DEVELOPMENT OF GLYCEROL BASED MICROFLUIDIC FUEL CELL

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by

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CHAPTER 6

CONCLUSIONS

It is clearly seen from the thorough studies on glycerol based air breathing MFC that it can be used for powering portable electrical and electronic devices. The fuel glycerol is formed as the byproduct during the biodiesel production and has comparable energy density as that of methanol and ethanol. The oxidant at cathode side is oxygen from air. Thus, operation cost of developed MFC would be low. Moreover, the microfluidic fuel cells eliminate the use of costly Nafion® membrane which is used in the PEM fuel cells. In this thesis, low cost laboratory synthesized Pd-Pt/C and Pd-Ni/C anode electrocatalyst were used in laboratory fabricated Y-shaped and T-shaped air breathing microfluidic fuel cell. Due to these reasons, the fabrication cost of MFC is lower than the membrane electrolyte based conventional fuel cell.

The laboratory constructed Y-shaped and T-shaped membraneless air breathing microfluidic fuel cell design is new and innovative in nature. The cell was fabricated using PMMA sheet, where the microchannel was designed with the help of CNC milling machine. Specially designed air breathing cathode was fabricated to enhance the mass transport of air/oxygen to the cathode active zones. The constructed single cell was operated at very low temperature i.e., 35 ^{o}C. Thus, the developed MFC system could be used for sustainable and clean energy production at low cost. The active component of anode electrode i.e., electrocatalysts were synthesized in laboratory and further characterized by physicochemical characterization and electrochemical characterization techniques for the use in air breathing Y-shaped and T-shaped MFC. The performance of synthesized anode electrocatalysts were promising in terms of power density.

6.1 Anode electrocatalyst characterization

6.1.1 Physicochemical characterization

The anode electrocatalyst Pd-Pt/C and Pd-Ni/C of various metal ratios were synthesized using impregnation reduction method. The metal loading in both the Pd-Pt and Pd-Ni was 20 wt. % and support material acetylene black of 80 wt. % was fixed in all synthesized electrocatalyst. The physicochemical characterization was performed using XRD, SEM, EDX and TEM. The XRD analysis shows the crystal structures of synthesized electrocatalyst Pd/C and bimetallic Pd-Pt (16:4)/C, Pd-Pt (10:10)/C, and Pd-Pt (4:16)/C, Pd-Ni (16:4)/C, Pd-Ni (10:10)/C, and Pd-Ni (4:16)/C of various metal ratios. The diffraction patterns show the characteristics of crystalline face-centered cubic (FCC) Pd, with peaks at 2θ position corresponding to (111), (200), and (220) planes. The lattice parameters of all Pd-Pt/C alloy electrocatalysts (0.3891, 0.3892, 0.3893 and 0.3896 nm) are smaller than the value for pure Pt (0.3923 nm) but higher than that of pure Pd (0.3890 nm). It indicates the decrease in the lattice parameters is due to replacement of Pt by Pd in the structure of the Pd-Pt alloy. The crystalline size of Pd-Pt/C was strongly affected by the addition of Pt element on the electrocatalyst. Similar trend was also observed for the Pd-Ni/C electrocatalysts. The electrocatalyst Pd-Pt (16:4)/C and Pd-Ni (10:10)/C shows highest degree of alloying than other ratio of Pd-Pt/C and Pd-Ni/C, respectively.

The surface morphology of all synthesized electrocatalysts Pd/C, Pd-Pt (16:4)/C, Pd-Pt (10:10)/C, Pd-Pt (4:16)/C, Pd-Ni (16:4)/C, Pd-Ni (10:10)/C, and Pd-Ni (4:16)/C were investigated by SEM analysis. The surface morphology of electrocatalysts show spherical and uniform particles of nano range irrespective of electrocatalyst types. The surface composition and concentration of metals and carbon support in all electrocatalysts were obtained from EDX analysis. The EDX analysis displays the presence of all the elements i.e., Pd, Pt, and C for all the Pd-Pt/C and Pd, Ni, and C for all the Pd-Ni/C electrocatalyst

for all different ratios of synthesized electrocatalyst. The elemental analyses obtained from EDX are not exactly the same as that of initial nominal composition. The reason for these changes is due to the heterogeneous surface nature of electrocatalyst and thus, the EDX result of elemental composition varies from point to point. The average particle size and its distribution of all synthesized electrocatalyst were obtained with the help of TEM analysis. The TEM images show that the all electrocatalysts comprise of nano range size and reasonably distributed on the support material. The physicochemical characterization show that the synthesized electrocatalysts and Pd-Pt (16:4)/C and Pd-Ni (10:10)/C are better than other ratios.

