
CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, the results related to the electrodes morphology, reaction mechanisms for methanol, ethanol, and sodium borohydride electrooxidation at anode and oxygen electroreduction at the cathode by cyclic voltammetry are discussed in detail in the first two sections. The effect of different parameters, e.g., fuel and electrolyte concentration, electrocatalyst loading electrocatalyst type at the anode, temperature, GDL types and oxidant type at cathode on j-v characteristics of the air breathing microfluidic fuel cell are discussed in the third section. Finally, the efficiency of the fuel cell and lifetime test of the microfluidic fuel cell are reported. The model predictions on the fuel cell voltage and current density at different load conditions for the variation of different experimental data on (i) fuel concentration, (ii) electrolyte concentration and (iii) temperature are discussed at the end of the chapter.

5.1 Scanning Electron Microscope (SEM) of Electrodes

The surface morphology of the sintered electrodes of different electrocatalyst loading of the anode, cathode and blank GDL is investigated through scanning electron micrographs. The observations of SEM are described in the following section.

5.1.1 Blank Gas Diffusion Layer (GDL)

The SEM of Toray TGP-H-60 and IIT (BHU) laboratory made GDL, i.e., the blank substrate on which electrocatalyst ink was pasted is shown in fig (5.1a) and fig (5.1b). As

already mentioned that Toray carbon paper (TGP-H-60) was used for all electrodes if not mention otherwise laboratory made GDL was used only in some experiments for comparison with commercial Toray carbon paper. Fig (5.1a) and (5.1b) show the SEM of blank GDL, Toray TGP-H-60 and laboratory made carbon cloth, respectively. Both the SEM shows the even distribution of comparatively larger carbon particle over GDL surface with PTFE interconnecting film.

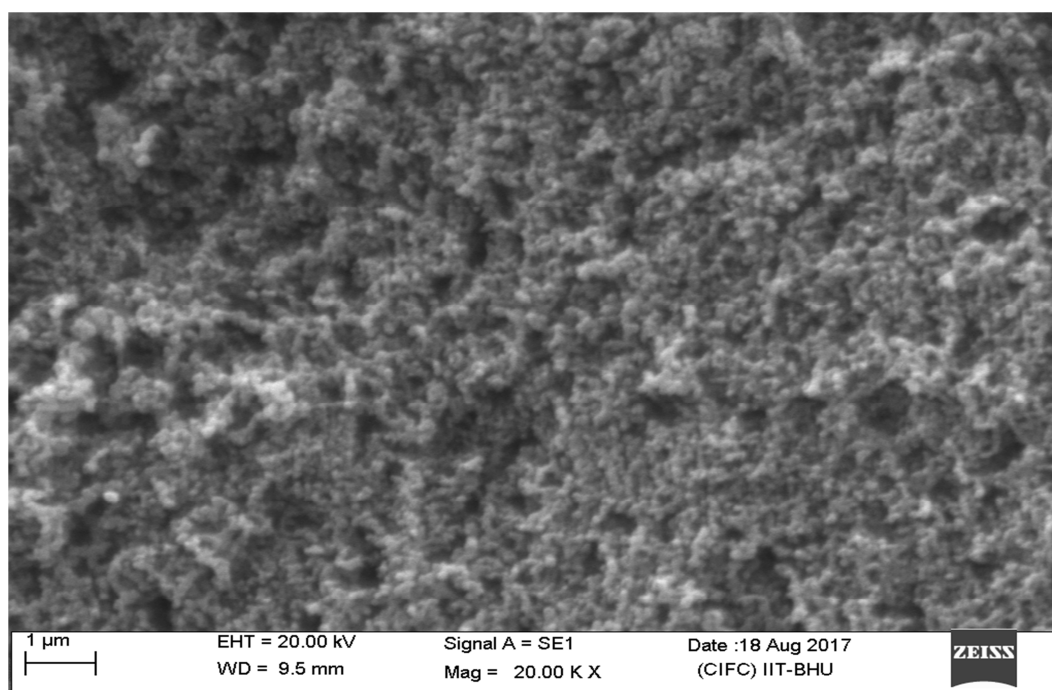


Figure 5.1a SEM of blank GDL (Toray TGP-H-60, Alfa Aesar)

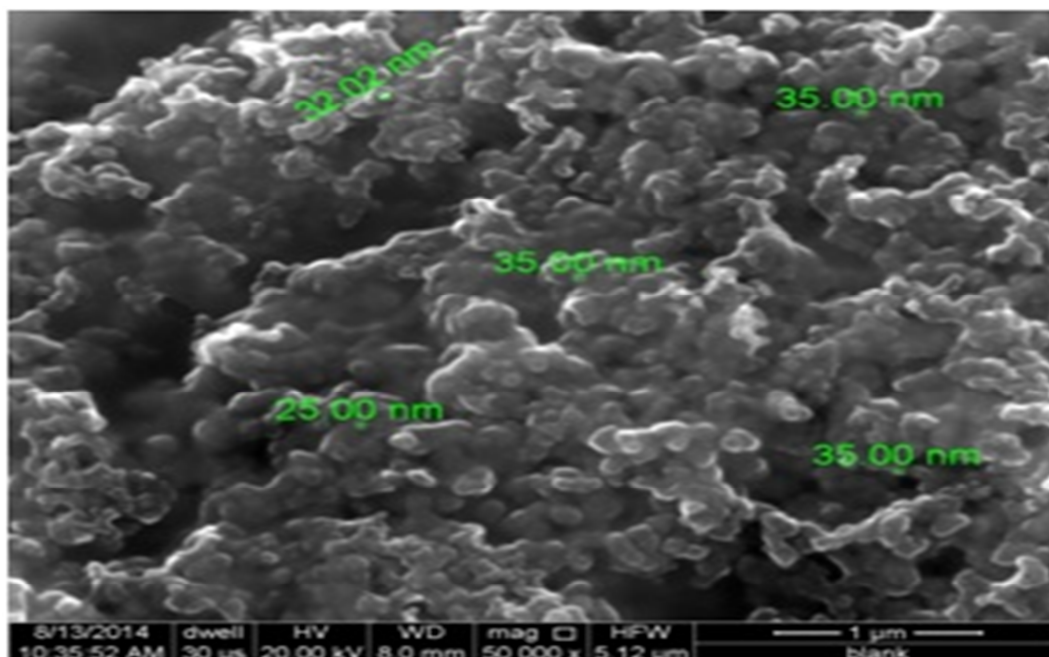


Figure 5.1b SEM of blank GDL (IIT (BHU) laboratory made

5.1.2 Anode Electrode

Fig (5.2a) to (5.2c) show the SEM of anode for different type of electrocatalyst loading ranging from 0.5 mg/cm^2 to 2 mg/cm^2 of Pt-Ru (30 %:15 % by wt.)/C_{HSA}. Fig (5.2a) shows the uneven distribution of Pt-Ru/C at low electrocatalyst loading of 0.5 mg/cm^2 on Toray carbon paper and larger carbon particles are prominent at the surface. Fig (5.2b) represents the SEM of Pt-Ru/C anode of 1 mg/cm^2 , where the smaller sizes of electrocatalyst particles are uniformly distributed on carbon paper and this result in the improved electronic conductivity of electrocatalyst layer. However, further increase in electrocatalyst loading from 1 mg/cm^2 to 2 mg/cm^2 , electrocatalyst particles agglomeration occurs (Fig 5.2c), and thus, the active surface area of electrocatalyst layer is also decreased.

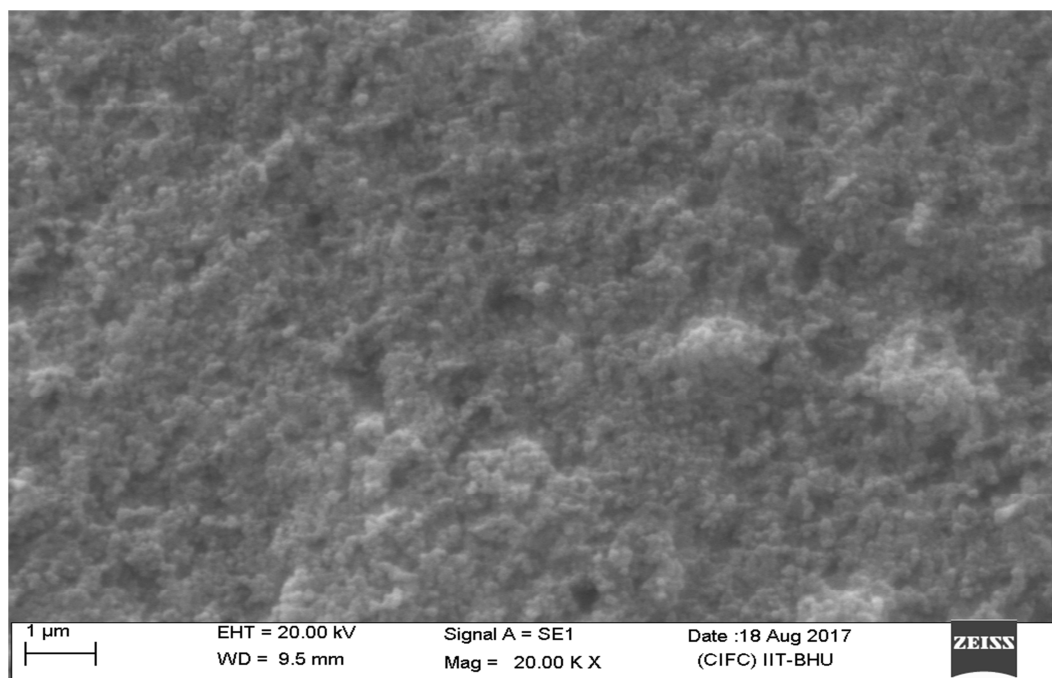


Figure 5.2a SEM of Pt-Ru/C_{HSA} (0.5 mg cm⁻²)

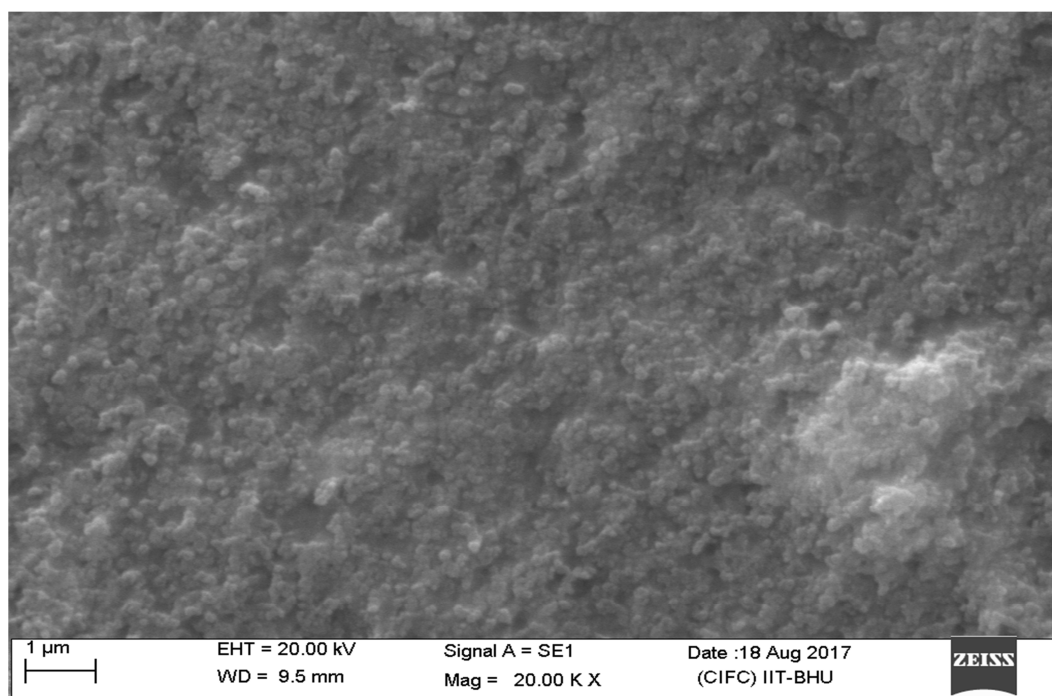


Figure 5.2b SEM of Pt-Ru/C_{HSA} (1 mg cm⁻²)

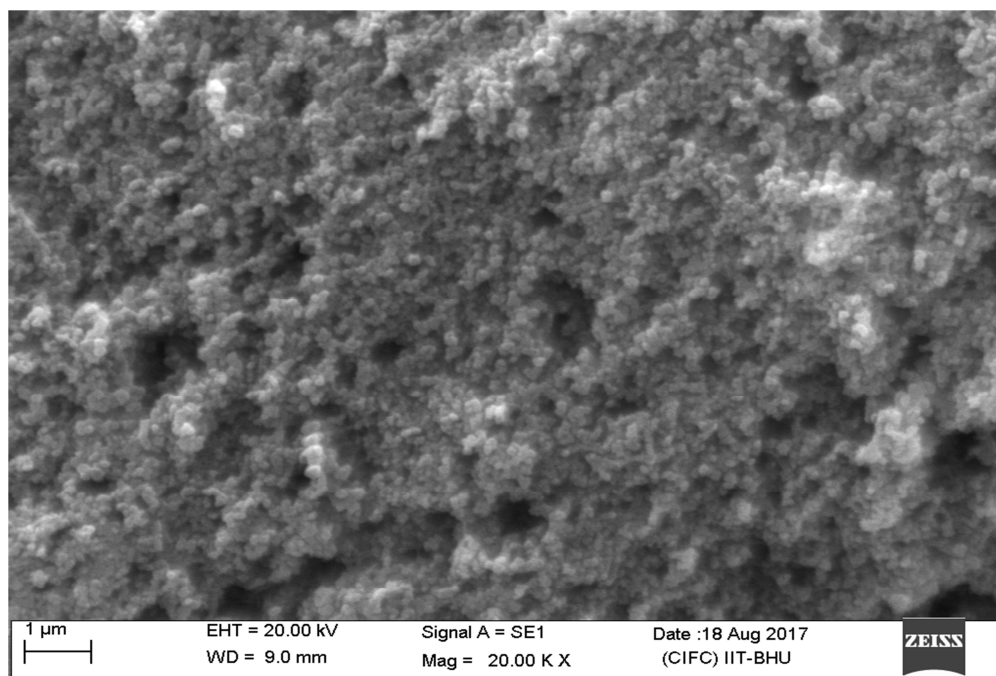


Figure 5.2c SEM of Pt-Ru/C_{HSA} (2 mg cm⁻²)

The porosity of the electrocatalyst layer also decreases, which results in poor mass transfer at the active electrocatalyst zones. The porous structure ensures the fuel supply at the anode electrocatalyst layer.

5.1.3 Cathode Electrode

Fig (5.3a) to (5.3c) show the SEM of cathode electrodes of varying electrocatalyst loading ranging from 0.5 mg/cm² to 2 mg/cm² of Pt (40 % by wt.)/C_{HSA}. Fig (5.3b) shows the even distribution of Pt/C_{HSA} electrocatalyst over the GDL for the loading of 1 mg/cm² compare to that in fig (5.3a) (0.5 mg/cm²). Fig (5.3c) is the SEM for the cathode of 2 mg/cm² Pt/C_{HSA} which shows that the electrocatalyst layer is compact and less porous due to agglomeration of the high amount of electrocatalyst on a same geometric area.

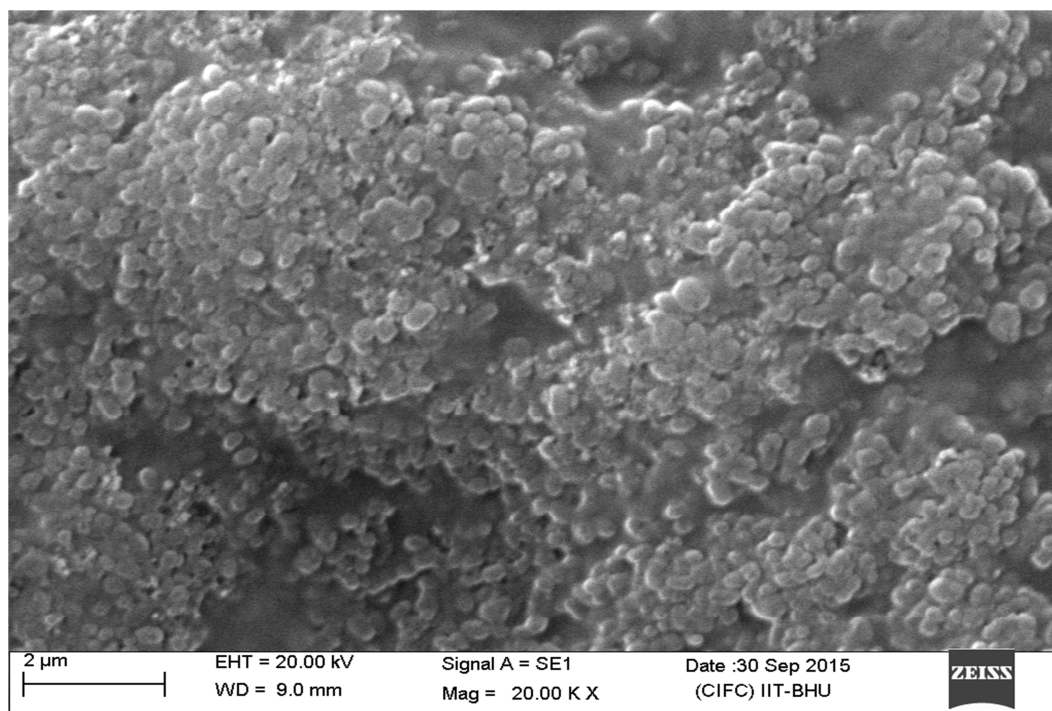


Figure 5.3a SEM of Pt/C_{HSA} (0.5 mg cm⁻²)

