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## CHAPTER 5

### CONCLUSIONS

The problems of liquid electrolyte in alkaline fuel cell have inspired scientists to develop solid alkaline electrolyte. The solid alkaline electrolyte membrane conducts  $\text{OH}^-$  ions and separates the anode and cathode from each other. Many materials have been utilized to fabricate and characterize alkaline membrane. Polyvinyl alcohol is one such membrane which has gained interests of scientist due to its many favorable properties like cheap and large availability, easy to manufacture and synthesize membrane, biodegradable, hydrophilic and availability of sites for crosslinking. Many works have been done using PVA in alkaline fuel cell. However, they lack a systematic approach and detail membrane characterization and optimization of various parameters. Thus, in this study PVA based solid alkaline membrane electrolytes were synthesized in laboratory and characterized extensively. Single cell analysis was also performed using methanol or ethanol or their mixture. Various parameters were optimized to get maximum power density and current density.

#### 5.1 Direct alcohol fuel cell (DAFC) components and construction

The direct alcohol fuel cell was fabricated by assembling various individual components such as anode, cathode, membrane electrolyte, flow channels, current collectors and bipolar plates. The membrane electrode assembly (MEA) also called as the heart of the fuel cell was fabricated in the laboratory. The anode and cathode were fabricated using Pt–Ru/C (30 % : 15 % by wt) and Pt/C<sub>HSA</sub> (40 % by wt.) electrocatalyst, respectively. The electrocatalyst ink was prepared by ultrasonically mixing electrocatalysts with certain amount of acetylene black carbon, isopropyl alcohol, Nafion<sup>®</sup> and PTFE dispersion. Nafion<sup>®</sup> 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<sup>2</sup> using

paintbrush technique. The painted electrodes were sintered at high temperature. 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<sup>-</sup> conductivity. 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.

## 5.2 Membrane electrolyte characterization

Polyvinyl alcohol (PVA) based solid alkaline electrolyte were fabricated using three different methods (i) physical crosslinking (ii) chemical crosslinking and (iii) without crosslinking. The freeze thaw method was used for physical crosslinking and glutaraldehyde of different weight percent was used for chemical crosslinking. The 2.5 wt % GA crosslinked PVA membrane showed optimum results in terms of KOH uptake and ionic conductivity. The pristine PVA membrane showed the highest water uptake of 130 wt %, while the water uptake decreased for physical crosslinked PVA membrane (70 wt %) and 2.5 wt % GA crosslinked PVA membrane (29.3 wt %). The decrease in water uptake was due to the formation of more ordered pattern and reduction in void volume. The highest KOH uptake of 59.4 wt % was observed for 2.5 wt % GA crosslinked PVA membrane doped with 6 M KOH. Whereas, the KOH uptake of 37.8 wt % and 37.9 wt % were obtained using PVA membrane doped with 6 M KOH solution for pristine and physical crosslinked, respectively. The KOH uptake of pristine PVA membrane was found to be lower in comparison to crosslinked PVA membrane. The ionic conductivity is correlated with KOH uptake and thus, the ionic conductivity for 2.5 wt % GA crosslinked PVA membrane doped with 6 M KOH was highest, in the order of  $9 \times 10^{-3}$  S/cm. However, the ionic conductivity of pristine ( $0.89 \times 10^{-3}$  S/cm) and

physical crosslinked PVA ( $5.6 \times 10^{-3}$  S/cm) membrane are lower in comparison to chemical crosslinked PVA membrane. The morphology study of plane surface reveals cracks for pristine PVA membrane. However, the cracks disappear, and membrane becomes more compact and denser with crosslinking. The cross-sectional SEM observation of crosslinked membrane doped with 6 M KOH reveals the uniform pores and embedded KOH molecules are observed as spike like structures. The XRD analysis showed that the membrane becomes amorphous as the crosslink of GA is increased. The membrane becomes brittle for 3 wt % GA crosslinked PVA membrane as observed visually and by the XRD graph. FTIR analysis showed the characteristics functional groups present in the PVA membrane. The mechanical testing showed that the tensile strength of 2.5 wt % GA crosslinked membrane (44 MPa) is higher than pristine PVA membrane (37 MPa) and physical crosslinked PVA membrane (40 MPa).

