DAFC are the low emission of pollutants, high energy density, and easy handling and transportation, since it uses liquid fuel alcohol. Currently, the widely used electrolyte in proton exchange membrane (PEM) fuel cell is Nafion®. The Nafion® is very costly which does not permit its large and commercial scale use. The PEMFC has many drawbacks like fuel crossover, low thermal stability, hydrogen storage problem and slow cathode kinetics. The solid alkaline membrane used as electrolyte offer many benefits like improved water management, reduced crossover problem, excellent electrode kinetics in alkaline medium at a low temperature and provides low resistance to ion transport across the membrane. The electrooxidation of oxygen is excellent in an alkaline medium than under acidic medium. Polyvinyl alcohol (PVA) based alkaline membrane has been received more attention as promising solid alkaline electrolyte material to be used in fuel cell. The PVA is low cost, chemically stable, good film forming ability, hydrophilic and with more number of crosslinking sites, environment friendly, biodegradable and non toxic.

Many research works on PVA based alkaline membrane have been studied either by physical crosslinking or chemical crosslinking for fuel cell applications. No work on physical crosslinked membrane was found in the open literature for DAFC. No detailed study on direct alcohol fuel cell (DAFC) has been carried out using physical and chemical crosslinked PVA based alkaline membrane. The detailed study on chemical crosslinking of PVA membrane by glutaraldehyde and thorough characterization of the membrane are not reported in the published literature till date. 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.

The electrolyte membranes were synthesized using PVA by physical crosslinking, chemical crosslinking and without any crosslinking methods. The PVA membrane with no crosslinking was designated as pristine PVA membrane. All the membranes were doped with KOH for OH^- conductivity. The membranes were characterized for various physicochemical properties such as water uptake, KOH uptake, ionic conductivity, surface morphology, functional groups, crystallinity and mechanical property.

The anode and cathode were fabricated using Pt–Ru/C (30 % : 15 % by wt) and Pt/C_{HSA} (40 % by wt.) electrocatalyst, respectively. The electrocatalyst ink was prepared by ultrasonically mixing electrocatalysts with certain amount of acetylene black carbon, isopropyl alcohol, Nafion® and PTFE dispersion. Nafion® and PTFE function as binders and assist in creation of pores and channels. The inks were then loaded onto carbon paper/gas diffusion layer of area about 6.25 cm^2 using paintbrush technique. The painted electrodes were sintered at high temperature. The electrodes were characterized by scanning electron microscopy and cyclic voltammetry in half-cell mode using three-electrode cell assemblies.

The physical and chemical crosslinked both types of membranes showed optimum KOH uptake and ionic conductivity at 6 M KOH. The scanning electron microscopy analysis shows that with the increase in crosslinking, the membrane became dense and compact. The XRD analysis showed decrease in crystallinity upon crosslinking. FTIR analysis confirmed presence of functional groups corresponding to crosslinking. The tensile properties showed that crosslinked membrane is more mechanically stable than pristine membrane.

The synthesized alkaline membrane electrolytes were used for MEA fabrication. The performance of PVA based membranes were evaluated in a single DAFC using methanol and ethanol as fuel. The single cell performance of chemical crosslinked membrane was found to be excellent in comparison to physical crosslinked membrane for methanol, ethanol and their mixture keeping all process parameters constant. The anode and cathode optimum loading of 1 mg/cm^2 was observed for both the fuels and both types of alkaline PVA membrane electrolyte. The optimum KOH doping concentration of 6 M KOH was found for both physical and chemical crosslinked PVA membranes. At optimum doping concentration of KOH (6 M), conductivity of membranes were 9 x 10^{-3} S/cm for chemical crosslinked, 5.6 x 10^{-3} S/cm for physical crosslinked and 0.89 x 10^{-3} S/cm for pristine PVA membrane. The power density increases with the increase in fuel concentration irrespective of PVA membranes types. The optimum concentration of methanol for physical and chemical crosslinked PVA membrane were 2 M and 3 M, respectively. Whereas, the optimum concentration of ethanol was 2 M for both types of membranes.

The electrolyte (KOH) concentration of 6 M and 1 M were found as optimum for methanol and ethanol using physical crosslinked PVA membrane. Whereas, same KOH concentration of 6 M and 1 M were found optimum for methanol and ethanol using chemical crosslinked PVA membrane.

In single cell experiment, using chemical crosslinked PVA membrane (2.5 wt % GA), the maximum OCV of 0.63 V and power density of 7.10 mW/cm^2 at a current density of 23.53 mA/cm^2 were obtained for the fuel of 3 M methanol mixed with 6 M KOH. Whereas, the maximum OCV of 0.75 V and power density of 3.57 mW/cm^2 at a current density of 17.76 mA/cm^2 were obtained for the fuel of 2 M ethanol mixed with 1 M KOH.

Similarly, using physical crosslinked PVA membrane, the maximum OCV of 0.656 V and power density of 2.59 mW/cm^2 at a current density of 9.06 mA/cm^2 were obtained for the fuel of 2 M methanol mixed with 6 M KOH. Whereas, the maximum OCV of 0.73 V and power density of 1.93 mW/cm^2 at a current density of 8.06 mA/cm^2 were obtained for the fuel of 2 M ethanol mixed with 1 M KOH.

It should be noted that the performance of pristine PVA membrane was always low compared to physical and chemical crosslinked PVA membrane. The maximum OCV of 0.577 V and power density of 1.39 mW/cm^2 at a current density of 8.8 mA/cm^2 were obtained for the fuel of 2 M methanol mixed with 6 M KOH. Whereas, the maximum OCV of 0.582 V and power density of 1.17 mW/cm^2 at a current density of 4.8 mA/cm^2 were obtained for the fuel of 2 M ethanol mixed with 1 M KOH.

The results obtained are discussed and presented in this thesis. The subject matter contained in the thesis has been arranged in five different chapters. General introduction about the energy scenario, basic principle of the fuel cell, methanol or ethanol as fuel along with their benefits and alkaline membrane electrolyte are discussed in detail in **Chapter 1**. **Chapter 2** presents the literature review 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. The fabrication of anode, cathode, and membrane electrode assembly, fabrication of single cell set up, cyclic voltammetry for half cell analysis, and cell performance are also discussed at the end of **Chapter 3**. **Chapter 4** presents the results 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, etc. The electrodes morphology, half cell analysis and the experimental results of the single cell are also discussed in detail in this chapter. 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.