
CHAPTER 6

CONCLUSIONS

Air breathing microfluidic fuel cell working in alkaline medium is one of the low temperature fuel cell suitable for powering milliwatt (mW) to kilowatt (kW) range of electrical appliances. Hydrogen based proton exchange membrane fuel cell is the top competitor of air breathing microfluidic fuel cell in this low temperature segment. However, hydrogen has many drawbacks, which have emphasized to consider the use of hydrogen-rich molecules like methanol, ethanol, or sodium borohydride in the air breathing microfluidic fuel cell. In this thesis, microfluidic fuel cell in the alkaline medium using methanol or ethanol or sodium borohydride as fuels along with air as an oxidant is developed for power generation.

6.1 Microfluidic Fuel Cell Components and Constructions

Air breathing microfluidic fuel cell was constructed with Pt-Ru (30 %:15 % by wt.)/C_{HSA} or Pt (40 % by wt.)/C_{HSA} as the anode electrocatalysts, Pt (40 % by wt.)/C_{HSA} as cathode electrocatalyst and KOH as an electrolyte. Air (atmospheric oxygen) was used as the oxidant. Anode and cathode were fabricated using electrocatalyst ink made by the above electrocatalyst. The electrocatalyst ink was prepared using electrocatalysts, Nafion[®] and PTFE dispersions, which was spread homogeneously over the carbon paper through paint-brush technique. Painted electrodes were sintered at high temperature. Nickel mesh was attached on the other side of the sintered electrode using the hot press. Nickel mesh was used as the

current collector at the electrodes. The air breathing microfluidic fuel cell was continuously fed with fuel mixed with electrolyte KOH. The oxidant (for H₂O₂) mixed with liquid electrolyte KOH was fed at the cathode, and for air breathing condition, only KOH solution was fed at the cathode.

6.2 SEM and Half-cell Analyses

First of all, the fabricated electrodes were characterized individually using three cell-electrode assemblies in the half-cell mode and through scanning electron micrographs (SEM). SEM of the anode and cathode electrodes shows the uniform distribution of electrocatalysts particles over the electrode surfaces at an optimum loading (1 mg/cm²) of the electrocatalyst. The cyclic voltammetry experiments show that initially, the current density peaks increases with the increase in methanol or ethanol or electrolyte KOH for a given applied voltage in cyclic voltammogram because of sufficient availability of adsorbed OH_{ad} and HCO_{ad} or CH₃CO_{ad} species on active sites. The current density decreases at a higher concentration of electrolyte (KOH) because of the formation of the Pt-O layer and remaining OH_{ad} species hinders the electrooxidation of fuel (methanol or ethanol). On the other hand, current density decreases at higher concentration of fuel (methanol or ethanol) because of the coverage of the electrocatalyst layer by fuel residues increases. Hence, the concentration of OH_{ad} species on the active sites of the electrocatalysts reduces, therefore, the mobility of anions decreases. A similar effect was observed with NaBH₄ when the concentration was increased up to a certain limit (0.1 M), and beyond 0.1 M no electrooxidation peak was observed. The current density peaks increase with the increase in electrocatalyst loading from 0.5 mg/cm² to 1 mg/cm²

for methanol, ethanol, and NaBH_4 , respectively. However, further increase in the loading, the peak current density decreases. The reason for this decrease may be electrocatalyst particle agglomeration at higher loading in a given specific volume of the electrode. Agglomeration results in the decrease in active sites of the electrocatalyst per unit area of electrode. The porosity of the electrocatalyst layer also decreases, which offers increased diffusional resistance to mass transport of fuel from bulk to the electrocatalyst layer. On the other side the active sites, and electronic conductivity of electrocatalyst layer increases with the increase in electrocatalyst loading. The analysis of electrode in SEM also shows the agglomeration of the electrocatalyst at higher electrocatalyst loading. The electrocatalyst loading of 1 mg/cm^2 Pt-Ru (30 %:15 % by wt.)/ C_{HSA} gives the best performance for methanol or ethanol fuel. Pt (40 % by wt.)/ C_{HSA} of 1 mg/cm^2 gave the best performance for sodium borohydride electrooxidation. A combination of fuel, methanol of (0.5 M) mixed with KOH or ethanol of (0.5 M) mixed with KOH or sodium borohydride of (0.1 M) mixed with KOH solution results in maximum electrooxidation peak current density (methanol: 124.1 mA/cm^2 at -0.14 V ; ethanol: 237.3 mA/cm^2 at 0.18 V ; sodium borohydride 73.18 mA/cm^2 at -0.18 V). Based on cyclic voltammetry results and as reported in published literature, it is predicted that electrooxidation of methanol and ethanol follows a single step four electron mechanism. In case of sodium borohydride electrooxidation, the reaction path was primarily follows two-step eight electron reaction mechanism. The reduction mechanism of the oxygen electro-reduction on Pt/C electrocatalyst proceeds by 2+2 electrons mechanism. When H_2O_2 is mixed with oxygen saturated solution, it also shows the 2+2 electron ORR pathway with low activation overpotential due to the

increase in the concentration of oxidant at cathode electrocatalyst site by shifting the peak to less negative potential.