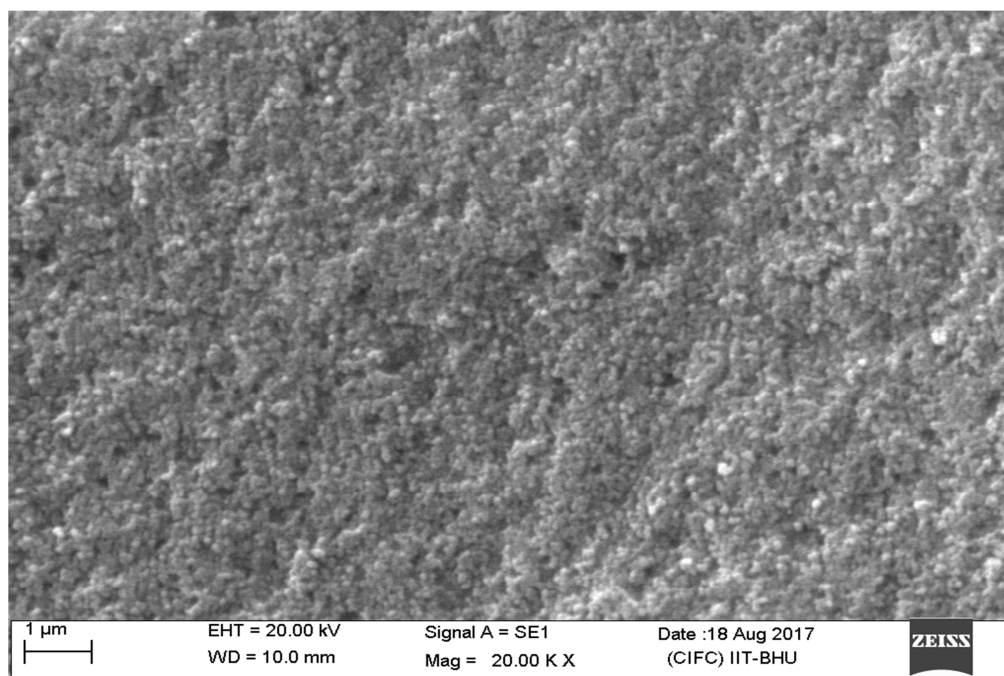


Figure 5.3b SEM of Pt/C_{HSA} (1 mg cm⁻²)

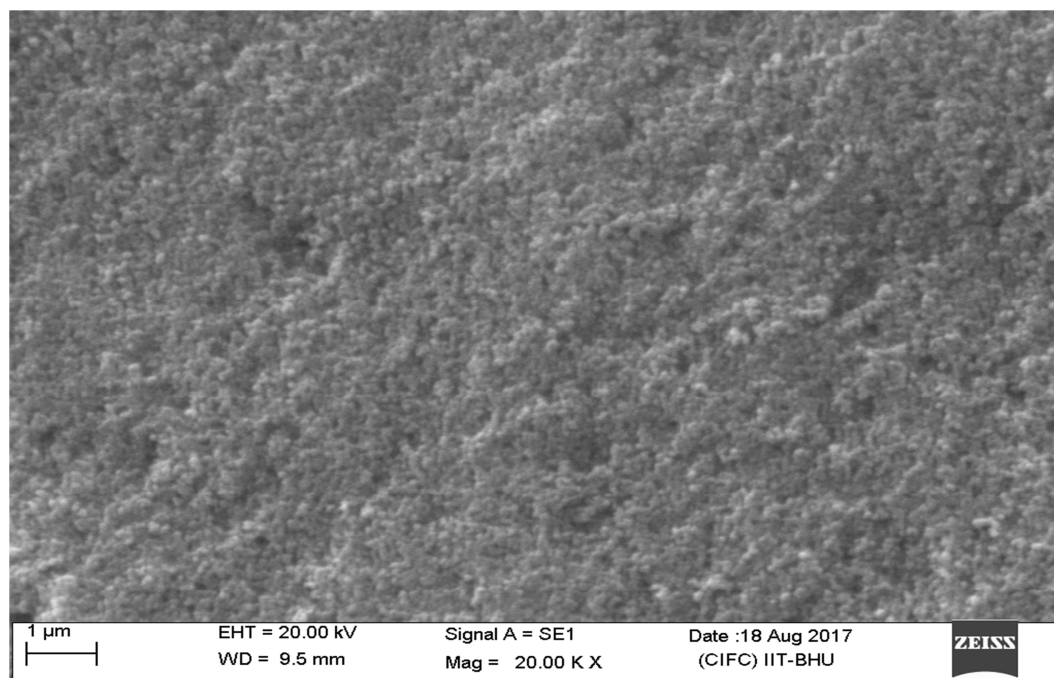


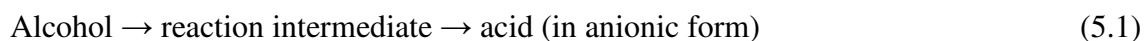
Figure 5.3c SEM of Pt/C_{HSA} (2 mg cm⁻²)

5.2 Half-cell Study

The results of cyclic voltammetry analysis for methanol, ethanol on Pt-Ru (30 %:15 % by wt.)/C_{HSA} electrocatalyst and for sodium borohydride in the presence of the Pt (40 % by wt.)/C_{HSA} (Alfa Aesar, USA) electrocatalysts are discussed in this section 5.2.1. The oxygen reduction reactions (ORR) on Pt (40 % by wt.)/C_{HSA} are discussed in section 5.2.2. The oxidant types and ORR kinetics are studied in detail. The different parameters related to cyclic voltammetry studied are scan rate, fuel concentration, electrolyte (KOH) concentration and electrocatalyst loading for methanol, ethanol, and sodium borohydride electrooxidation at the anode. For the cathode study, oxidant types and mixed oxidant are considered.

5.2.1 Anode

The cyclic voltammetry studies of methanol, ethanol and sodium borohydride with KOH electrolyte were systematically conducted. It can suggest a suitable combination of electrocatalysts and fuel/electrolyte mixtures, such that the electrooxidation reaction occurs at lowest potential and the formation of poisoning species is reduced. During alcohol (methanol, ethanol, n-propanol and n-butanol) electrooxidation the reactive intermediate and the inactive intermediates (poisoning species) generated follows a dual path reaction mechanism (Equation 5.1 and 5.2), which is summarized as (Tripkovic et al., 2001) and has already been discussed in literature review section (Page no. 36):



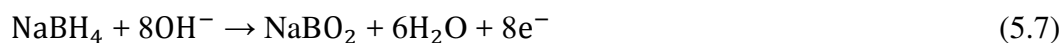
Equation (5.1) shows the main reaction path and assumes the formation of reactive intermediates, weakly bonded to the surface, in contrast with the poisoning intermediates, which are strongly bonded (Morallon et al. 1995). Tripkovic et al. (2001) proposed the following general mechanism for the electrooxidation of alcohol (Equation 5.3 to 5.6) on the noble metal catalyst in alkaline medium:





The adsorption of alcohol on catalyst site initiates dehydrogenation reaction where alcohol reacts with hydroxyl ion to produce water molecule and electrons. Adsorbed OH_{ad} species reacts with the adsorbed molecule to produce acid. The acid remains as an anion in the electrolyte. The detail mechanisms of methanol and ethanol have been discussed in the chapter literature review (section 2.1.5.1, page no. 36). Equation (5.7) and (5.10) shows the single step electrooxidation of methanol and ethanol.

Similarly, this has already been mentioned in the literature review section 2.1.5.1 (Page no. 41) that there are two types of possible routes for the electrooxidation of NaBH_4 . In the first type NaBH_4 is directly oxidized as per equation (5.7) below (Amendola et al. 1999 and Li et al. 2003):



Hydrogen gas is liberated (Equation 5.8) in the second type of possible route at high temperature, or pH less than 7 and this hydrogen gas reacts with OH^- to produce electrons (Equation 5.9)



Because of the hydrolysis reaction, 7 electrons are utilized per molecule of borohydride electrooxidation rather than theoretically 8 electrons (Wang et al. 2014).

5.2.1.1 Effect of Scan Rate

The electron transfer reactions and concerned chemical reactions depend upon the time scale of the experiments, which is controlled by the scan rate. Fig (5.4a), (5.4b) and (5.4c) show the effect of scan rate on the response of cyclic voltammogram for 0.5 M methanol, 0.5 M ethanol and 0.1 M NaBH₄ in 1 M KOH solution, respectively. The electrocatalyst loading of 1 mg/cm² was maintained for all anodes. In the cyclic voltammetry study, the electrooxidation peaks for methanol, ethanol, and NaBH₄ were found in forward and reversed scan. It should be noted in fig (5.4a) to (5.4c) that the peak current densities for forward and reverse scan increases with the increase in scan rate. The size and appearance of the electrooxidation peak in the reverse scan are explained in terms of the adsorbed methanol, or ethanol, or NaBH₄ on the electrode surface. As the methanol, ethanol or NaBH₄ is used up by the reaction, a concentration layer or diffusion gradient establishes. The size of the concentration gradient depends upon the voltage scan rate. There will be enough time for the diffusion layer to form a thicker layer in slow scan rate than that for fast scan rate. Thus, the flux at the electrode surface is considerably smaller at slow scan rate than at the faster scan rate (Pramanik et al., 2011 and Verma A., 2005). The current is proportional to the flux at the electrode. Thus, the magnitude of the current will be lower at slow scan rates. On the other hand, fuel is consumed high at higher scan rates during forward scan, and thus, a smaller amount of fuel is available for the further electrooxidation in the reverse scan. Therefore, the electrooxidation peak current density is found lower during a reverse scan at a faster scan rate. However, in fig (5.4a) to (5.4c) 50 mV/s was found as intermediate scan rate at which all sharp peaks are observed at relatively low over

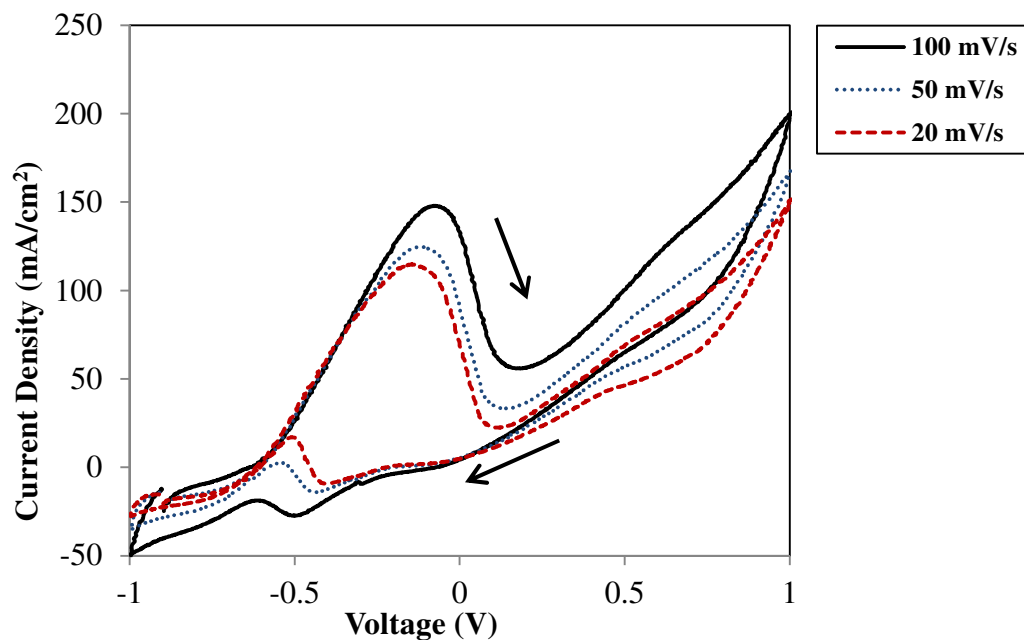


Figure 5.4a Cyclic voltammetry for 0.5 M methanol in 1 M KOH at different scan rate on Pt-Ru/C_{HSA} anode at the loading of 1 mg/cm²; Temperature 34 °C.

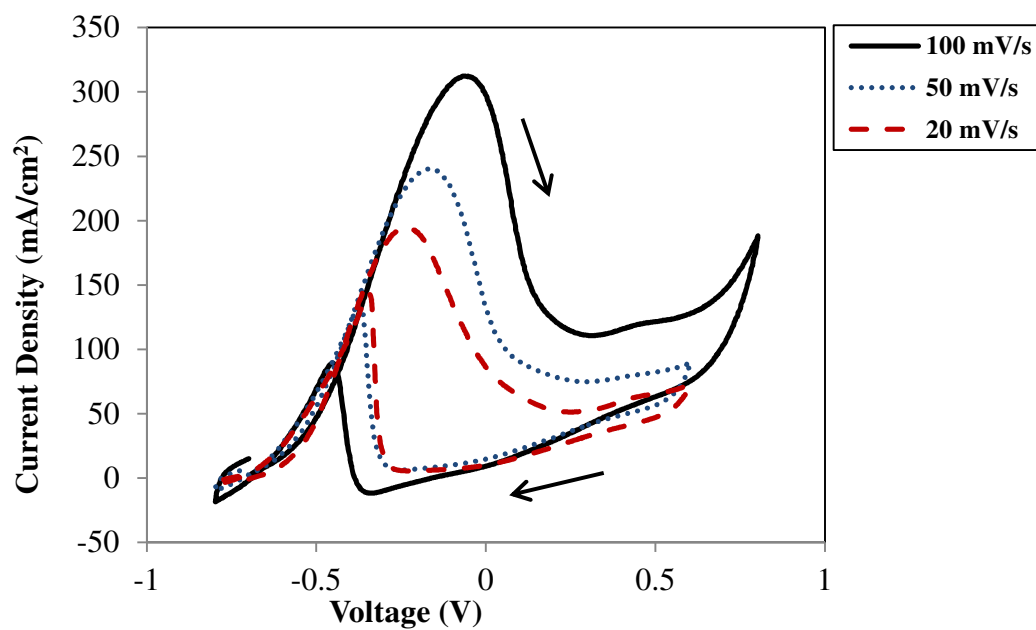


Figure 5.4b Cyclic voltammetry for 0.5 M ethanol in 1 M KOH at different scan rate on Pt-Ru/C_{HSA} anode at the loading of 1 mg/cm²; Temperature 34 °C.

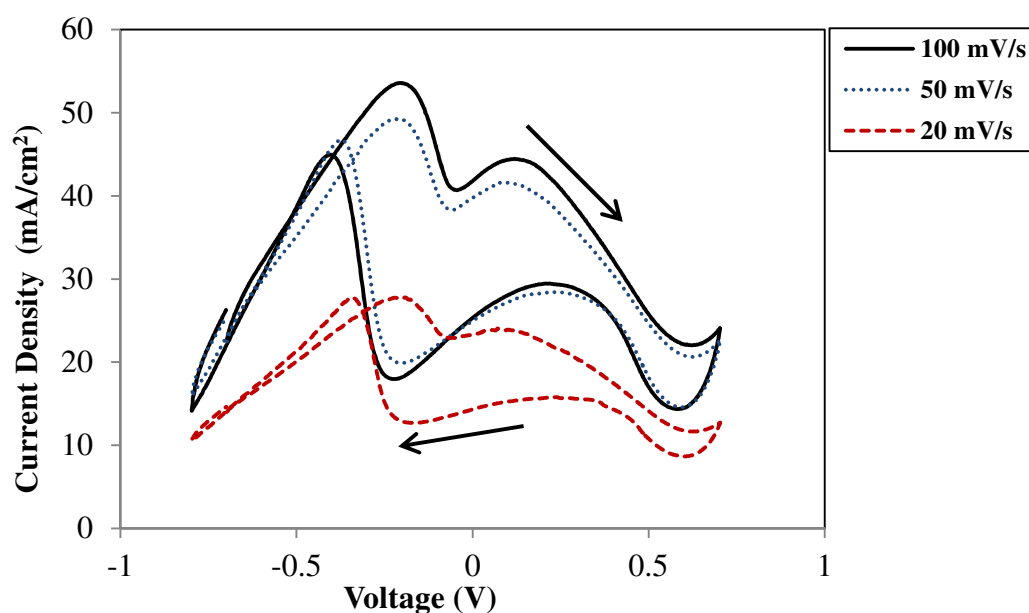


Figure 5.4c Cyclic voltammetry for 0.1 M NaBH₄ in 1 M KOH at different scan rate on Pt/C_{HSA} anode at loading of 1 mg/cm²; Temperature 40 °C.

the potential for all fuels, methanol, ethanol, and NaBH₄, respectively. Thus, 50 mV/s scan rate was considered for comparison of other parameters in cyclic voltammetry experiments.

It is observed from fig (5.4a) to (5.4c), the peak current density of 123.1 mA/cm² at a voltage of -0.15 V, 237.3 mA/cm² at a voltage of -0.19 V and 49.1 mA/cm² at a voltage of -0.23 V were obtained for methanol, ethanol and NaBH₄, respectively in the forward scan. However, the peak current density of 6.5 mA/cm² at a voltage of -0.57 V, 137.6 mA/cm² at a voltage of -0.37 V and 45.8 mA/cm² at a voltage of -0.35 V were achieved at reverse scan rate for the same cycle, respectively. It may be because the concentration of the adsorbed species was less in the reverse scan rate, released less number of electrons.

5.2.1.2 Effect of Fuel Concentration

Figs (5.5a) to (5.5c) show the effect of methanol, ethanol and NaBH_4 concentration on cyclic voltammetry in 1 M KOH solution, respectively. Fig (5.5a) shows that the peak current density increases with the increase in methanol concentration from 0.25 M to 0.5 M. However, further increases in fuel concentration from 0.5 M to 1 M, peak current density falls slightly. As per anode reaction (eq. 2.7, page no. 39), the presence of methanol and OH^- ions both are essential at anode electrode. Thus, there is delicate balance between methanol concentration and OH^- ion required to achieve maximum electrode performance. Moreover, the fuel concentration of 0.5 M methanol is the optimum at which activation loss is minimum and thus, it produces maximum peak current density at more negative potential (-0.144 V) in comparison to other concentrations of methanol fuel. Larminie and Dicks (2003) also explained that activation loss can be reduced by increasing the concentration of the reactant and system pressure. The maximum peak current density of 124.1 mA/cm^2 at a voltage of -0.14 V was obtained during the forward scan for the 0.5 M concentration of methanol. However, the peak current density of 6.5 mA/cm^2 at a voltage of -0.57 V was obtained at reversed scan for the same fuel concentration. The initial increase in peak current density may be because of the increase in methanol concentration. However, the availability of OH^- ion at the electrocatalyst site decreases with the further increase in methanol concentration. This implies the decrease in methanol electrooxidation reaction due to lesser availability of adsorbed OH^- on the catalyst sites. Hence, the peak current density decreases at higher concentration of methanol. The similar pattern is observed for the ethanol electrooxidation (Fig 5.5b) (Verma A., 2005). The maximum peak current density of 237.3 mA/cm^2 at a voltage of -0.19 V was obtained during the forward scan for the 0.5 M concentration of ethanol. However, the peak current density of 137.6

mA/cm^2 at a voltage of -0.37 V was obtained at reversed scan for the same fuel concentration.

It is seen in fig (5.5c) that the peak current density increases with the increase in NaBH_4 concentration from 0.05 M to 0.1 M . However, further increase in NaBH_4 concentration beyond 0.1 M no peak is observed in the forward and reverse scan as well. The maximum peak current density of $73.18 \text{ mA}/\text{cm}^2$ at a voltage of -0.18 V was obtained during the forward scan for the 0.1 M concentration of NaBH_4 . However, the peak current density of $70.6 \text{ mA}/\text{cm}^2$ at a voltage of -0.42 V was obtained at reversed scan for the same NaBH_4 concentration. This is because of the relative concentration of KOH to NaBH_4 reduces with the increase in NaBH_4 concentration.