### 5.3 Electrode characterization

The fabricated anode and cathode were characterized for morphology using SEM and half-cell analysis using cyclic voltammetry. SEM of the electrodes revealed uniform distribution of electrocatalyst over GDL layer. However, agglomeration was also observed at higher loading. The cyclic voltammetry analysis for alcohol oxidation showed important trends and were further validated with single cell experiments. At higher scan rates less poisoning of electrodes occurs, thus scan rate of 100 mV/s was chosen for CV study. It was observed that initially with increase in fuel (methanol or ethanol) and KOH concentration the current density increases. However, after certain limit the current density values decreases. The formation of PtO layer at higher KOH concentration is responsible for decrease in current density since it hinders the electrooxidation of methanol or ethanol. The decrease in current density values at higher fuel concentration is due to the reduction in availability of  $\text{OH}_{\text{ad}}$  ion on the active sites of anode. The

electrocatalyst loading of  $1 \text{ mg/cm}^2$  for both anode (Pt-Ru/C) and cathode (Pt/C<sub>HSA</sub>) was found to be optimum for both the fuels. A combination of 3 M methanol mixed with 6 M KOH gave higher current density values of  $453 \text{ mA/cm}^2$  at a potential of 0.87 V. The highest current density of  $287 \text{ mA/cm}^2$  at a potential 0.34 V was observed for 2 M ethanol mixed with 1 M KOH. The electrooxidation of mixture of methanol: ethanol gave an optimum value for molar ratio 1:3 methanol: ethanol with current density of  $141.09 \text{ mA/cm}^2$  at a potential of 0.7 V. The cyclic voltammetry of oxygen reduction reaction using Pt/C<sub>HSA</sub> cathode showed two peaks at around - 0.5 V and - 0.6 V corresponding to 2+2 electron pathway mechanism. No peaks were observed for alkaline solution saturated with nitrogen.

#### 5.4 Performance of DAFC

The laboratory fabricated direct alcohol fuel cell set up was tested to evaluate the performance of synthesized PVA based alkaline membranes which were used in the MEA. The optimum conditions of DAFC were found by varying different parameters like KOH doping in PVA membrane, fuel concentration, electrolyte concentration, electrocatalyst loading at anode and cathode, electrocatalyst type at anode, cell temperature, oxidant types and membrane types such that maximum cell performance is obtained in terms of current density and power density. The anode and cathode optimum loading of  $1 \text{ mg/cm}^2$  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  $9 \times 10^{-3} \text{ S/cm}$  for chemical crosslinked and  $5.6 \times 10^{-3} \text{ S/cm}$  for physical crosslinked PVA membrane. The power density increases with the increase in fuel concentration for both types of PVA membranes. The optimum value of methanol for physical and chemical crosslinked PVA

membrane were 2 M and 3 M, respectively. Whereas, the optimum value of ethanol was 2 M for both types of membranes. The optimum electrolyte (KOH) concentration of 6 M and 1 M were found using physical crosslinked PVA membrane for methanol and ethanol, respectively. Whereas, same KOH concentration of 6 M and 1 M were found using chemical crosslinked PVA membrane for methanol and ethanol, respectively.

In single cell experiment, using chemical crosslinked PVA membrane (2.5 wt % GA), the OCV of 0.63 V and power density of 7.10 mW/cm<sup>2</sup> at a current density of 23.53 mA/cm<sup>2</sup> 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<sup>2</sup> at a current density of 17.76 mA/cm<sup>2</sup> 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<sup>2</sup> at a current density of 9.06 mA/cm<sup>2</sup> 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<sup>2</sup> at a current density of 8.06 mA/cm<sup>2</sup> 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 low compared to physical and chemical crosslinked PVA membrane. The OCV of 0.577 V and power density of 1.39 mW/cm<sup>2</sup> at a current density of 8.8 mA/cm<sup>2</sup> 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<sup>2</sup> at a current density of 4.8 mA/cm<sup>2</sup> were obtained for the fuel of 2 M ethanol mixed with 1 M KOH.