6.3 Fuel Cell Performance

The air breathing microfluidic fuel cell fabricated with above anode and cathode using methanol or ethanol or sodium borohydride as fuel was tested and current density vs. cell voltage characteristic curves were generated by varying experimental parameters, e.g., fuel concentration, electrolyte concentration at anode and cathode side, electrocatalyst loading and type at anode and cathode side and operating temperature GDL types and oxidant types at cathode. The cell performance increases initially with the increase in fuel (methanol, or ethanol, or sodium borohydride) concentration but it does not increase proportionally with the further increase in fuel concentration. The optimum concentration of methanol of 0.5 M, ethanol of 0.5 M and NaBH_4 of 0.1 M, respectively were found for the maximum power density of the cell. This may be due to the adsorbed fuel species occupy the electrocatalyst active sites with the increase in the concentration of fuel, which prevents adsorption of enough hydroxyl ions for the fuel electrooxidation reaction. Also, the air breathing microfluidic fuel cell performance increases with the increase in electrolyte (KOH) concentration from 0.5 M to 1 M and then it starts decreasing with the further increase in KOH concentration. At higher electrolyte concentration, OH_{ad} are not entirely consumed in the electrooxidation of fuel, and the remaining OH_{ad} may begin to behave as a poison species by blocking the active sites of the electrocatalysts layer. Thus the rate of the electrooxidation reaction decreases. Among the electrocatalysts, Pt-Ru/ C_{HSA} and Pt/ C_{HSA} tested at the anode, Pt-Ru (30 %: 15 % by wt.)/ C_{HSA} shows better performance for air breathing microfluidic fuel cell using

methanol and ethanol as fuel. The performance of the air breathing microfluidic fuel cell using sodium borohydride as fuel does not show a significant difference on different electrocatalysts at the anode. However, Pt/C_{HSA} shows little better performance for NaBH₄ electrooxidation. This may be due to Pt-Ru/C_{HSA} play a bi-functional role for electrooxidation of methanol and ethanol. However, there is no role of a bi-functional mechanism for sodium borohydride electrooxidation. The performance of the air breathing microfluidic fuel cell increases with the increase in anode electrocatalyst loading from 0.5 mg/cm² to 1 mg/cm² irrespective of fuel used at the anode. However, beyond electrocatalyst loading of 1 mg/cm², the performance starts decreasing. The performance of the air breathing microfluidic fuel cell increases with the increase in electrocatalyst loading at the cathode (Pt/C_{HSA}) from 0.5 mg/cm² to 1 mg/cm² and then decreases with further increase in the electrocatalyst loading. This may be due to agglomeration of electrocatalyst particles at high loading which reduces the active sites and the porosity of the electrocatalyst layer. The performance of the air breathing microfluidic fuel cell also increases with the temperature for different fuels (methanol, or ethanol, or sodium borohydride) because of the improved reaction kinetics. In some experiments, the performance of air breathing microfluidic fuel cell was evaluated with two types of GDL/carbon paper. The performance of the air breathing microfluidic fuel cell shows a better result in case of commercial GDL (Toray Carbon paper, TGP-H-60) in comparison to the IIT (BHU) laboratory made GDL because of the lower hydrophobicity and higher porosity of the commercial GDL (Toray Carbon paper, TGP-H-60). The more elevated hydrophobicity of IIT (BHU) made GDL results in reduced spreading of the electrocatalyst on the carbon paper. The air breathing microfluidic fuel cell was

operated with air/atmospheric oxygen and air breathing combined with H_2O_2 (mixed oxidant) at the cathode. Mixed oxidant condition increase the power density of the microfluidic fuel cell due to the decrease in concentration polarization at the cathode.