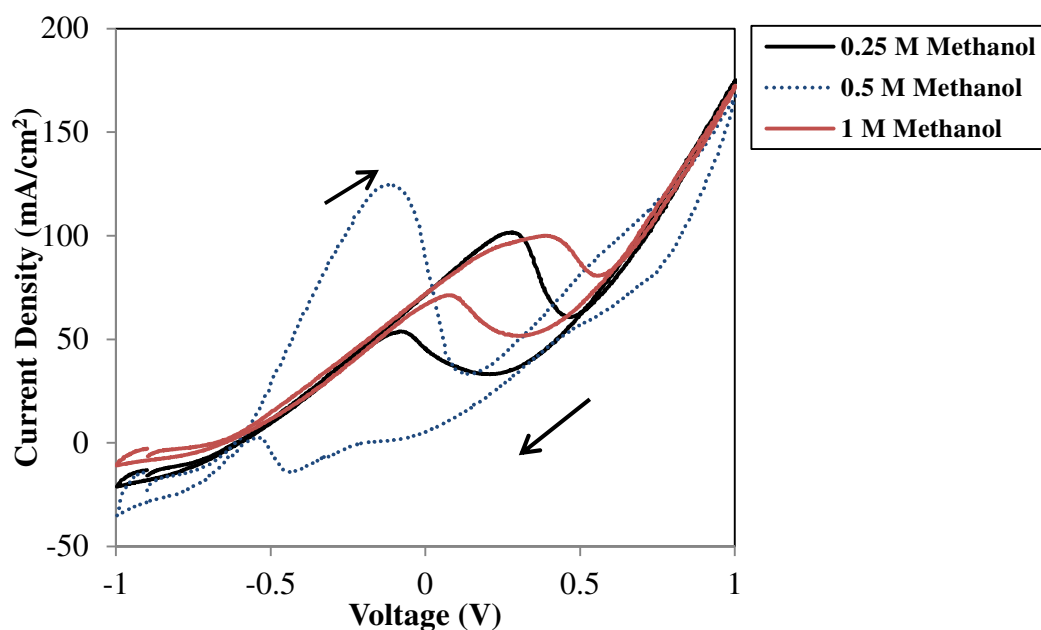


Figure 5.5a Cyclic voltammetry for different concentration of methanol in 1 M KOH as the electrolyte at 50 mV/s scan rate on $\text{Pt-Ru}/\text{C}_{\text{HSA}}$ anode of $1 \text{ mg}/\text{cm}^2$ loading; Temperature 34°C .

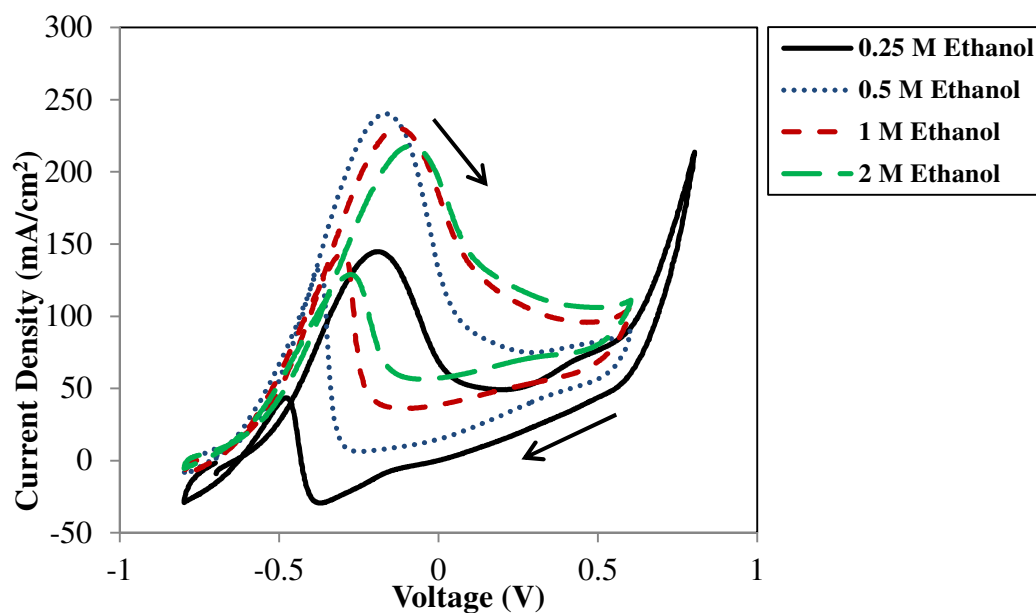


Figure 5.5b Cyclic voltammetry for different concentration of ethanol in 1 M KOH as the electrolyte at 50 mV/s scan rate on Pt-Ru/C_{HSA} anode of 1 mg/cm² loading; Temperature 34 °C.

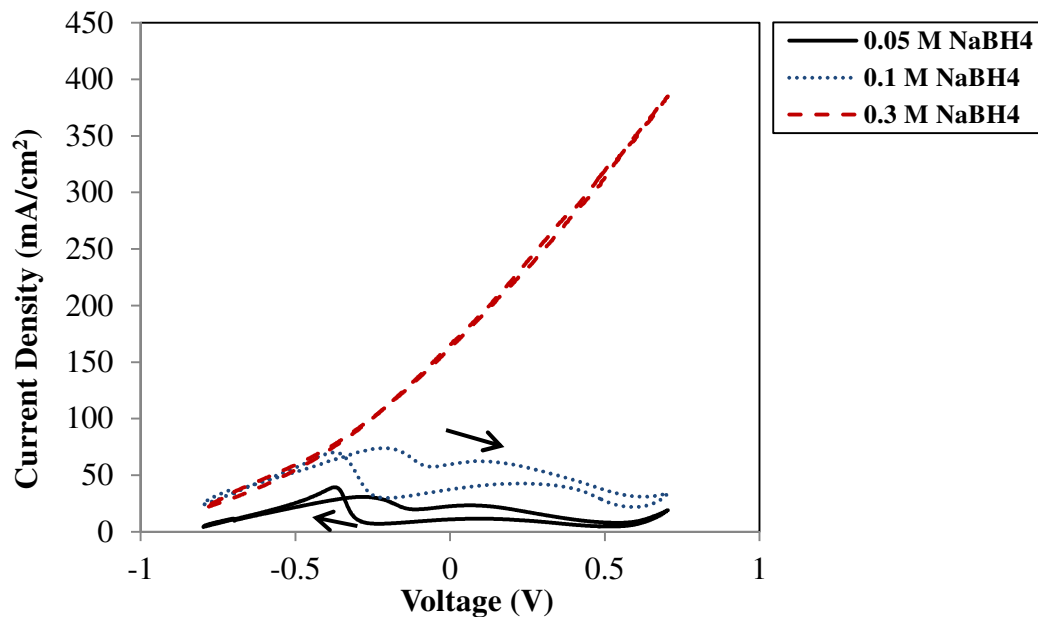


Figure 5.5c Cyclic voltammetry for different concentration of NaBH₄ in 1 M KOH as the electrolyte at 50 mV/s scan rate on Pt/C_{HSA} anode of 1 mg/cm² loading; Temperature 40 °C.

Thus, on increasing the NaBH_4 concentration, the hydrolysis dominates (Equation 5.8), and peak for NaBH_4 electrooxidation via hydrogen reduces (Equation 5.9) (Verma A., 2005).

5.2.1.3 Effect of Electrolyte Concentration

Fig (5.6a) to (5.6c) shows the cyclic voltammograms for different concentration of KOH solutions mixed with the fixed concentration of methanol, ethanol, and NaBH_4 as fuel, respectively. The electrolyte KOH perform the dual role in fuel electrooxidation process in the form of OH_{ad} species. First it takes part as an active intermediate in the fuel oxidation, and further, it helps in the formation of oxide species (Literature review section 2.1.5.1, page no. 36). It is noted that the peak current density increases with the increase in KOH concentration in the forward and reverse scan as well for all fuels. It may be because the increase in KOH concentration increases the OH_{ad} species on the electrocatalyst surface, which increases the electrooxidation of the fuel. However, the current density decreases with further increase in KOH concentration beyond 1 M. The maximum peak current density of 124.46 mA/cm^2 at a voltage of -0.13 V was observed for methanol fuel in the forward scan. However, the peak current density of 6.8 mA/cm^2 at a voltage of -0.58 V was achieved at reverse scan (Fig 5.6a). It may be due to the higher adsorption of OH^- ions on the electrocatalyst site compared to that of fuel molecules. The adsorption of OH^- on catalyst site at the higher concentration of KOH results in the PtO layer formation and create the hindrance for the electrooxidation of fuel molecules. Thus, the rate of electrooxidation reaction is slows down at electrocatalyst layer (Verma A., 2005).

A similar pattern was observed for 1 M ethanol fuel at the different concentration of KOH as shown in fig (5.6b) and reason could be similar as explained in case of methanol fuel.

The maximum peak current density of 239 mA/cm^2 at a voltage of -0.18 V was observed for methanol fuel in the forward scan. However, the peak current density of 132.5 mA/cm^2 at a voltage of -0.39 V was achieved at reverse scan (Fig 5.6b). Fig (5.6c) shows the cyclic voltammograms NaBH_4 fuel mixed with the different concentration of KOH solutions. The current density increases with the increase in KOH concentration from 0.5 M to 1 M . However, further increase in KOH concentration from 1 M to 1.5 M the peak current density decreases. The maximum peak current density of 72.9 mA/cm^2 at a voltage of -0.25 V was observed for NaBH_4 fuel in the forward scan. However, the peak current density of 68.3 mA/cm^2 at a voltage of -0.35 V was observed at reverse scan (Fig 5.6c). It implies that the hydrogen generation from NaBH_4 is the only preferential reaction at the concentration of 1 M KOH. On increasing the concentration of KOH from 0.5 M to 1 M the current density peaks are formed for NaBH_4 or hydrogen (Equation 5.7 and 5.8) (Page no. 101).

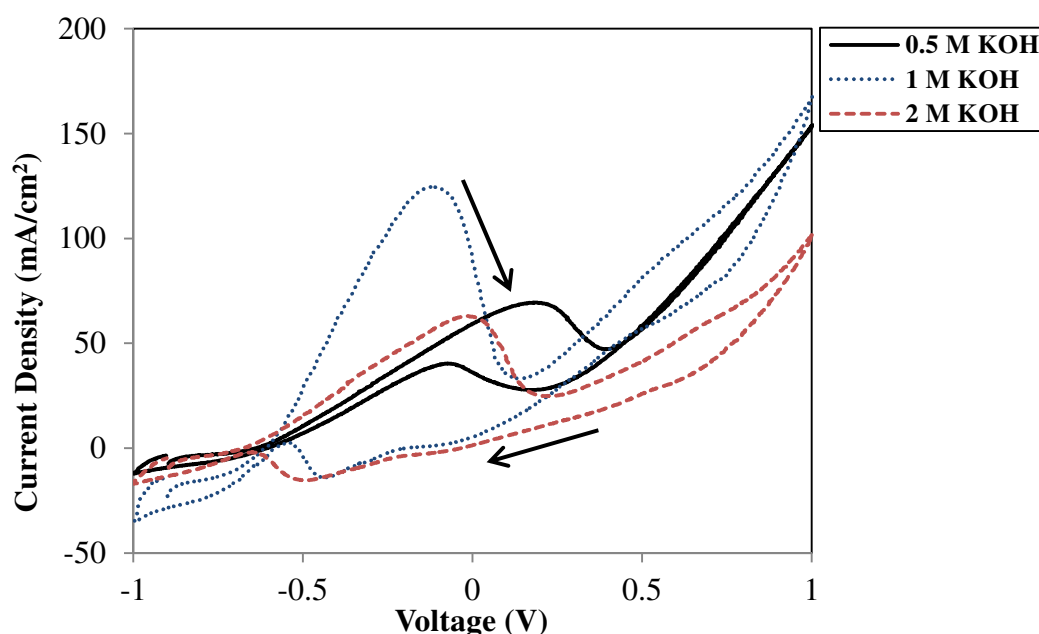


Figure 5.6a Cyclic voltammetry for 0.5 M methanol as fuel mixed with the different concentration of KOH at 50 mV/s scan rate on Pt-Ru/ C_{HSA} anode of 1 mg/cm^2 loading; Temperature 34°C .

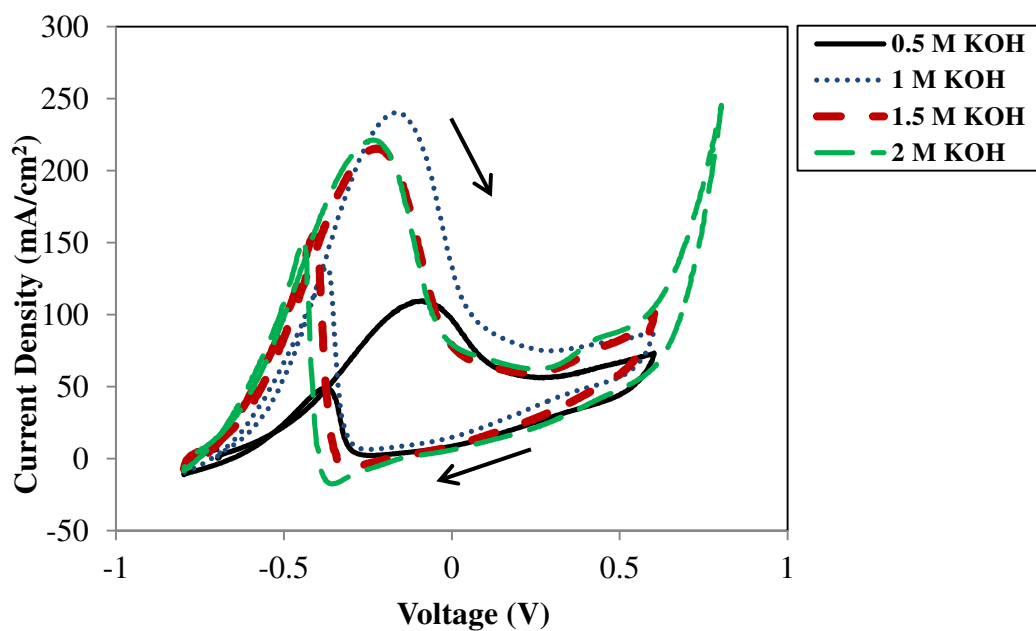


Figure 5.6b Cyclic voltammetry for 0.5 M ethanol as fuel mixed with the different concentration of KOH at 50 mV/s scan rate on Pt-Ru/C_{HSA} anode of 1 mg/cm² loading; Temperature 34 °C.

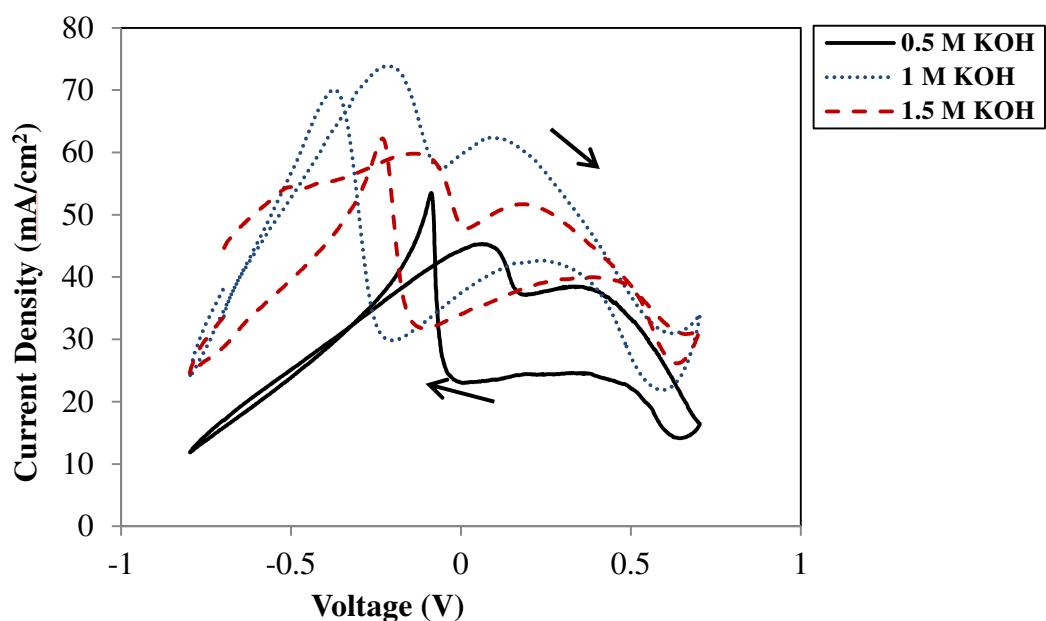


Figure 5.6c Cyclic voltammetry for 0.1 M NaBH₄ as fuel mixed with the different concentration of KOH at 50 mV/s scan rate on Pt/C_{HSA} anode of 1 mg/cm² loading; Temperature 40 °C.

electrooxidation. On further increasing the concentration of KOH from 1 M to 1.5 M the peaks reduces because of hindrance created due to the high amount of OH^- ion species for electrooxidation of fuel at the electrode surface.