It is observed that the performance of DAFC based on methanol and ethanol fuel increases with the increase in temperature of up to 50 °C for physical crosslinked PVA membrane and 60 °C for chemical crosslinked PVA membrane. The optimum

temperature for physical crosslinked membrane using methanol as fuel was 50 °C as the maximum power density of 3.90 mW/cm<sup>2</sup> at a current density of 11.17 mA/cm<sup>2</sup> were obtained from the single cell. The initial increase may be due to higher reaction kinetics at higher temperature. However, for physical crosslinked PVA membrane the reduction in cell performance at 60 °C may be due to poor crosslinking thereby the membrane degrades at high temperature. Similarly, the optimum temperature for chemical crosslinked membrane using same fuel methanol was 60 °C which is higher than that of physical crosslinked membrane. The maximum power density of 11.07 mW/cm<sup>2</sup> at a current density of 31.03 mA/cm<sup>2</sup> were obtained at 60 °C. In case of chemical crosslinked PVA membrane the membrane gets severely damaged at 70 °C and no readings could be taken.

Out of the two types of electrocatalyst Pt/C<sub>HSA</sub> and Pt-Ru/C tested at anode, Pt-Ru/C produced excellent performance for methanol and ethanol fuel, respectively. Similarly, the effect of oxygen and air was also evaluated, and oxygen gave higher performance in terms of power density in comparison to air. The evaluation of fuel mixture showed a similar trend as observed in CV. The molar ratio 1:3 of methanol to ethanol results in higher power density. The stability test study showed that the chemical crosslinked membrane is more stable than physical crosslinked membrane. After 15 hrs of cell performance, negligible drop in OCP i.e., 0.583 V to 0.563 V, 0.612 V to 0.595 V and 0.548V to 0.536 V were observed for chemical crosslinked PVA membrane using methanol, ethanol and their mixture, respectively. After same duration of cell operation a major drop in OCP i.e., 0.513 V to 0.267, 0.540 V to 0.310 V and 0.484 V to 0.218 V was observed for physical crosslinked PVA membrane using methanol, ethanol and their mixture, respectively. The calculated Total efficiency of direct alcohol fuel cell for methanol and ethanol were 48 % and 39 % for PVA based physical crosslinked

membranes. Whereas, for the chemical crosslinked PVA membranes total efficiency of 46 % and 40 %, were recorded for methanol and ethanol, respectively.

Experimental results prove that the PVA based chemical crosslinked alkaline membrane could be used in DAFC using methanol and ethanol as fuel for powering portable applications. The results from cyclic voltammetry studies validates the experimental data of single alkaline membrane fuel cell.

#### **5.4 Future scope**

Alkaline direct alcohol fuel cell holds a bright future for powering electronic equipments. The other considerable reasons are simplicity and low cost of alkaline fuel cell. The development of low cost PVA based alkaline membrane reported in this thesis can be taken as a “roadmap” for further improvement and development of alkaline fuel cell in terms of higher current density and power density. The alkaline fuel cell in future could replace the expensive proton exchange membrane fuel cell in zero emission vehicles.

However, many challenges need to be overcome before successful commercialization of alcohol based alkaline fuel cell. The development of low cost highly effective electrocatalyst is very much essential for reducing the cost of power produced from fuel cell. Non noble metal electrocatalyst or platinum based alloy electrocatalyst could be used in future in place of pure platinum based electrocatalyst. The electrooxidation of ethanol is slower in comparison to methanol. Thus, a suitable electrocatalyst need to be developed for easily breaking the C-C bond of ethanol at low temperatures and lower loading of electrocatalysts. The membranes developed in this work perform well under low temperature conditions. Future work could focus on developing composite membrane with efficient membrane properties such as ionic conductivity, high water retention and stable at high operating temperature. The suitability of the alkaline membrane for other

higher aliphatic alcohols e.g., ethylene glycol and glycerol could be studied in future. The thickness of membrane is important parameters on which many properties of membrane and cell performance depends. The alkaline membrane of different thickness needs to be fabricated and studied thoroughly to optimize various parameters for generation of high power density. The statistical analysis of the experimental results could be performed in future for designing more efficient single cell. Although single cell DAFC shows promising results, the stack development and testing is necessary for obtaining useful and workable voltage and current, making the alkaline fuel cell commercially viable.