

PREFACE

A continuously growing demand for miniaturized power sources for portable electronic telecommunication and computing devices such as mobile phones, laptop computers, and biomedical appliances has promoted research and development activities in the area of fuel cell technology. The energy demand is generally met by primary sources of energy like fossil fuels such as natural gas, petroleum oil, and coal and to a lesser extent, nuclear by fission of radioactive elements, solar indirect heating and photovoltaic cells, hydroelectricity, wind, geothermal and biomass. However, about 75% of the today's energy demand is fulfilled by fossil fuels. Fossil fuels generate energy by combustion and produce pollutants, e.g., oxides of sulfur, nitrogen, carbon and unburned hydrocarbons, which are introduced into the atmosphere resulting in a large number of problems to the environment. Currently, fuel cells are found to be very promising energy generating devices for the stationary and mobile applications with significant environmental advantages. In this context, low temperature fuel cells based on proton exchange membrane (PEM) technology are found very promising energy generating devices for smaller electronic devices. However, the use of membranes electrolyte (e.g., Nafion[®]) adds a certain amount of ohmic polarization losses and allows fuel crossover, both of which lower the fuel cell performance. Furthermore, the use of membranes requires complex water and thermal management strategies to enable high charge transfer rates. All these problems have propelled to develop a low cost miniaturized fuel cell which eliminates the use of static physical barrier (membrane) termed as the membraneless microfluidic fuel cell.

A microfluidic fuel cell (MFC) is defined as a device that incorporates all fundamental components of a fuel cell within a single micro channel (channel width $<1000\ \mu\text{m}$) and its walls. Microfluidic fuel cells have several advantages as compared to traditional proton exchange membrane (PEM)-based fuel cells. The benefits are (i) fuel and oxidant streams may be combined in a single microchannel (ii) fuel and/or oxidant crossover can be mitigated by adjusting the flow rate of the co-laminar streams (iii) no ion exchange membrane is required (iv) sealing, manifolding, and fluid delivery infrastructure requirements are reduced and (v) issues related to membrane hydration and water management are eliminated. In addition, microfluidic fuel cells may be manufactured using inexpensive microfabrication methods and low-cost materials. There are several types of fuel cells reported in literature among them air breathing MFC promises one as oxidant is atmospheric air which is freely available in the atmosphere. Thus, air breathing MFC is selected for further study in this research. Although, it is quite possible that the development work on various type MFC is being carried out in different research and development organizations, but their detailed studies on various operating parameters are not reported in the present literature.

The electrocatalysts used to prepare anode and cathode were Pt-Ru (30%:15% by wt.)/ C_{HSA} , Pt (40% by wt.)/ C_{HSA} (Alfa Aesar, USA) and Pt (40% by wt.)/ C_{HSA} (Alfa Aesar, USA) respectively. The electrodes were prepared by spreading catalyst ink homogeneously over the surface of the gas diffusion layer (GDL) using paint brush technique. Toray Carbon paper, TGP-H-60, (Alfa Aesar, USA) was used as substrate or gas diffusion layer (GDL) for electrodes. However, The IIT (BHU) laboratory made GDL was used for the anode and cathode fabrication for some experiments using methanol and ethanol as fuel.

Nickel mesh was used as the current collector. A mixture of electrocatalyst, isopropanol, Nafion[®] and PTFE dispersion was used for catalyst ink preparation. The electrodes were characterized by scanning electron microscopy and cyclic voltammetry in half-cell mode using three electrode cell assembly. Air breathing microfluidic fuel cell (MFC) tests were performed with a single cell design. The cell voltage and current density were measured for different fuel (methanol, ethanol and sodium borohydride) concentration, electrolyte (KOH) concentration, temperature, electrocatalyst loading and type of electrocatalyst at anode and cathode, respectively. Mixed oxidant condition experiment was performed for methanol MFC to check the mixed oxidant effect on cell performance.

The maximum open circuit voltage (OCV) of 0.47 V and power density of 1.3 mW/cm² at a current density of 8.86 mA/cm² was obtained at a temperature of 34 °C for 0.5 M methanol as fuel mixed with 1 M KOH. 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/cm² at a current density of 7.87 mA/cm² was obtained when the cell was operated at a temperature of 65 °C. Whereas, the maximum OCV of 0.69 V and power density of 5.45 mW/cm² at a current density of 29.15 mA/cm² was for 0.5 M methanol mixed with 1 M KOH at anode side and 2 M H₂O₂ in the presence of continuous diffusion of fresh ambient air as oxidant mixed with 1 M KOH at cathode side at temperature of 34 °C. Using IIT (BHU) laboratory made GDL, the maximum open circuit voltage (OCV) of 0.47 V and power density of 1.08 mW/cm² at a current density of 6.86 mA/cm² were obtained at a temperature of 34 °C for methanol. The maximum OCV of 0.43 V, and power density of 4.1 mW/cm² at a current density of 26.5 mA/cm² were obtained at 34 °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/cm² at a current density of 29.38 was obtained at a temperature of 65 °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 a temperature of 65 °C for NaBH₄.

A mathematical model for the air breathing MFC for methanol, ethanol and sodium borohydride was developed based on reaction mechanism proposed earlier. The model was developed by taking into account activation, ohmic and concentration over-potentials. The influence of process variables such as, fuel concentration and temperature on the cell performance is fairly well reflected in the model.

The data of life time test were recorded for 11 hours of at constant load to analyze the durability of an air breathing microfluidic fuel cell. The anode electrocatalyst loading was 1 mg/cm² of Pt-Ru/C_{HSA} for methanol and ethanol, respectively. For sodium borohydride, it was 1 mg/cm² Pt/C_{HSA}. The cathode electrocatalyst was Pt/C_{HSA} of 1 mg/cm² for all fuels. The cell voltage reduces in 11 hours from 0.55 V to 0.46 V, 0.6 V to 0.5 V and 0.69 V to 0.61 V, for methanol, ethanol and sodium borohydride, respectively.

The results obtained are discussed and presented in this thesis. The subject matter contained in the thesis has been arranged in ten different chapters including references. General

introduction about the energy scenario, basic principle of the microfluidic fuel cell, methanol, ethanol or sodium borohydride as fuel and their benefits are discussed in **Chapter 1**. **Chapter 2** presents the literature review and specific objectives of the thesis. **Chapter 3** describes the Experimental details related to the development of air breathing microfluidic fuel cell, e.g., fabrication of cell, gas diffusion layer preparation, anode and air breathing cathode preparation and properties, half-cell analysis through cyclic voltammetry and cell performance. **Chapter 4** presents the details of the mathematical model development of methanol, ethanol, and sodium borohydride-based air breathing microfluidic fuel cell. In **Chapter 5** results and discussion based on the characterization of anode and cathode regarding their surface morphology, half-cell analysis is discussed. The experimental results of single cell and model development are also presented in this chapter. Finally, **Chapter 6** summarizes the essential conclusions of the thesis, and some useful recommendations for further work in this area too presented. The appendices and the references are provided at the end of the thesis.