5.2.1.4 Effect of Electrocatalyst Loading

Fig (5.7a) to (5.7c) shows the cyclic voltammograms for different loading of electrocatalyst at anode for methanol, ethanol, and NaBH_4 ranging from 0.5 mg/cm^2 to 2 mg/cm^2 . It should be noted that anode electrocatalyst for methanol and ethanol was Pt-Ru/ C_{HSA} and for sodium borohydride Pt/ C_{HSA} , respectively. Fig (5.7a) to (5.7c) show that the peak current density increases with the increase in electrocatalyst loading from 0.5 mg/cm^2 to 1 mg/cm^2 . However, further increase in electrocatalyst loading beyond 1 mg/cm^2 current density peak starts decreasing. This may be due to the increase in active sites of the electrocatalyst with the increase in electrocatalyst loading from 0.5 mg/cm^2 to 1 mg/cm^2 . Also, the electronic conductivity of the electrocatalyst layer increases. However, further increase in loading beyond 1 mg/cm^2 , results in electrocatalyst particle agglomeration and the electrocatalyst layer becomes compacted to the same size and the thickness of the electrode. Hence, the porosity of the electrocatalyst layer decreases, which results in poor mass transfer at the active electrocatalyst zone. The maximum peak current density of 182.28 mA/cm^2 , 142.65 mA/cm^2 , and 73.4 mA/cm^2 at a voltage of -0.14 V , -0.24 V and -0.24 V were obtained for methanol, ethanol and NaBH_4 , respectively in the forward scan at anode loading of 1 mg/cm^2 . However, the peak current density of -34.95 mA/cm^2 , 47.18 mA/cm^2 and 68.3 mA/cm^2 at a voltage of -0.57 V , -0.49 V and -0.35 V were obtained for methanol, ethanol, and NaBH_4 , respectively at reverse scan rate (Fig 5.7a to 5.7c). The electrocatalyst loading of 0.5 mg/cm^2 produces the peak current density of 123.3 mA/cm^2 , 86.44 mA/cm^2 and

51.20 mA/cm² at a voltage of -0.15 V, -0.27 V and -0.18 V for methanol, ethanol and NaBH₄, respectively. Thus, 1 mg/cm² of electrocatalyst loading is found to be optimum irrespective of fuel used in the cyclic voltammetry experiments

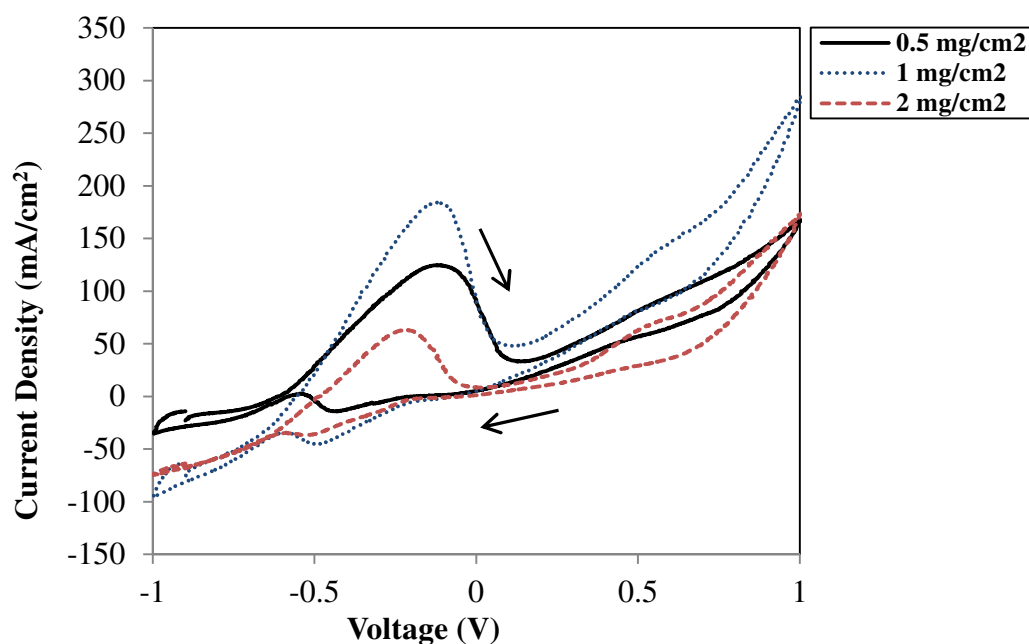


Figure 5.7a Cyclic voltammetry for 0.5 M methanol in 1 M KOH as the electrolyte at 50 mV/s scan rate using different anode loading of Pt-Ru/C_{HSA}; Temperature 34 °C.

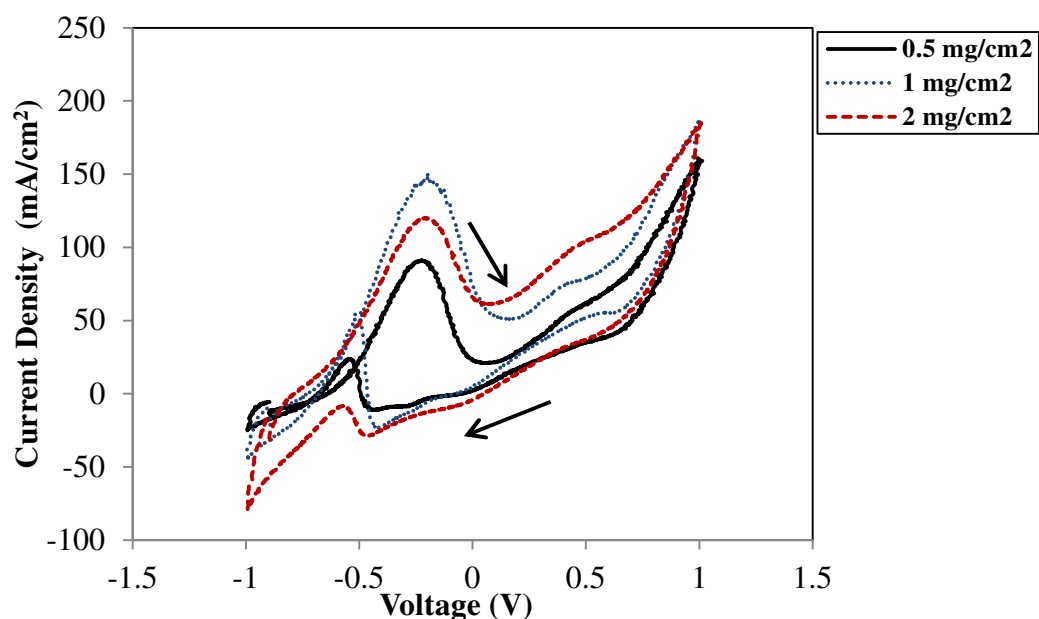


Figure 5.7b Cyclic voltammetry for 0.5 M ethanol in 1 M KOH as the electrolyte at 50 mV/s scan rate using different anode loading of Pt-Ru/C_{HSA}; Temperature 34 °C.

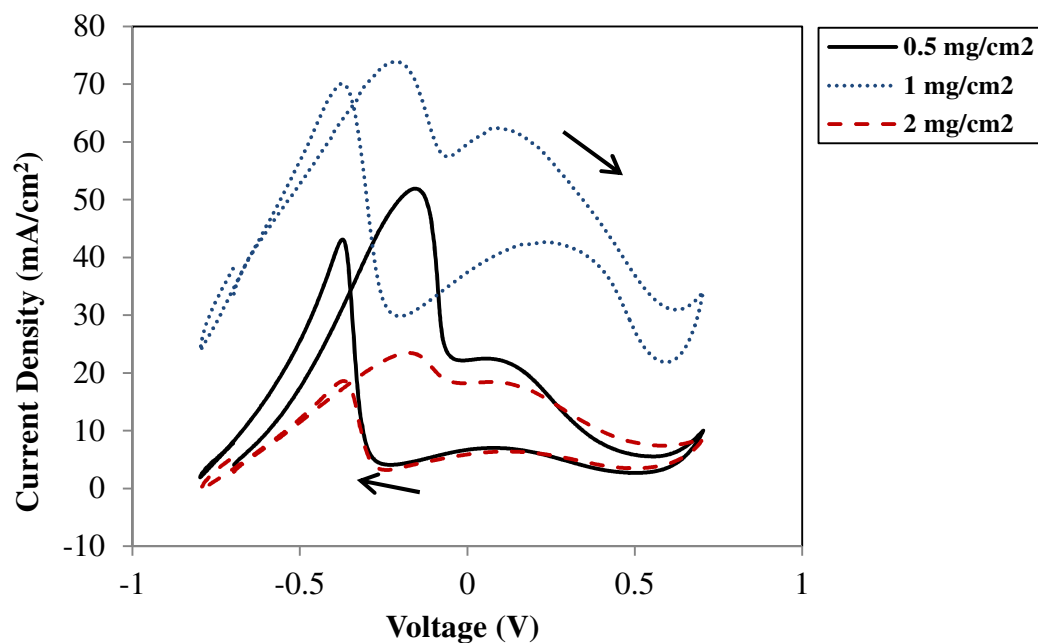


Figure 5.7c Cyclic voltammetry for 0.1 M NaBH₄ in 1 M KOH as the electrolyte at 50 mV/s scan rate using different anode loading of Pt/C_{HSA}; Temperature 40 °C.

5.2.2 Cathode

5.2.2.1 Oxygen as Oxidant

It is known from the literature that reaction kinetics of oxygen reduction is superior in an alkaline medium compared to acidic medium. The reduction reaction of oxygen in the alkaline medium generally precedes either by one or two pathways (Ortiz et al. 2003). (Equation 4.58 to 4.60) is described in chapter 4 (Page no. 87).

Fig (5.8a) shows the cyclic voltammogram of Pt/C_{HSA} electrode at loading of 1 mg/cm² and 10 mV/s scan rate using 1 M KOH in a nitrogen saturated solution. In fig (5.8a), no reduction peak is observed due to the absence of oxygen and thus, no reduction reactions cathode. Fig (5.8b) shows the cyclic voltammogram of Pt/C_{HSA} electrode at loading of 1 mg/cm² and 10 mV/s scan rate using 1 M KOH in an oxygen saturated solution from -1 to -0.2 V voltage span. The current density peaks for oxygen reductions are observed at -0.4 V and -0.8 V in the reverse scan corresponding to 2+2 electron pathways mechanism equation (4.59) and (4.60) (Page no. 87).

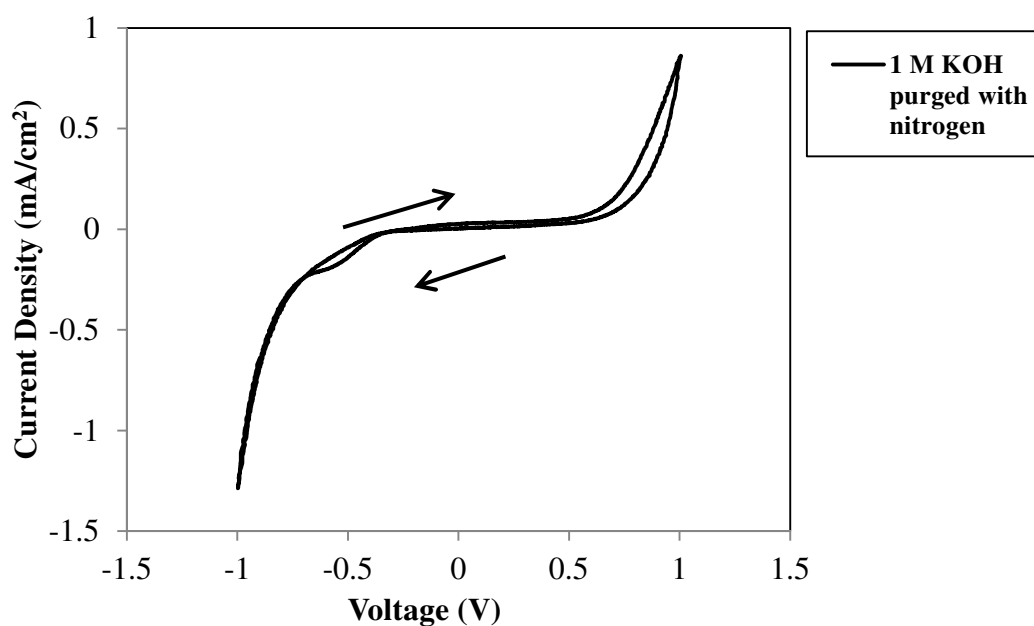


Figure 5.8a Cyclic voltammetry for Pt/C_{HSA} cathode at loading of 1 mg/cm² and 10 mV/s scan rate using 1 M KOH in a nitrogen saturated solution.

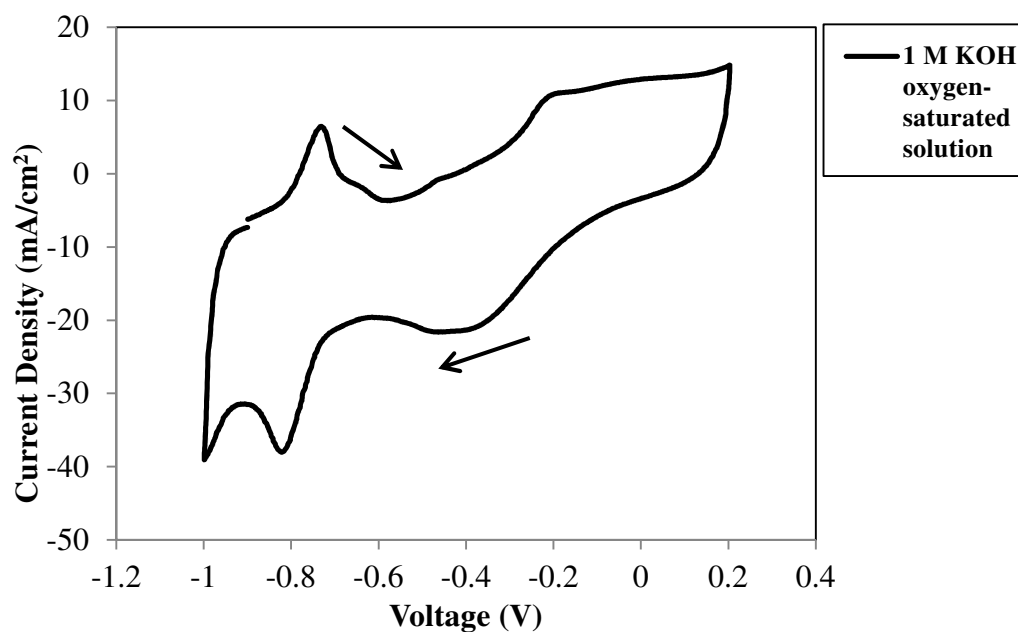


Figure 5.8b Cyclic voltammetry for Pt/C_{HSA} cathode at loading of 1 mg/cm² and 10 mV/s scan rate using 1 M KOH in an oxygen saturated solution.

5.2.2.2 Mixed Oxidant (H_2O_2 combined with oxygen saturated solution)

Fig (5.9) shows the cyclic voltammogram on Pt/ C_{HSA} electrode at loading of 1 mg/cm^2 and 10 mV/s scan rate using $2 \text{ M H}_2\text{O}_2$ mixed with 1 M KOH in an Oxygen-saturated solution (Mixed oxidant) from -1 V to 0.2 V voltage span. The reduction reactions with mixed oxidant also support 2+2 electrons mechanism. However, the first peak of oxygen reduction shifts from -0.4 V to -0.2 V (towards less negative potential) when H_2O_2 is mixed with oxygen saturated solution (Fig 5.9). The second reduction peak was observed at the same potential of -0.8 V for oxygen saturated and mixed oxidant conditions (Fig 5.9). The shifting of first reduction peak from -0.4 V to -0.2 V (towards less negative potential) shows that H_2O_2 mixed with oxygen saturated solution reduce activation loss due to the increase in the concentration of oxidant at cathode electrocatalyst sites followed by HO_2^- (Equation 4.59) formation at the cathode surface. This results in the elimination of the mass transfer limitations at high current density (Fig 5.9).

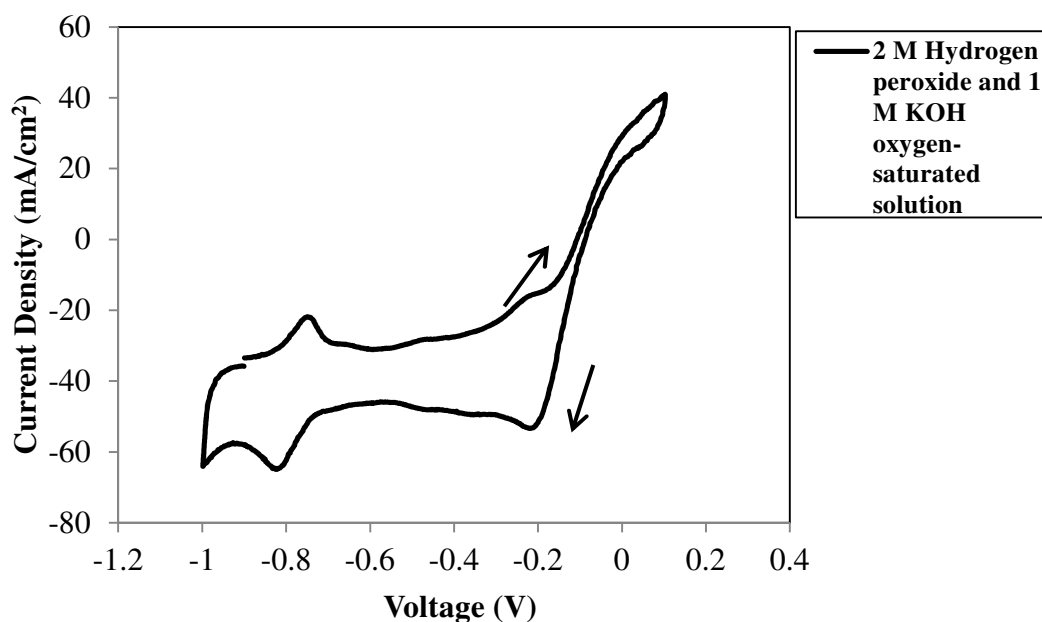


Figure 5.9 Cyclic voltammetry for Pt/ C_{HSA} cathode at the loading of 1 mg/cm^2 and 10 mV/s scan rate using $2 \text{ M H}_2\text{O}_2$ mixed with 1 M KOH in an oxygen saturated solution.

5.3 Single Cell Study

The performance of single air breathing microfluidic fuel cell was investigated after studying the electrooxidation of methanol, ethanol and sodium borohydride, and oxygen reduction on the prepared anode and cathode through half-cell analyses using cyclic voltammetry. The experimental results on single cell microfluidic fuel cell are presented below. The reasons for electrocatalyst selection at anode for methanol, ethanol, and NaBH_4 have been discussed in the section 5.3.6 effect of the electrocatalyst type (Page no. 131). Air (atmospheric oxygen) was used as oxidant at the air breathing cathode side unless it is mentioned specifically about another oxidant (H_2O_2 mixed with air). The air breathing microfluidic fuel cell experiments were performed to determine optimum condition of different parameters, such that maximum power density is obtained. The different parameters studied are electrolyte concentrations at anode and cathode, the concentration of fuel, electrocatalyst loading at anode and cathode, electrocatalyst type, cell temperature, type of gas diffusion layer and oxidant types.