6.1.2 Electrochemical characterization

The electrochemical characterizations of synthesized electrocatalyst were performed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis. In the CV analysis, the more negative peak potential (-0.189 V Vs. Ag/AgCl) and -0.174 V (vs. Ag/AgCl) were obtained for Pd-Pt (16:4)/C and Pd-Ni (10:10)/C electrocatalyst. Whereas, from the EIS analysis, the least charge transfer resistance of 115.2 Ω and 272.6 Ω were obtained for Pd-Pt (16:4)/C and Pd-Ni (10:10)/C electrocatalyst, respectively in their respective ratios. The physical and electrochemical characterization confirms that Pd-Pt (16:4)/C and Pd-Ni (10:10)/C are better among all Pd-Pt/C and Pd-Ni/C.

6.2 Single cell performance

6.2.1 Y-shaped air breathing MFC

The synthesized anode electrocatalyst Pd-Pt/C and Pd-Ni/C of different ratios were tested in Y-shaped air breathing MFC. Among all Pd-Ni/C i.e., Pd-Ni (16:4)/C, Pd-Ni (10:10)/C and Pd-Ni (4:16)/C anode electrocatalyst the best electrocatalyst was Pd-Ni (10:10)/C in terms of cell performance. The optimum anode and cathode electrocatalyst loading were

1.5 mg/cm^2 of Pd-Ni (10:10)/C and Pt/C_{HSA}, respectively. The optimum anode fed was 0.5 M glycerol mixed with 0.5 M KOH electrolyte and cathode fed was 0.5 M KOH electrolyte. The maximum OCV 0.74 V and maximum power density 1.16 mW/cm^2 at a current density of 2.92 mA/cm^2 was obtained at room temperature i.e., 35 ^{o}C. Whereas, at the higher temperature of 75 ^{o}C the maximum OCV 0.8 V and power density was 1.7 mW/cm^2 at a current density of 4.41 mA/cm^2. Similarly, Pd-Pt (16:4)/C resulting in better performance among all others ratios i.e., Pd-Pt (10:10)/C, Pd-Pt (4:16)/C and Pd/C. The optimum anode and cathode electrocatalyst loading were 2 mg/cm^2 of Pd-Pt (16:4)/C and Pt/$_{CHSA}$, respectively. The optimum anode fed was 0.5 M glycerol mixed with 0.5 M KOH electrolyte and cathode electrolyte was 0.5 M KOH. The maximum OCV of 0.88 V and maximum power density 1.6 mW/cm^2 at a current density of 4 mA/cm^2 were obtained at room temperature of 35 ^{o}C. Whereas, at higher temperature of 75 ^{o}C the maximum OCV of 0.93 V and power density of 2.11 mW/cm^2 at a current density of 5.01 mA/cm^2 were obtained. Among all electrocatalysts, Pd-Pt (16:4)/C exhibited highest cell performance at room temperature (35 ^{o}C) and optimum cell temperature (75 ^{o}C) both in Y-shaped MFC.

6.2.2 T-shaped air breathing MFC

Similar to Y-shaped MFC, in T-shaped air breathing MFC, the synthesized anode electrocatalyst Pd-Ni/C and Pd-Pt/C of different ratios were also tested. The Pd-Ni (10:10)/C gives better performance among all others ratios i.e., Pd-Ni (16:4)/C and Pd-Ni (4:16)/C. The optimum anode and cathode electrocatalyst loading were 1 mg/cm^2 of Pd-Ni (10:10)/C and Pt/C_{HSA}, respectively. The optimum anode fed was 1 M glycerol mixed with 1 M KOH electrolyte and cathode electrolyte was 1 M KOH. The maximum OCV 0.42 V and power density obtained 1.27 mW/cm^2 at a current density of 5.7 mA/cm^2 obtained at room temperature of 35 ^{o}C. Whereas, at higher temperature of 75 ^{o}C, the

maximum OCV 0.51 V and power density 2.14 mW/cm^2 at a current density of 8.96 mA/cm^2 were obtained.