The maximum open circuit voltage (OCV) of 0.47 V and power density of 1.3 mW/cm^2 at a current density of 8.86 mA/cm^2 was obtained at $34 \text{ }^\circ\text{C}$ for 0.5 M methanol as fuel mixed with 1 M KOH and fresh atmospheric air as oxidant combined with 1 M KOH at the cathode. The maximum OCV of 0.5 V and power density of 1.75 mW/cm^2 at a current density of 7.87 mA/cm^2 was obtained when the cell was operated at a temperature of $65 \text{ }^\circ\text{C}$. Whereas, the maximum OCV of 0.69 V and power density of 5.45 mW/cm^2 at a current density of 29.15 mA/cm^2 was for 0.5 M methanol mixed with 1 M KOH at anode side and 2 M H_2O_2 in the presence of continuous diffusion of fresh ambient air as oxidant mixed with 1 M KOH at cathode side at temperature of $34 \text{ }^\circ\text{C}$. Using IIT (BHU) laboratory made GDL, the maximum open circuit voltage (OCV) of 0.47 V and power density of 1.08 mW/cm^2 at a current density of 6.86 mA/cm^2 were obtained at a temperature of $34 \text{ }^\circ\text{C}$ for methanol.

The maximum OCV of 0.43 V, current density of 33.33 mA/cm^2 and power density of 4.1 mW/cm^2 at a current density of 26.5 mA/cm^2 were obtained at $34 \text{ }^\circ\text{C}$ for 0.5 M ethanol as fuel mixed with 1 M KOH as electrolyte and the concentration of electrolyte at cathode side was 1 M KOH mixed with ambient air as oxidant. Whereas, the maximum open circuit voltage of 0.46 V and power density of 5.09 mW/cm^2 at a current density of 29.38 mA/cm^2 was obtained at a temperature of $65 \text{ }^\circ\text{C}$ for ethanol.

The maximum OCV of 0.66 V and power density of 8.46 mW/cm² at a current density of 34.04 mA/cm² was obtained at 40 °C using 0.1 M NaBH₄ as fuel mixed with 1 M KOH as electrolyte, and the concentration of electrolyte at cathode side was 1 M KOH mixed with ambient air as oxidant. Whereas, the maximum open circuit voltage of 0.60 V and power density of 11.22 mW/cm² at a current density of 34.9 mA/cm² was obtained at the temperature of 65 °C for NaBH₄.

Experimental results prove that the air breathing microfluidic fuel cell based on methanol, or ethanol or sodium borohydride as fuel can be used for portable power applications. The Cyclic voltammetry experiments substantiate the experimental data of single air breathing microfluidic fuel cell.

6.4 Model Development and Prediction

A mathematical model for air breathing microfluidic fuel cell using methanol, or ethanol, or sodium borohydride as a fuel is developed by taking into account of activation, ohmic and concentration overpotentials. The activation overpotential term is obtained using the reaction mechanism proposed earlier in the literature based on the half-cell analysis and reaction product analyses. Ohmic overpotential term is derived based on the conductivity of the electrolyte, and the cell interconnects resistances measured with a multimeter. The concentration term is modeled using Fick's law of diffusion, modified Butler-Volmer equation and transport process through diffusion layer. The model equation predicts reasonably well the experimental data on cell voltage and current density. Model prediction equation

fairly reflected the influence of process variables such as, fuel concentration and cell temperature on the prediction.

6.5 Future Scope

The development of air breathing microfluidic fuel cell presented in the thesis is the starting work of the energy laboratory, IIT (BHU). It can be further improved in terms of higher power density by taking the thesis as the "roadmap." The future scope of the air breathing microfluidic fuel cell using methanol, or ethanol, or sodium borohydride is promising in nature for powering small and portable electronic equipment, i.e., pacemakers, healthcare diagnostics, mobile phones and DNA analysis devices, as the single cell result shows the reasonable performance at a mild condition.

However, there are specific issues, which need to be addressed. These are the formation of CO poisoning species during the electrooxidation of methanol and ethanol. The low reaction kinetics of ethanol electrooxidation is still a challenging to researchers to improve the cell efficiency. A suitable electrocatalyst should be developed, which can break the C-C bond in ethanol and enhance the electrooxidation mechanism of the fuel followed by CO removal from the active sites of the electrocatalyst. Bubble generation over anode due to electrooxidation of fuel can be removed by using a micro pumping mechanism (Shaegh et al., 2012). Mass transfer limitation losses, electrochemical kinetics, and ohmic loss should be addressed to achieve high power density.

Moreover, the performance of air breathing microfluidic fuel cell depends on the successful development of higher porous anode, air breathing cathode, fuel and electrolyte concentration, electrocatalyst type and loading, channel geometry, fuel cell stacks and the operating temperature. Finally, stack design and stack testing are necessary as it is key to the success of air breathing microfluidic fuel cell to provide high electrical power and makes the cell commercially viable.