5.3.1 Effect of Electrolyte Concentration at Anode

Figs (5.10a) to (5.10b) show the polarization and power density curves for fixed electrolyte concentration of 1 M KOH at the cathode with air breathing condition and varying electrolyte (KOH) concentration at anode mixed with 0.5 M methanol, 0.5 M ethanol and 0.05 M NaBH_4 as fuel, respectively. Ambient air was used as oxidant at the cathode. The anode and cathode electrocatalysts loading were 1 mg/cm^2 of Pt-Ru/ C_{HSA} and Pt/ C_{HSA} for methanol and ethanol, respectively. For NaBH_4 fuel, the electrocatalyst loading at anode and cathode were 1 mg/cm^2 of Pt/ C_{HSA} at both electrodes. All experiments were performed at room temperature (34°C for methanol, ethanol and 40°C for NaBH_4). Figs (5.10a) to

(5.10c) show that the cell voltage increases with the increase in KOH concentration from 0.5 M to 1 M for a particular load and then it decreases with further increase in KOH concentration for all fuels. Fig (5.10a) to (5.10c) indicate that 1 M KOH mixed with 0.5 M of methanol, 0.5 M of ethanol and 0.05 M of NaBH_4 results in maximum power density of 1.3 mW/cm^2 , 4.1 mW/cm^2 and 5.35 mW/cm^2 at a current density of 8.8 mA/cm^2 , 26.5 mA/cm^2 and 20 mA/cm^2 , respectively. Whereas, 2 M electrolyte (KOH) mixed with 0.5 M of methanol, 0.5 M of ethanol and 1.5 M KOH mixed with 0.05 M of NaBH_4 resulting in power density of 0.72 mW/cm^2 , 2.9 mW/cm^2 and 3.06 mW/cm^2 at a current density of 5.7 mA/cm^2 , 18.5 mA/cm^2 and 14 mA/cm^2 , respectively. The reason for the decrease in current density and voltage may be because of the relative decrease in concentration of fuel in the presence of high concentration of KOH. At higher concentration of electrolyte OH_{ad} species are not entirely consumed in the electrooxidation of fuel and the remaining OH_{ad} may begin to behave as poison species by blocking the active sites of the electrocatalyst. Hence, the rate of the electrochemical reaction slows down. This results in the decrease in cell performance in terms of voltage and current density. The similar trend was observed in cyclic voltammetry experiments also, as explained in the cyclic voltammetry analysis (Page no. 107).

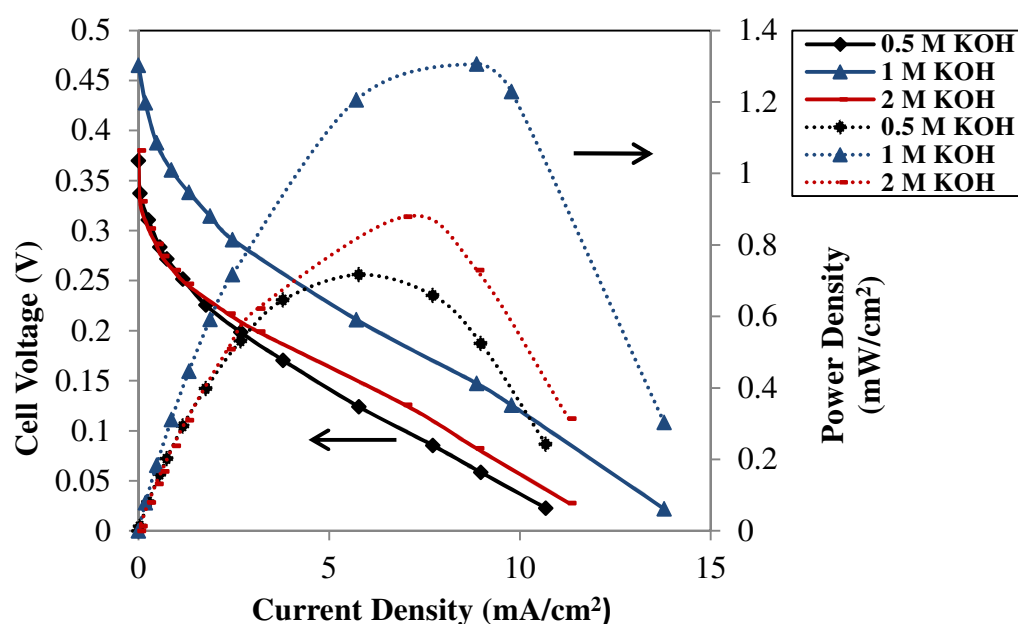


Figure 5.10a Current density vs. cell voltage and current density vs. power density curves for 0.5 M methanol mixed with the different concentration of KOH at the anode and fixed cathode electrolyte of 1 M KOH and air as an oxidant; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

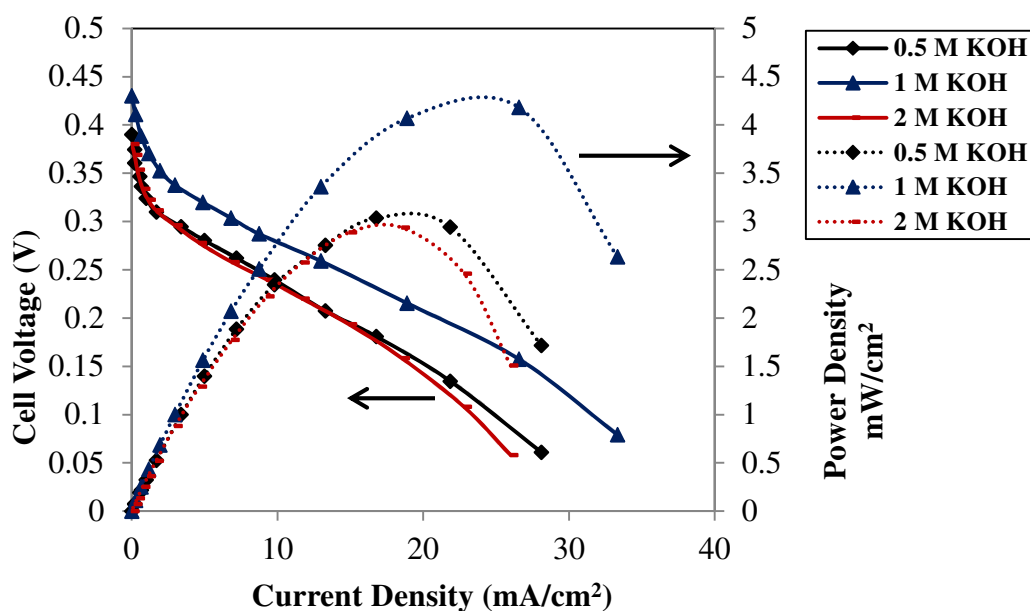


Figure 5.10b Current density vs. cell voltage and current density vs. power density curves for 0.5 M ethanol mixed with the different concentration of KOH at the anode and fixed cathode electrolyte of 1 M KOH and air as an oxidant; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

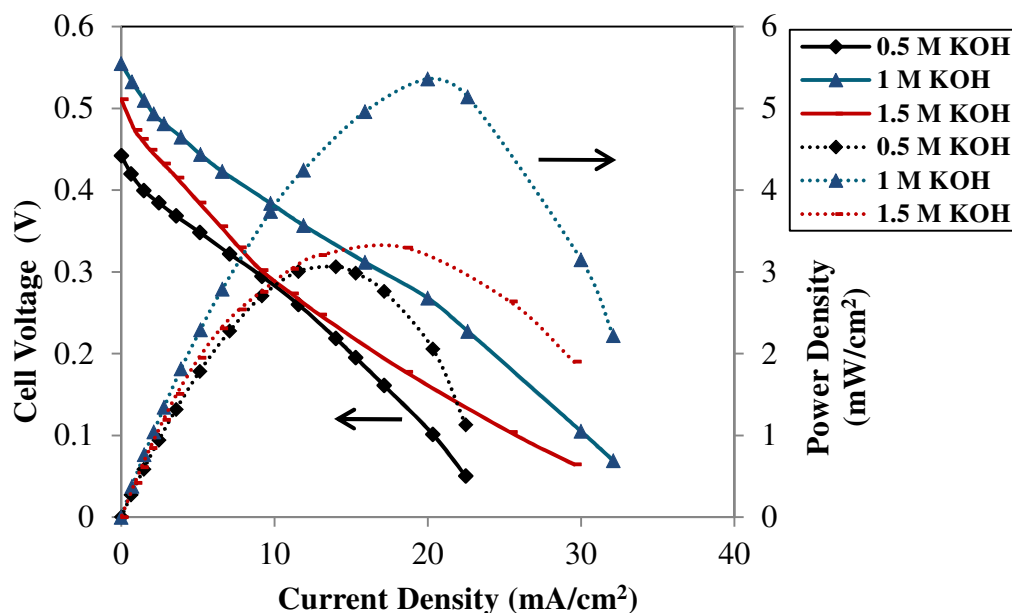


Figure 5.10c Current density vs. cell voltage and current density vs. power density curves for 0.05 M NaBH_4 mixed with the different concentration of KOH at the anode and fixed cathode electrolyte of 1 M KOH and air as an oxidant; Temperature 40 °C; Solid lines-polarization curves; Dotted lines-power density curves.

5.3.2 Effect of Electrolyte Concentration at Cathode

Figs (5.11a) to (5.11c) show the polarization and power density curves for different concentration of electrolyte (KOH) at cathode for a fixed electrolyte concentration at anode mixed with 0.5 M of methanol, 0.5 M of ethanol and 0.05 M of NaBH_4 as fuel, respectively. Ambient air was used as oxidant at the cathode. The anode and cathode electrocatalyst loadings were 1 mg/cm^2 Pt-Ru/ C_{HSA} and Pt/ C_{HSA} for methanol and ethanol, respectively. Whereas, for NaBH_4 the electrocatalyst loading at anode and cathode were Pt/ C_{HSA} of 1 mg/cm^2 . All experiments were performed at room temperature (34 °C for methanol, ethanol and 40 °C for NaBH_4). Figs (5.11a) to (5.11c) show that the cell voltage increases with the increase in KOH concentration from 0.5 M to 1 M for a particular load and then it decreases with further increase in KOH concentration for different fuels.

Initially, the current density and OCV increases with the increase in KOH concentration from 0.5 M to 1 M because the over potential reduces. However, at higher electrolyte concentration beyond 1 M, the coverage of the electrocatalyst layer by KOH increases and at the same time water concentration decreases in the solution. Thus, the cell performance decreases. It is shown in the reaction mechanism (Chapter 2 section 2.1.5.1, page no. 36) that the presence of water molecules is essential in the reaction at the cathode.

It is seen in Fig (5.11a) to (5.11b) that 1 M KOH results in a maximum power density of 0.65 mW/cm², 3.35 mW/cm² and 5.35 mW/cm² at a current density of 5.5 mA/cm², 18.15 mA/cm² and 20 mA/cm² for methanol, ethanol and NaBH₄, respectively. However, higher concentration of 2 M KOH for methanol and ethanol results in a maximum power density of 0.47 mW/cm² and 4.7 mW/cm² at current density of 4.7 mA/cm² and 11.8 mA/cm² and 1.5 M KOH for NaBH₄ results maximum power density of 4.6 mW/cm² at a current density of 18.2 mA/cm², respectively.

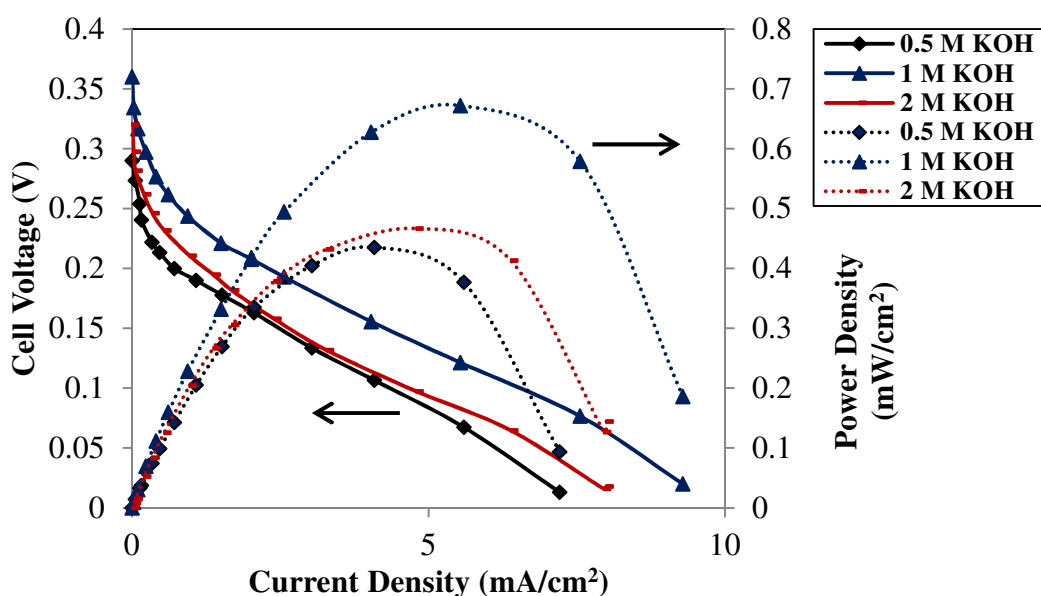


Figure 5.11a Current density vs. cell voltage and current density vs. power density curves for 0.5 M methanol and 0.5 M KOH as fuel using the different concentration of KOH at cathode and air as oxidant; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

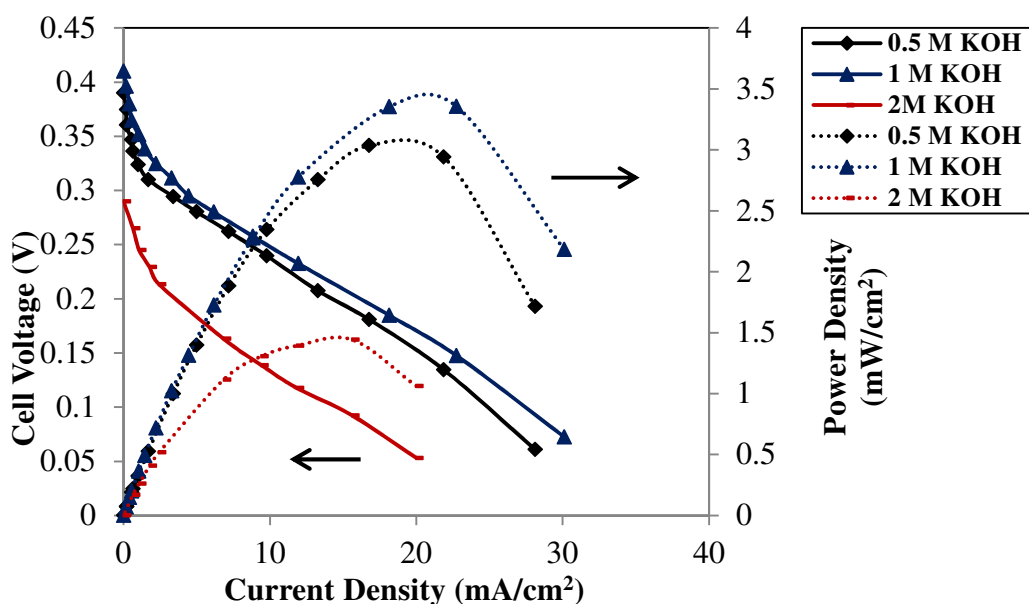


Figure 5.11b Current density vs. cell voltage and current density vs. power density curves for 0.5 M ethanol and 0.5 M KOH as fuel using the different concentration of KOH at cathode and air as oxidant; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

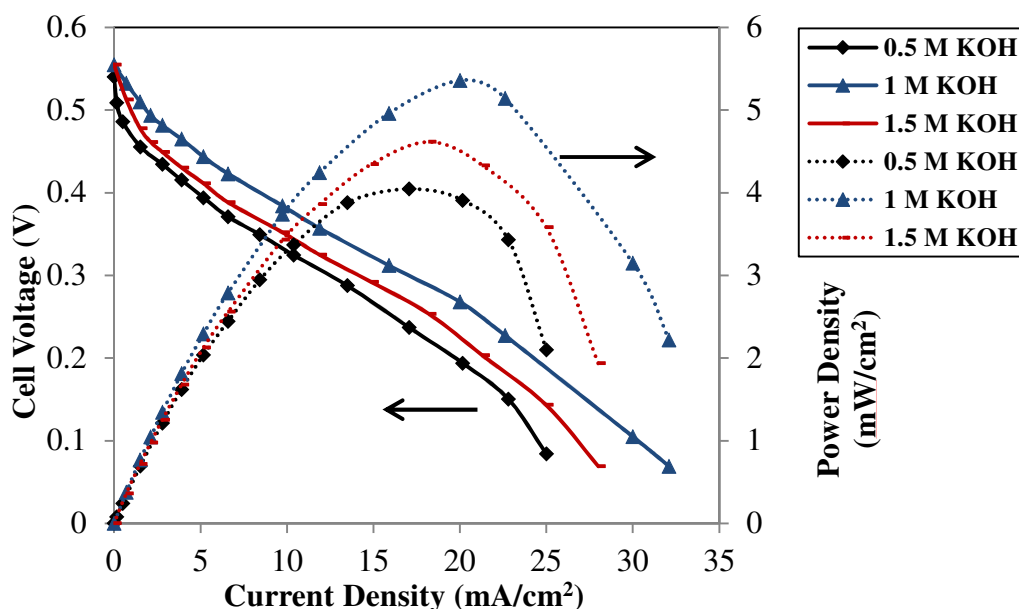


Figure 5.11c Current density vs. cell voltage and current density vs. power density curves for 0.05 M NaBH₄ and 1 M KOH as fuel using the different concentration of KOH at cathode and air as oxidant; Temperature 40 °C; Solid lines-polarization curves; Dotted lines-power density curves.

5.3.3 Effect of Fuel Concentration

Figs (5.12a) to (5.12c) show the polarization and power density curves for different concentration of methanol, ethanol and NaBH₄ mixed with an optimum concentration of electrolyte (1 M KOH). The concentration of electrolyte at cathode was optimum KOH of 1 M in the presence of atmospheric oxygen as oxidant. The anode and cathode electrocatalysts loading were 1 mg/cm² of Pt-Ru/C_{HSA} and Pt/C_{HSA} for methanol and ethanol, respectively. Whereas, for NaBH₄, the electrocatalyst of Pt/C_{HSA} loading at anode and cathode were 1 mg/cm². The Cell was operated at room temperature (34 °C for methanol, ethanol and 40 °C for NaBH₄). The cell performance in terms of voltage and current density increases with the increase in concentration from 0.25 M to 0.5 M of methanol and ethanol, respectively. However, further increase in concentration beyond 0.5

As the cell performance decreases (Fig 5.12a and 5.12b). Whereas, for NaBH_4 , the cell performance increases with the increase in the concentration of fuel from 0.05 M to 0.1 M and further increase in concentration the cell performance decreases (Fig 5.12c). Thus, the optimum concentration of fuel methanol and ethanol were found 0.5 M, and it was 0.1 M for NaBH_4 . The reason may be because of the decrease in OH^- ion mobility with the increase in fuel concentration. Also, the fractional coverage of the electrocatalyst layer by the fuel increases with the increase in fuel concentration. Hence, the active sites for the adsorption of OH^- ion, which plays an important role for fuel oxidation as discussed in cyclic voltammetry section, is blocked by fuel molecules and thus, OH^- ion get less opportunity to come in contact with the active electrocatalyst sites. In the case of NaBH_4 , the hydrolysis reaction dominates in the presence of high concentration of fuel.