Similarly, Pd-Pt (16:4)/C gives better performance among all others ratios i.e., Pd-Pt (10:10)/C, Pd-Pt (4:16)/C and Pd/C. The optimum anode and cathode electrocatalyst loading were 1 mg/cm^2 of Pd-Pt (16:4)/C and Pt/$_{CHSA}$, respectively. The optimum anode fed was 1 M glycerol mixed with 1.5 M KOH electrolyte and cathode electrolyte was 0.5 M KOH. The maximum OCV of 0.69 V and maximum power density of 2.77 mW/cm^2 at a current density of 7.55 mA/cm^2 were obtained at room temperature of 35 ^{o}C. Whereas, at higher temperature of 75 ^{o}C, the maximum OCV 0.78 V and maximum power density 4.03 mW/cm^2 at a current density of 10.47 mA/cm^2 were obtained. As observed in Y-shaped MFC, the best performance was shown by the Pd-Pt (16:4)/C among all synthesized electrocatalyst in T-shaped MFC also. Moreover, T-shaped produces better power density in comparison to Y-shaped MFC irrespective of electrocatalyst types.

In additional study, using calcium hypochlorite and air as mixed oxidant at the optimum condition the performance of Pd-Ni (10:10)/C anode electrocatalyst and Pd-Pt (16:4)/C in T- shaped air breathing MFC was evaluated. MFC performance was significantly improved by adding calcium hypochlorite as oxidant at cathode side. The OCV increased from 0.42 V to 0.72 V and power density increases from 1.27 mW/cm^2 to 3.43 mW/cm^2 when mixture of calcium hypochlorite and air as used as mixed oxidant at cathode in comparison to air only at room temperature of 35 ^{o}C. The mixture of sodium hypochlorite and air as mixed oxidant produced OCV of 0.58 V and power density 1.53 mW/cm^2. For the anode electrocatalyst Pd-Pt (16:4)/C, the highest power density of 4.5 mW/cm^2 at a current density of 13.16 mA/cm^2 were obtained. The results suggested the using of calcium hypochlorite and air mixed oxidant in an air breathing MFC could be used to enhance the MFC performance.

6.2.3 Optimization of cell parameters using RSM

The Box Benkhen design (BBD) tool in response surface methodology (RSM) was used to investigate the effect of process parameters in T-shaped MFC i.e., glycerol concentration (A), anode electrolyte concentration (B), anode electrocatalyst loading (C) and cathode electrolyte concentration (D) on the power density as a response (Y) followed by optimization of process parameters to achieve highest power density. The F and P values obtained from ANOVA analysis show that the model is significant, it also indicates that the independent variables have a considerable impact on the response. The RSM analysis showed that the operating parameters have their effect on power density (Y) in the order of C>A>B>D and it means anode electrocatalyst loading (C) has higher impact on the power density, whereas cathode electrolyte concentration (D) has the lowest impact on the power density. The quadratic model was used to optimize operating conditions as it perfectly fitted the experimental data. The optimum conditions found for glycerol concentration (A), anode electrolyte concentration (B), anode electrocatalyst loading (C) and cathode electrolyte concentration (D) were 1.07 M, 1.62 M, 1.12 mg/cm^2 and 0.69 M, respectively. The predicted value for power density was 2.79 mW/cm^2, and the power density obtained from experiment at given optimum condition was 2.76 mW/cm^2 with 1.07 % deviation from predicted value. Thus, from the present study, it could be summarized that the optimization of the operating parameters by RSM is important to get the higher cell performance at their optimum values which reduces time and recommends to perform small number of experiments to achieve highest cell performance experimentally.

6.3 Future scope

The development of glycerol based microfluidic fuel cell presented in the thesis used different types of Pd based bimetallic anode electrocatalyst synthesized in laboratory. The Y-shaped and T-shaped air breathing microfluidic fuel were fabricated in laboratory, IIT-BHU. The small and portable devices with less power consuming like camcorder, cell phone, laptop, glucose sensor, and pacemaker etc. can be powered using microfluidic fuel cell. However, power density of a single MFC in the present thesis work is little low. As the simple scaleup by increasing the length or dimension of the electrodes and microchannel will not work here due to instability problem of laminar flow and hydrodynamics within the microchannel. Thus, scaleup of the microfluidic fuel cell adding large number of cells in a stack with series and parallel combination could be done as an extension of the present work in future. Although, glycerol as fuel in MFC has drawn much attention in recent times due to its several advantages however, activation loss, ohmic loss and mass transfer limitation must be reduced significantly to achieve high power density. The cell modification via suitable design of MFC is also required to increase active electrode area within small size of cell. Moreover, the present study is focused on the development of Pd based bimetallic with non-noble metal Ni i.e., Pd-Ni/C and noble metal Pt i.e., Pd-Pt/C electrocatalysts. However, the cell performance in terms of power density can be further enhanced by increasing reaction kinetics and reducing activation loss at the MFC electrodes. In view of this, trimetallic electrocatalysts should be developed in future work to achieve very high power density from the same size of the cell. Moreover, the longer duration cell operation is also necessary to study the durability test of the cell.