The maximum OCV of 0.47 V, 0.43 V, and 0.66 V were obtained for methanol, ethanol, and NaBH_4 . The maximum power density of 1.3 mW/cm^2 , 4.1 mW/cm^2 and 8.4 mW/cm^2 at a current density of 8.8 mA/cm^2 , 26.5 mA/cm^2 and 34 mA/cm^2 were obtained for 0.5 M methanol, 0.5 M ethanol and 0.1 M NaBH_4 as a fuel mixed with 1 M KOH as electrolyte, respectively. In the cyclic voltammetry study similar trend was found for all fuels (Page no. 106 to 107).

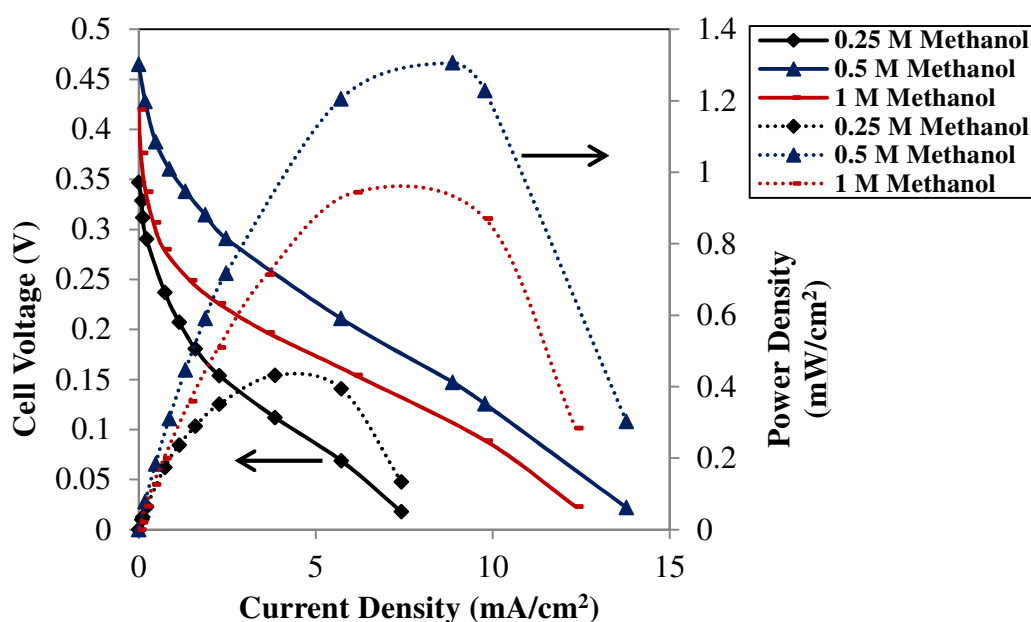


Figure 5.12a Current density vs. cell voltage and current density vs. power density curves for different concentration of methanol mixed with 1 M KOH as fuel using optimum concentration of electrolyte (1 M KOH) at cathode side and air as oxidant; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

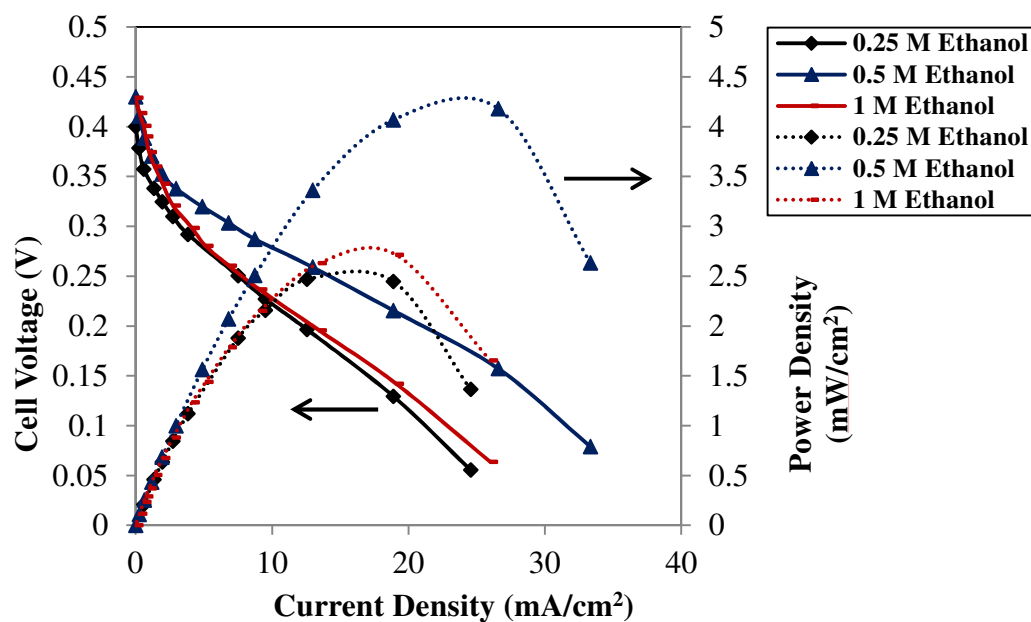


Figure 5.12b Current density vs. cell voltage and current density vs. power density curves for different concentration of ethanol mixed with 1 M KOH as fuel using optimum concentration of electrolyte (1 M KOH) at cathode side and air as oxidant; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

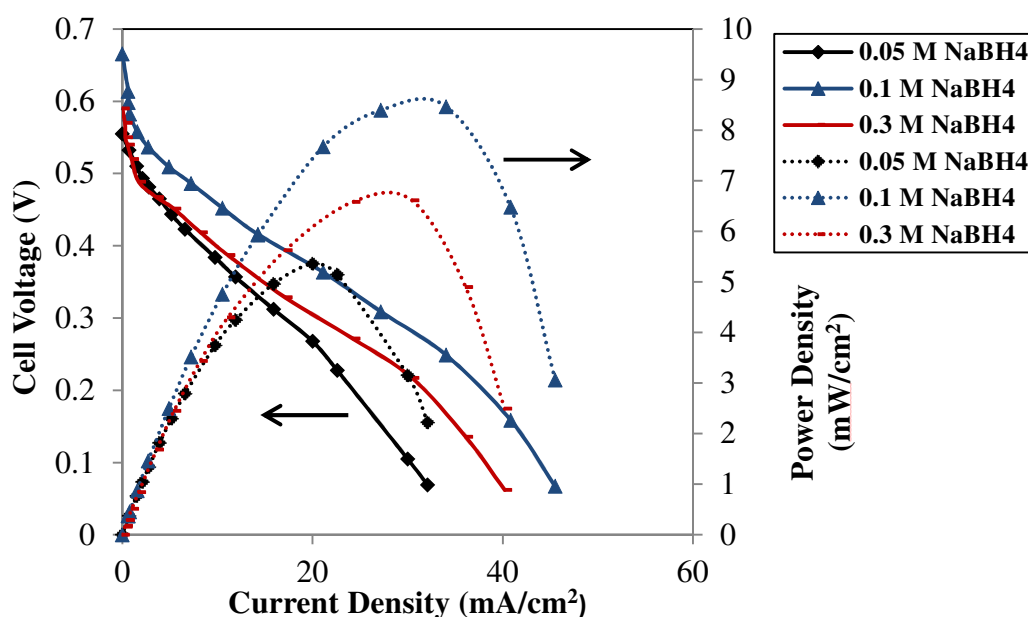


Figure 5.12c Current density vs. cell voltage and current density vs. power density curves for different concentration of NaBH₄ mixed with 1 M KOH as fuel using optimum concentration of electrolyte (1 M KOH) at cathode side and air as oxidant; Temperature 40 °C; Solid lines-polarization curves; Dotted lines-power density curves.

5.3.4 Effect of Electrocatalyst Loading at Anode

Fig (5.13a) to (5.13c) show the current density vs. cell voltage and current density vs. power density curves for methanol, ethanol and sodium borohydride fuels at different loadings i.e., 0.5 mg/cm², 1.0 mg/cm² and 2.0 mg/cm² at anode, respectively. The anode electrocatalyst was Pt-Ru/C_{HSA} for methanol and ethanol. For sodium borohydride, it was Pt/C_{HSA}. It is seen in fig (5.13a) to (5.13c) that the power density and current density increases with the increase in electrocatalyst loading from 0.5 mg/cm² to 1 mg/cm² at anode side irrespective of fuel used. While the further increase in electrocatalyst loading beyond 1 mg/cm², the cell performance starts decreasing. The reason for this decrease may be electrocatalyst particles agglomeration at higher loading in a same size and thickness of anode electrode. Due to agglomeration, the active sites of the electrocatalyst layer per unit

area of electrode decrease. This also results in the decrease in the porosity of the electrocatalyst layer, which offers increased diffusional resistance to mass transport of fuel from bulk to the electrocatalyst layer. The analysis of electrodes in SEM also shows the agglomeration of electrocatalyst layer at higher loading of anode and cathode electrode (Fig 5.2a to 5.2c and fig 5.3a to 5.3c, page no. 96 to 99). The above dependence of electrocatalyst loading is also observed in cyclic voltammograms (Fig 5.7a to 5.7c, page no. 112 to 113).

The maximum open circuit voltage of 0.47 V, 0.43 V and 0.65 V were obtained for anode loading of 1 mg/cm^2 using methanol, ethanol and sodium borohydride as fuel, respectively. The maximum power density of 1.3 mW/cm^2 , 4.1 mW/cm^2 and 5.6 mW/cm^2 at current density of 8.8 mA/cm^2 , 26.5 mA/cm^2 and 23 mA/cm^2 were achieved for methanol, ethanol and NaBH_4 fuels at the anode electrocatalyst loading of 1 mg/cm^2 . However, anode loading of 2 mg/cm^2 produced maximum power density of 0.95 mW/cm^2 , 2.3 mW/cm^2 and 1.8 mW/cm^2 at a current density of 5.1 mA/cm^2 , 20 mA/cm^2 and 10.6 mA/cm^2 for methanol, ethanol and sodium borohydride, respectively (Fig 5.13a to 5.13c).

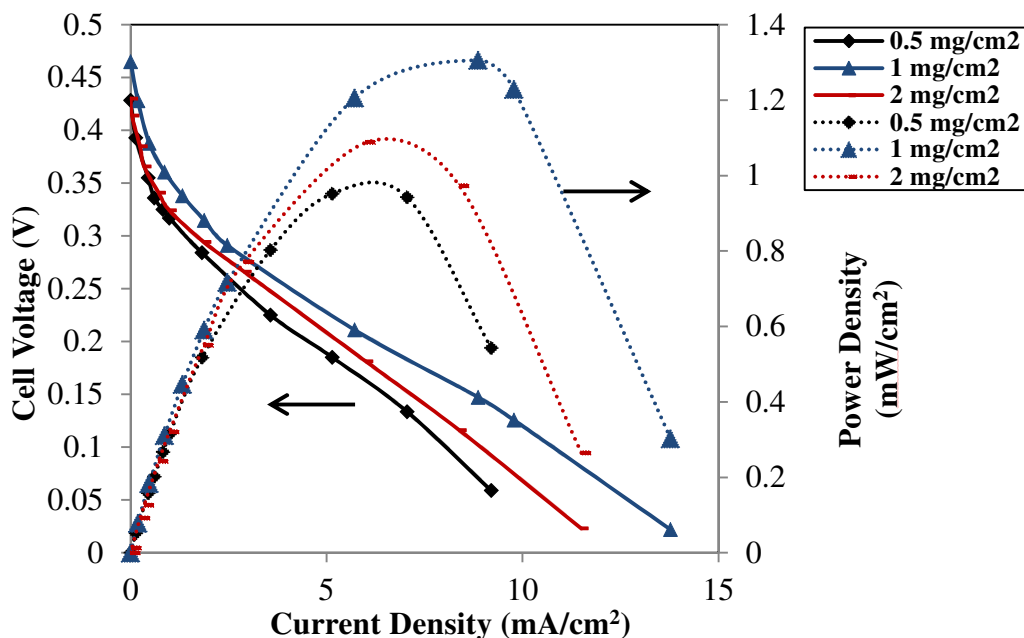


Figure 5.13a Current density vs. cell voltage and current density vs. power density curves for 0.5 M methanol mixed with 1 M KOH as electrolyte using different anode electrocatalyst loading of Pt-Ru/C_{HSA} and cathode at fixed loading of 1 mg/cm² Pt/C_{HSA}; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

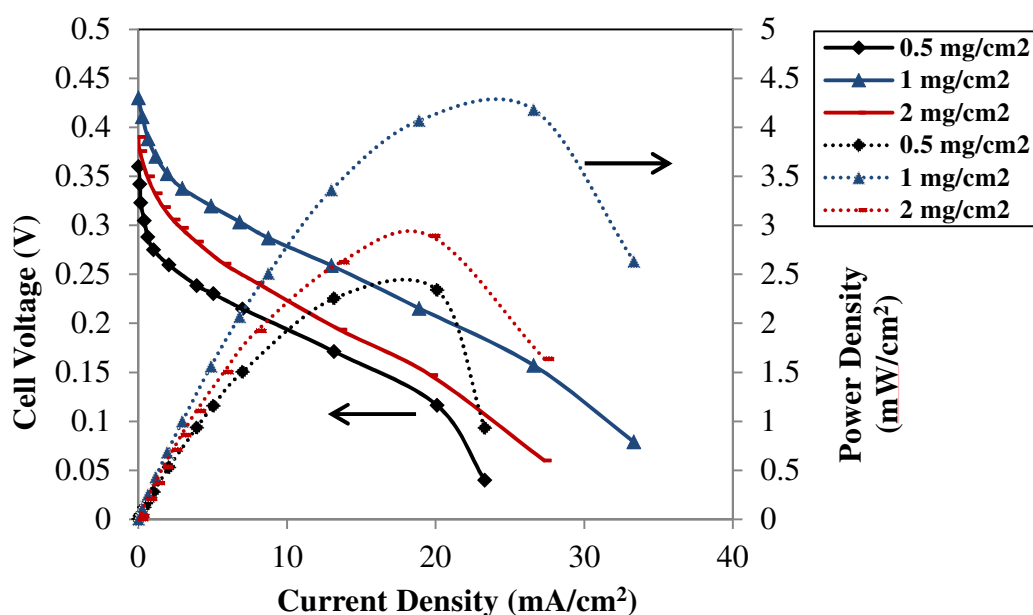


Figure 5.13b Current density vs. cell voltage and current density vs. power density curves for 0.5 M ethanol mixed with 1 M KOH as electrolyte using different anode electrocatalyst loading of Pt-Ru/C_{HSA} and cathode at fixed loading of 1 mg/cm² Pt/C_{HSA}; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

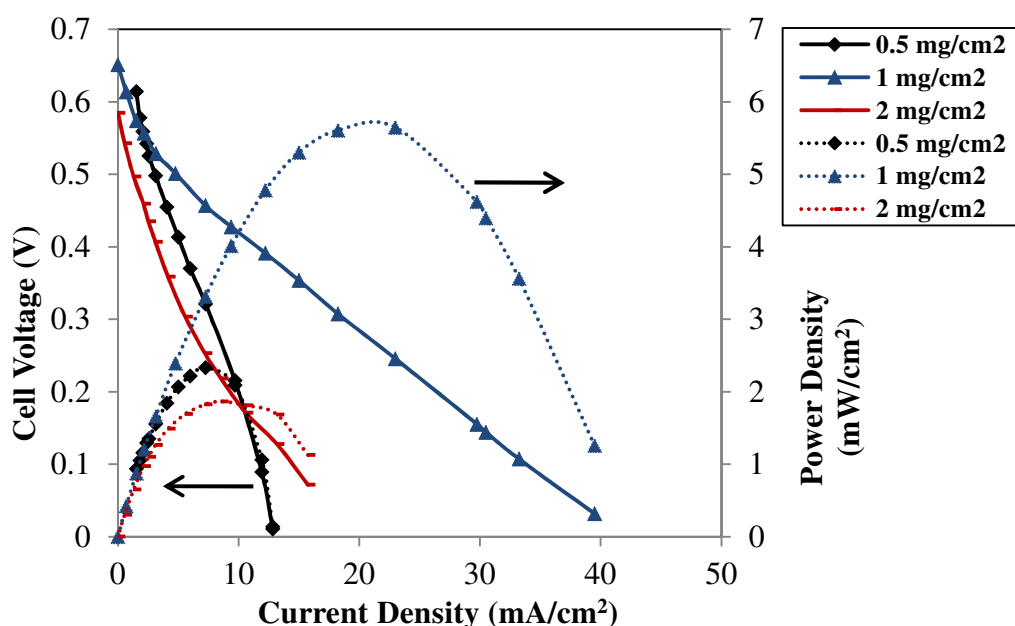


Figure 5.13c Current density vs. cell voltage and current density vs. power density curves for 0.1 M NaBH₄ mixed with 1 M KOH as electrolyte using different anode electrocatalyst loading of Pt/C_{HSA} and cathode at fixed loading of 0.5 mg/cm² Pt/C_{HSA}; Temperature 40 °C; Solid lines-polarization curves; Dotted lines-power density curves.

5.3.5 Effect of Electrocatalyst Loading at Cathode

Figs (5.14a) to (5.14c) show the current density vs. cell voltage and current density vs. power density curves. The similar trend was also noticed for varying cathode electrocatalyst loading as observed in fig (5.13a) to (5.13c). It is seen in the fig (5.14a) to (5.14c) the current density and power density increases with the increase in cathode electrocatalyst loading from 0.5 mg/cm² to 1 mg/cm² for all fuels. However, further increase in the electrocatalyst loading from 1 mg/cm² to 2 mg/cm² the cell performance decreases irrespective of the fuel used at the anode.

The maximum open circuit voltage of 0.47 V, 0.43 V and 0.66 V were obtained for cathode loading of 1 mg/cm² using methanol, ethanol and sodium borohydride as fuel, respectively.

The maximum power density of 1.3 mW/cm^2 , 4.1 mW/cm^2 and 8.46 mW/cm^2 at current density of 8.8 mA/cm^2 , 26.5 mA/cm^2 and 34.04 mA/cm^2 were achieved for methanol, ethanol and NaBH_4 fuels at cathode electrocatalyst loading of 1 mg/cm^2 . However, cathode loading of 2 mg/cm^2 produced maximum power density of 1.2 mW/cm^2 , 3.2 mW/cm^2 and 4.54 mW/cm^2 at a current density of 8 mA/cm^2 , 23.7 mA/cm^2 and 23.62 mA/cm^2 for methanol, ethanol and sodium borohydride, respectively (Fig 5.14a to 5.14c).

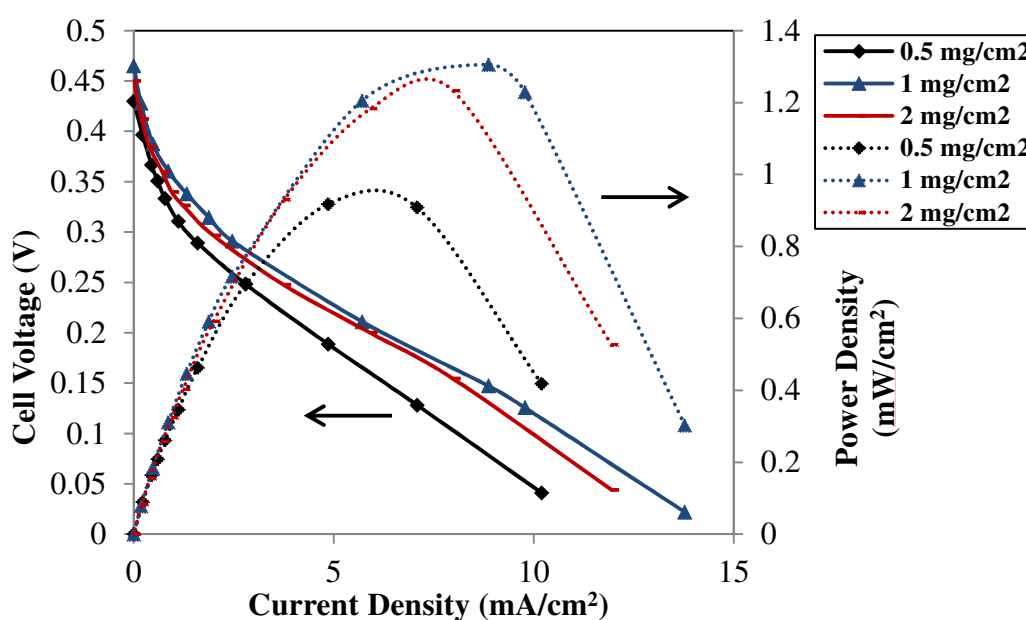


Figure 5.14a Current density vs. cell voltage and current density vs. power density curves for 0.5 M methanol mixed with 1 M KOH as electrolyte at different cathode electrocatalyst loading of Pt/ CHSA and anode at fixed loading of 1 mg/cm^2 Pt-Ru/ CHSA ; Temperature 34°C ; Solid lines-polarization curves; Dotted lines-power density curves.

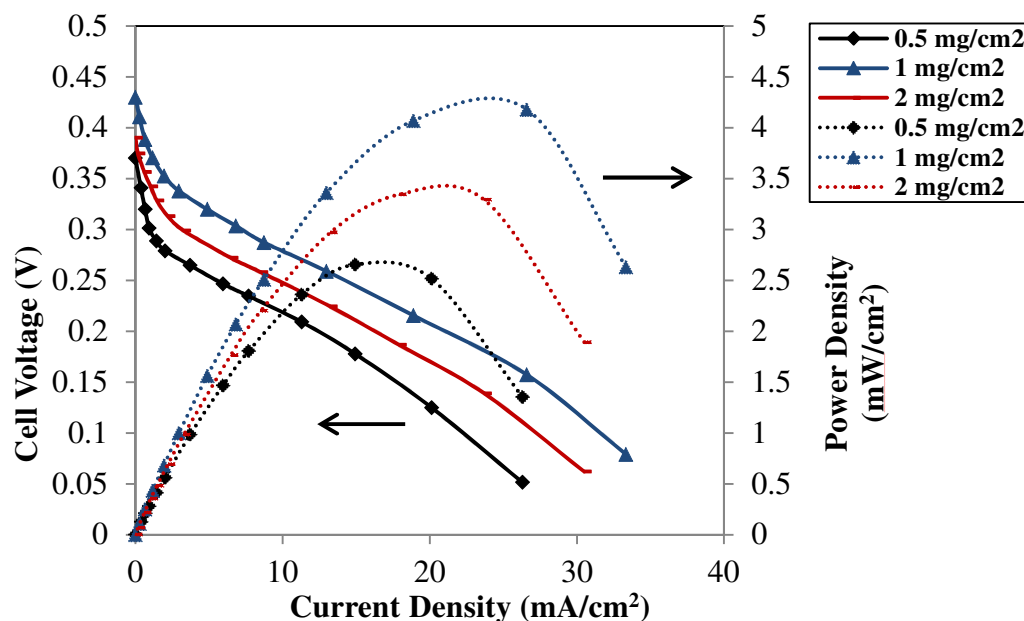


Figure 5.14b Current density vs. cell voltage and current density vs. power density curves for 0.5 M ethanol mixed with 1 M KOH as electrolyte at different cathode electrocatalyst loading of Pt/C_{HSA} and anode at fixed loading of 1 mg/cm² Pt-Ru/C_{HSA}; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

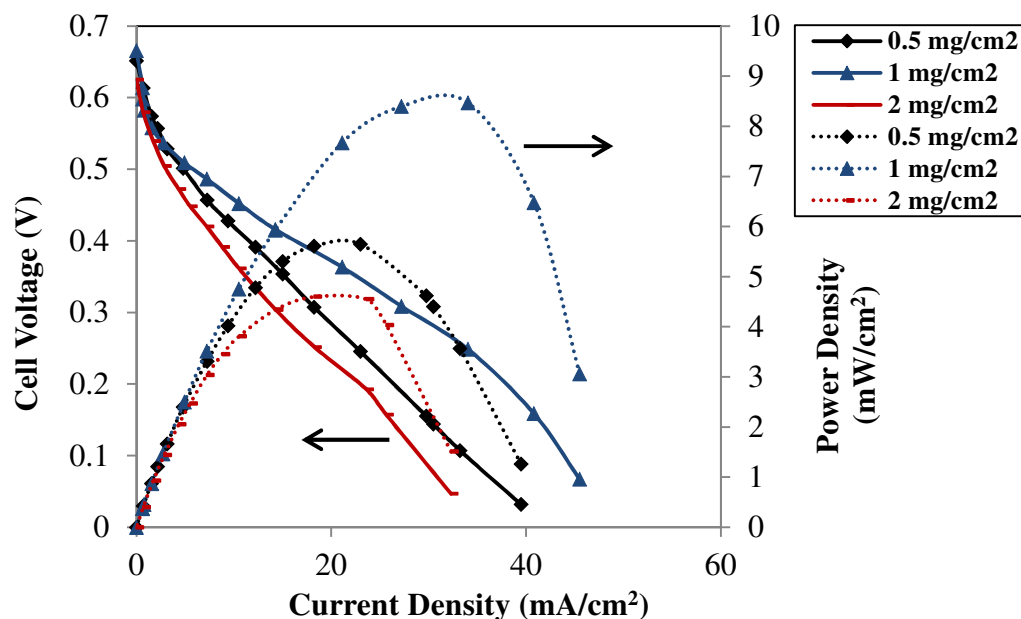


Figure 5.14c Current density vs. cell voltage and current density vs. power density curves for 0.1 M NaBH₄ mixed with 1 M KOH as electrolyte at different cathode electrocatalyst loading of Pt/C_{HSA} and anode at fixed loading of 1 mg/cm² Pt/C_{HSA}; Temperature 40 °C; Solid lines-polarization curves; Dotted lines-power density curves.

5.3.6 Effect of Electrocatalyst Type

The current density vs. cell voltage and current density vs. power density characteristics for methanol, ethanol, and sodium borohydride fuels for different anode electrocatalyst are shown in fig (5.15a) to (5.15b). The different anode electrocatalysts tested are Pt-Ru (30%:15% by wt.)/High Surface Area Carbon (C_{HSA}) (Alfa Aesar, USA) and Pt (40% by wt.)/ C_{HSA} (Alfa Aesar, USA) of 1 mg/cm^2 for each fuel. The cathode electrocatalyst used was Pt (40 % by wt.)/ C_{HSA} of 1 mg/cm^2 . Figs (5.15a) to (5.15b) show that the performance of the air breathing microfluidic fuel cell is slightly higher with Pt/Ru/ C_{HSA} electrocatalyst when methanol or ethanol was used as fuel. It is well known that Pt-Ru/ C_{HSA} plays a bi-functional role for methanol ethanol electrooxidation. Ru plays an important role in water dissociation followed by CO oxidation to CO_2 at low overpotential during methanol and ethanol electrooxidation. Moreover, Ru is a good CO tolerant catalyst for methanol and ethanol oxidation. The property of Ru is to supply OH_{ad} species to increase the oxidation of adsorbed CO and enhances the activity of electrocatalyst (Gasteiger et al. 1993). Thus, the CO formed as a side reaction is oxidized, and the poisoning effect is reduced (Tripkivic et al. 2002). There is no role of bimetallic electrocatalyst for the bi-functional mechanism in case of NaBH_4 as fuel. Hence, the performance of microfluidic fuel cell for NaBH_4 as fuel is not much affected irrespective of different anode electrocatalyst tested (Fig 5.15c). However, the cell performance for NaBH_4 fuel in the presence of Pt/ C_{HSA} electrocatalyst is slightly higher than that for Pt-Ru/ C_{HSA} electrocatalyst. The anode electrocatalyst Pt-Ru/ C_{HSA} produces the power density of 1.3 mW/cm^2 , 4.1 mW/cm^2 and 8.86 mW/cm^2 for methanol, ethanol and sodium borohydride, respectively. Whereas, Pt/ C_{HSA} anode produces the power density of 1.02 mW/cm^2 , 2.94 mW/cm^2 and 8.46 mW/cm^2 for methanol, ethanol and sodium borohydride, respectively. Thus, for air breathing

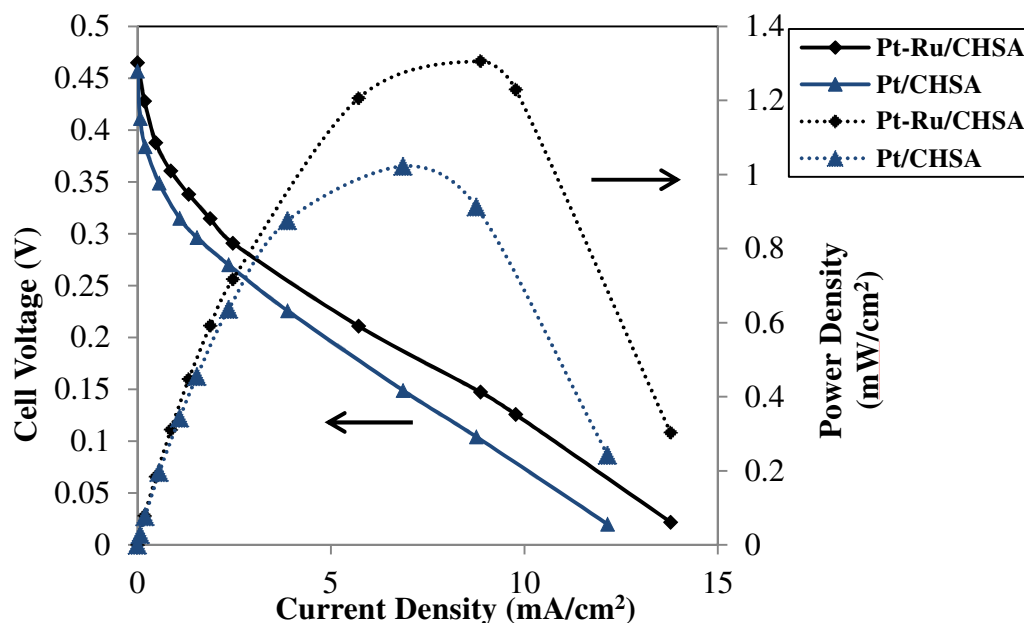


Figure 5.15a Current density vs. cell voltage and current density vs. power density curves for 0.5 M methanol mixed with 1 M KOH as electrolyte using different anode electrocatalyst at fixed cathode Pt/CHSA; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

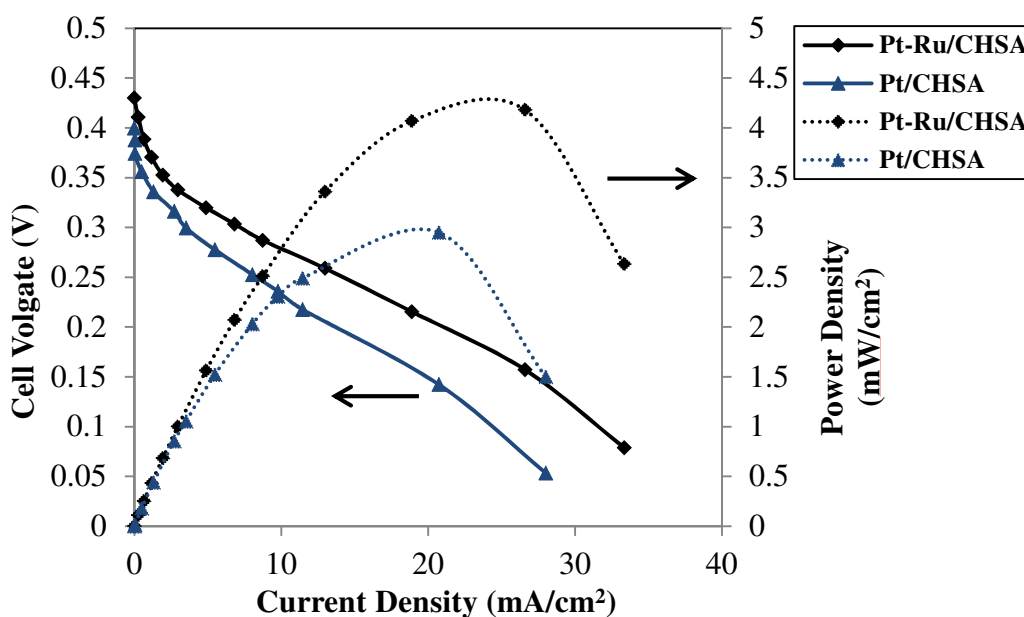


Figure 5.15b Current density vs. cell voltage and current density vs. power density curves for 0.5 M ethanol mixed with 1 M KOH as electrolyte using different anode electrocatalyst at fixed cathode Pt/CHSA; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

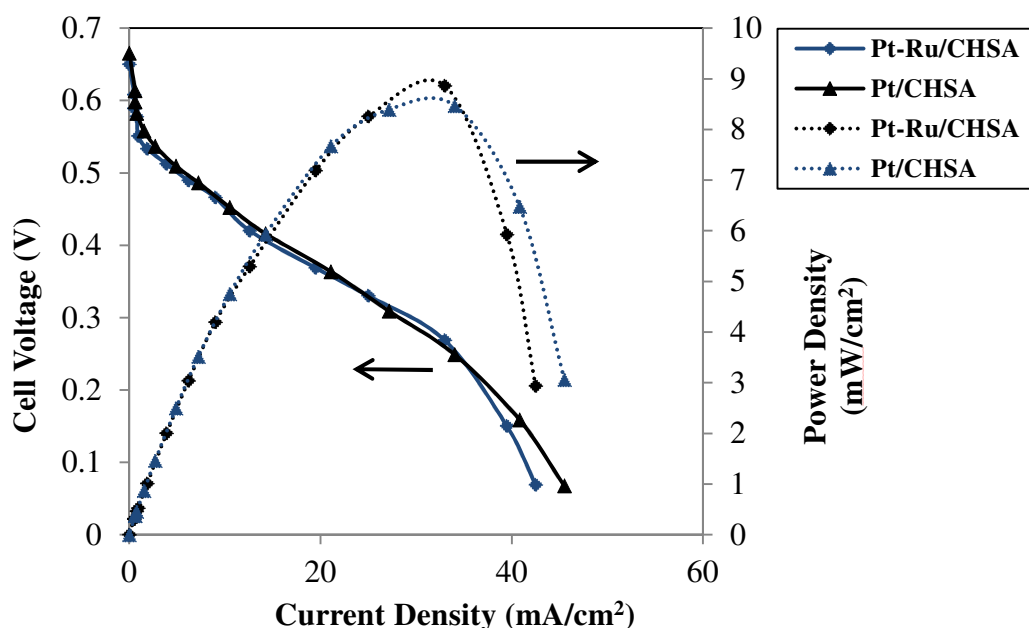


Figure 5.15c Current density vs. cell voltage and current density vs. power density curves for 0.1 M NaBH_4 mixed with 1 M KOH as electrolyte using different anode electrocatalyst at fixed cathode $\text{Pt}/\text{C}_{\text{HSA}}$; Temperature 40 °C; Solid lines-polarization curves; Dotted lines-power density curves.

microfluidic fuel cell study, $\text{Pt-Ru}/\text{C}_{\text{HSA}}$ was chosen as anode electrocatalyst for methanol and ethanol, respectively and for NaBH_4 fuel, $\text{Pt}/\text{C}_{\text{HSA}}$ was used as anode electrocatalyst in all experiments.

5.3.7 Effect of Temperature

The current density vs. cell voltage and current density vs. power density characteristics for methanol, ethanol and sodium borohydride fuels at 33 °C, 50 °C and 65 °C is shown in fig (5.16a) to (5.16c). It is seen in fig (5.16a) to (5.16c) that the microfluidic fuel cell performance increases with increase in temperature because of the decrease in activation overpotential, which results in higher rate of reactions and current density for all fuels. The

ionic conductivity and mobility also improved at high temperature, which results in the decrease in ohmic polarization. In addition, the performance of microfluidic fuel cell using sodium borohydride as fuel shows increasing trends in current density and cell voltage at the higher temperature. The reason for this increase may be, hydrogen gas generation from sodium borohydride by hydrolysis reaction (Equation 5.8) (Page no. 101). Generated hydrogen gas gets adsorbed on the surface of electrocatalyst which results in improved electrooxidation kinetics.

Fig (5.16a) to (5.16c) show that the maximum power density of 1.75 mW/cm^2 , 5.09 mW/cm^2 and 11.22 mW/cm^2 at a current density of 7.87 mA/cm^2 , 29.38 mA/cm^2 and 34.9 mA/cm^2 were obtained at the cell temperature of 65°C for methanol, ethanol and NaBH_4 , respectively. Whereas, at a room temperature (33°C), the maximum power density of 1.30 mW/cm^2 , 4.18 mW/cm^2 and 8.46 mW/cm^2 at a current density of 8.86 mA/cm^2 , 26.58 mA/cm^2 and 34.04 mA/cm^2 were obtained for methanol, ethanol and NaBH_4 , respectively. The experimental studies show the significant increase in microfluidic fuel cell performance in terms of current density and power density at high temperature. It should be noted that the microfluidic fuel cell temperature was not increased beyond 65°C , keeping in mind the low boiling point of methanol, ethanol and high dissociation of NaBH_4 at high temperature. The formation of fuel vapor and H_2 gas bubble would possibly create hindrance at high temperature.

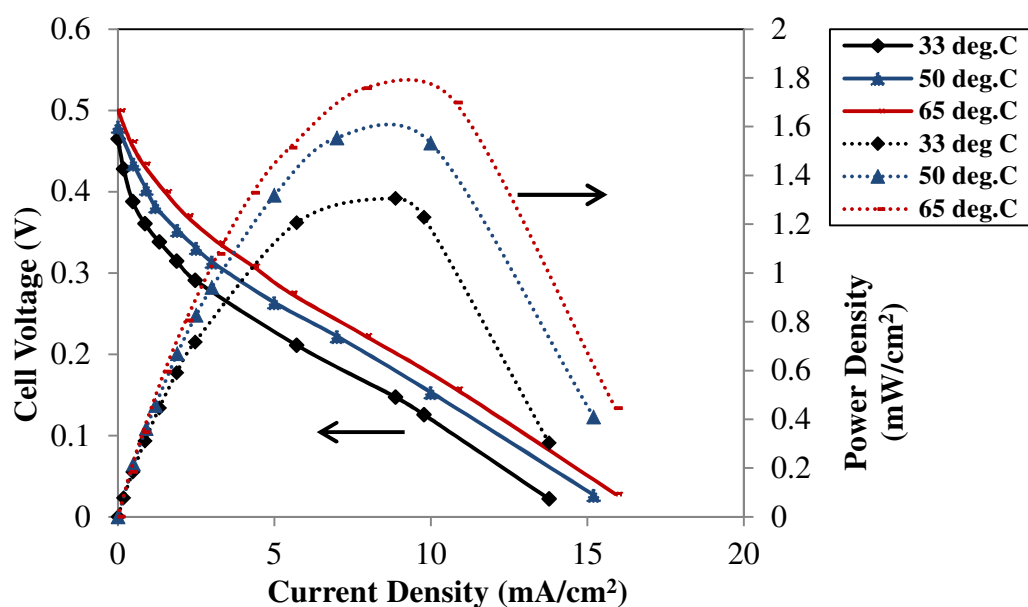


Figure 5.16a Current density vs. cell voltage and current density vs. power density curves using different temperatures of MFC for methanol concentration of 0.5 M mixed with 1 M KOH as electrolyte on Pt-Ru/C_{HSA} anode and Pt/C_{HSA} cathode at the loading of 1 mg/cm²; Solid lines-polarization curves; Dotted lines-power density curves.

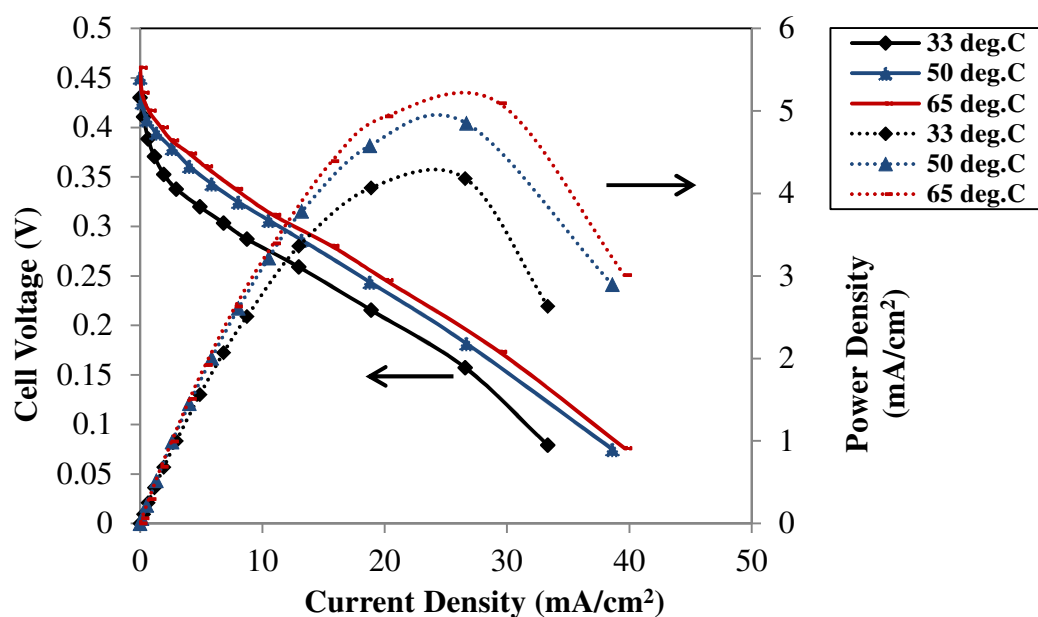


Figure 5.16b Current density vs. cell voltage and current density vs. power density curves using different temperatures of MFC for ethanol concentration of 0.5 M mixed with 1 M KOH as electrolyte on Pt-Ru/C_{HSA} anode and Pt/C_{HSA} cathode at the loading of 1 mg/cm²; Solid lines-polarization curves; Dotted lines-power density curves.

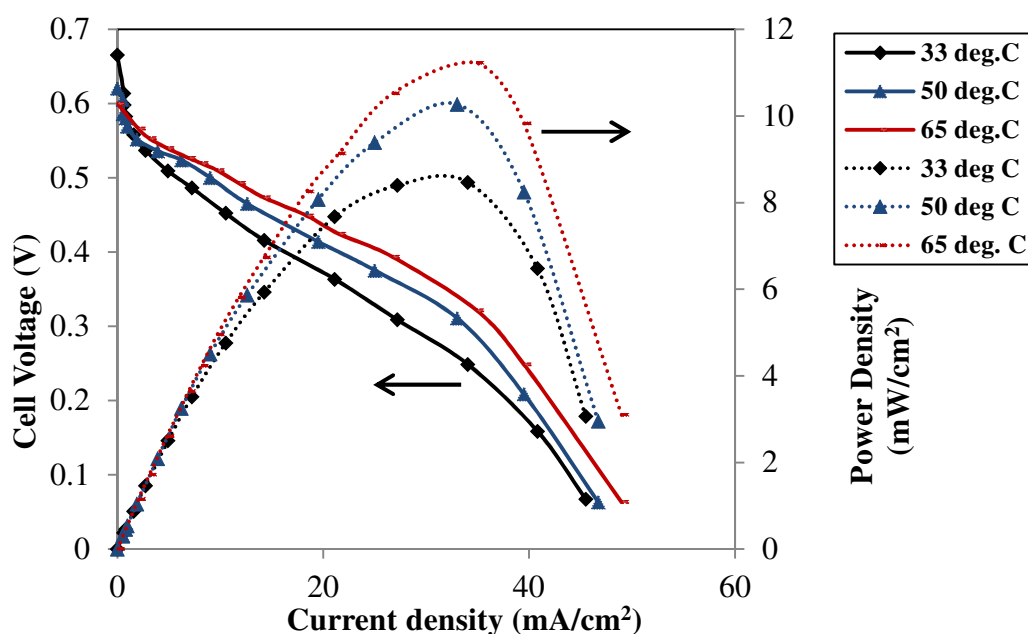


Figure 5.16c Current density vs. cell voltage and current density vs. power density curves using different temperatures of MFC for NaBH_4 concentration of 0.1 M mixed with 1 M KOH as electrolyte on Pt/C_{HSA} anode and cathode at the loading of 1 mg/cm^2 ; Solid lines-polarization curves; Dotted lines-power density curves.

5.3.8 Effect of Gas Diffusion Layer (GDL) or Carbon Paper

Fig (5.17) shows the current density vs. cell voltage, and current density vs. power density characteristics using commercial Toray Carbon paper, (TGP-H-60, Alfa Aesar, USA) and IIT (BHU) laboratory made carbon paper for anode fuel methanol and air as oxidant at the cathode. Commercial Toray carbon paper (TGP-H-60) in comparison to IIT (BHU) laboratory made carbon paper gives better performance when it is used as a substrate for anode and cathode fabrication (Fig 5.17). It may be due to higher ohmic resistance, and low porosity of IIT (BHU) lab made GDL carbon cloth. The higher ohmic resistance offers high ohmic polarization and similarly, high mass transfer resistance through the gas diffusion layer in the microfluidic fuel cell results in concentration polarization.

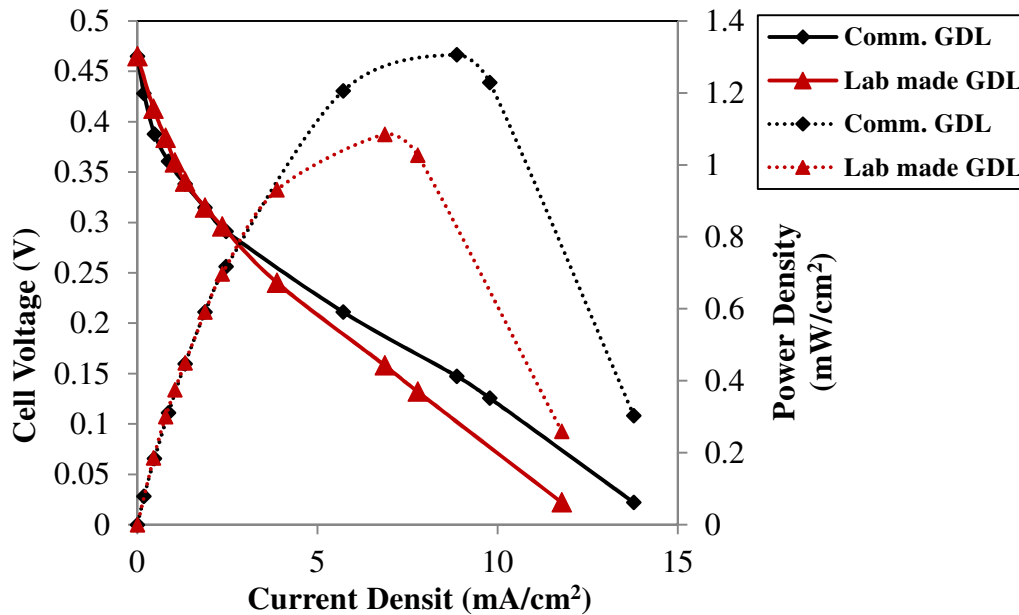


Figure 5.17 Current density vs. cell voltage and current density vs. power density curves using different Gas diffusion layers of MFC for methanol concentration of 0.5 M mixed with 1 M KOH as electrolyte on Pt-Ru/C_{HSA} anode and Pt/C_{HSA} cathode at loading of 1 mg/cm²; Solid lines-polarization curves; Dotted lines-power density curves.

Fig. (5.17) Shows the maximum power density of 1.3 mW/cm² at a current density of 8.86 mA/cm² for commercial Toray carbon paper. Whereas, the power density of 1.08 mW/cm² at a current density of 6.86 mA/cm² was obtained for IIT (BHU) laboratory made carbon paper, due to better performance of commercial GDL. Though, it was used in all experiments until unless it is not mentioned. Here, similar trends were observed for ethanol and NaBH₄ as anode fuels. The IIT (BHU) laboratory made GDL was used for the anode and cathode fabrication for some experiments using methanol and ethanol as fuel. The experimental results (j-v characteristics) are reported in the Appendix (A2).

5.3.9 Effect of Oxidant Type at Cathode

Fig (5.18) shows the polarization and power density curves for optimum fuel concentration of 0.5 M methanol mixed with optimum 1 M KOH as the electrolyte at the anode. The oxidants at cathode were H_2O_2 of different concentration mixed with 1 M KOH and combined with ambient oxygen through air breathing cathode (mixed oxidant). It noted from the fig. (5.43) that the polarization and power density curves shift upward with the increase in hydrogen peroxide concentration from 1 M to 2 M. However, the curve shifts downward with the further increase in H_2O_2 concentration beyond 2 M. The maximum open circuit voltage (OCV) 0.69 V was obtained for the 2 M H_2O_2 concentration.

The maximum current density of 38.4 mA/cm^2 was obtained from the microfluidic fuel cell for 2 M H_2O_2 oxidant mixed with 1 M KOH as an electrolyte in the presence of air breathing cathode conditions. Whereas, short circuit current density of 31.2 mA/cm^2 was obtained for 3 M H_2O_2 oxidant mixed with 1 M KOH in the presence of air breathing cathode condition. The maximum power density of 5.45 mW/cm^2 at a current density of 29.15 mA/cm^2 was obtained from the microfluidic fuel cell using 2 M H_2O_2 at the cathode with air breathing condition (mixed oxidant). Whereas, 3 M H_2O_2 with air breathing condition produced the power density of 4.1 mW/cm^2 at a current density of 19.5 mA/cm^2 .

It is noted from the fig (5.18) that the OCV at the cathode is increased for mixed oxidant compared to air as oxidant at the cathode. As discussed in the cyclic voltammetry experiments (Fig 5.18) the use of H_2O_2 combined with atmospheric oxygen increases the concentration of oxidant at the cathode side thus, it reduced the activation loss and

improved OCV. The current density is also improved due to the improved electrode kinetics.

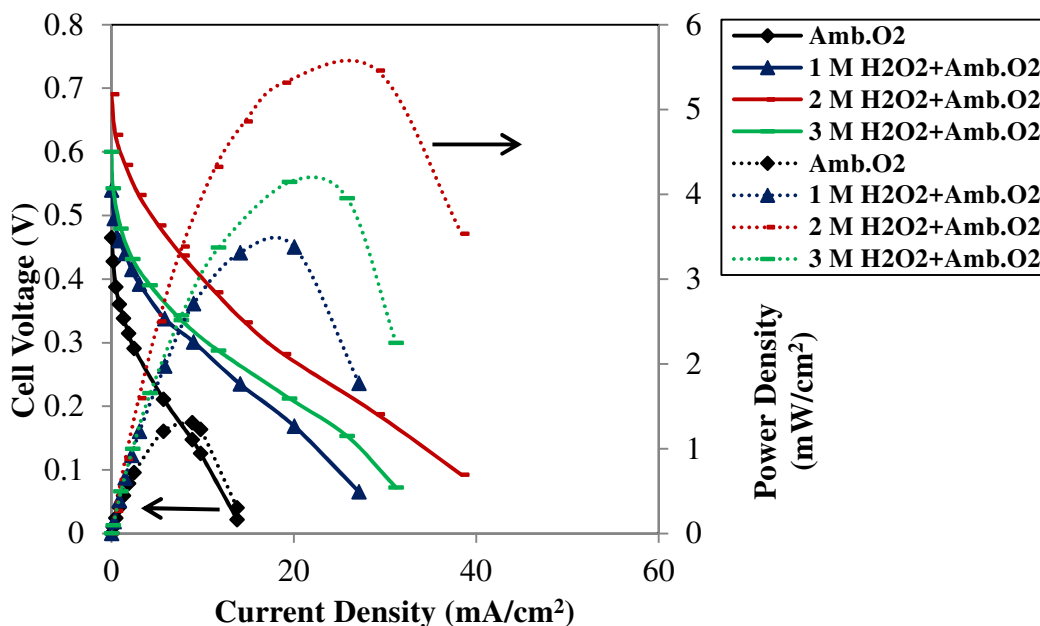


Figure 5.18 Current density vs. cell voltage and current density vs. power density curves for 0.5 M methanol mixed with 1 M KOH as fuel and 1 M KOH at cathode side mixed with the different concentration of H_2O_2 in the presence of air; Temperature 34 °C; Solid lines-polarization curves; Dotted lines-power density curves.

5.4 Life time Test of The Microfluidic Fuel Cell

Life time or stability of the cell was tested for methanol, ethanol and sodium borohydride as shown in fig (5.19). The anode electrocatalyst loading was 1 mg/cm^2 of Pt-Ru/ C_{HSA} for methanol and ethanol, respectively. For sodium borohydride, it was 1 mg/cm^2 Pt/ C_{HSA} . The cathode electrocatalyst was Pt/ C_{HSA} of 1 mg/cm^2 for all fuels. 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 microfluidic fuel cell performance deteriorated with time may be because of the carbonate layer formation in alkaline medium and adsorption of intermediate species on electrocatalyst surface.

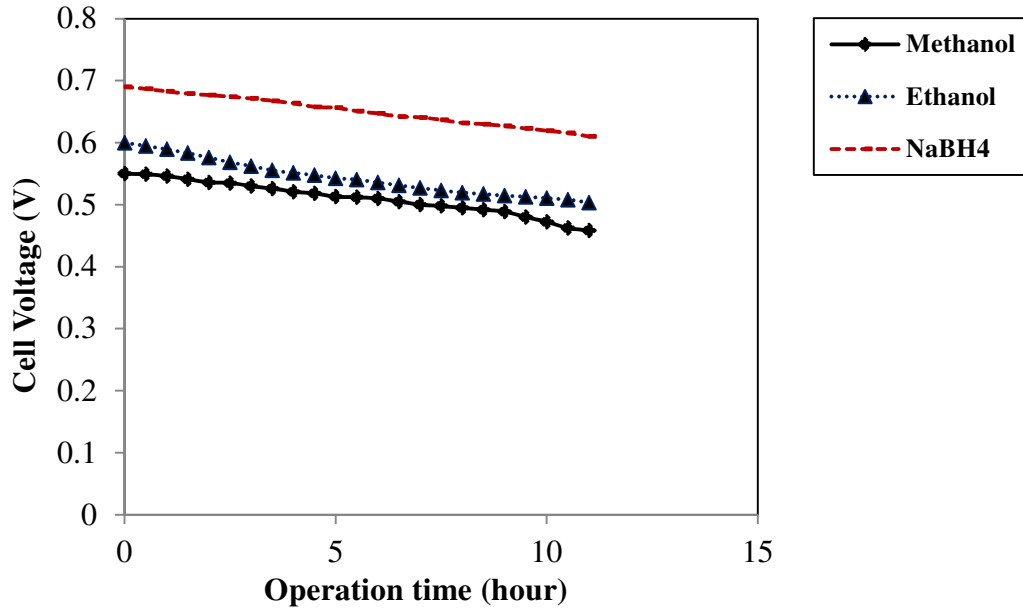


Figure 5.19 Life time or stability test of the microfluidic fuel cell using methanol, ethanol and sodium borohydride as fuel at constant load.

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 calculated rate of decay for methanol, ethanol and borohydride are 0.0079 Volt/hr., 0.0087 Volt/hr. and 0.0072 Volt/hr., respectively.

5.5 Efficiency of The Air breathing Microfluidic Fuel Cell

The total efficiency of a fuel cell is defined as the product of different efficiencies as given below (Carrette et al. 2001):

$$\eta_{FC} = \eta_r^{cell} \times \eta_V \times \eta_F \times \eta_U \times \eta_H \quad (5.10)$$

Where, η_{FC} = Total efficiency of the microfluidic fuel cell

η_r^{cell} = thermodynamics efficiency

η_V = electrochemical efficiency

η_F = Faraday efficiency

η_U = fuel utilization

η_H = heating value efficiency

Thermodynamic efficiency η_r^{cell} is calculated from the Gibbs free energy (ΔG) and the enthalpy change (ΔH) of the electrochemical reactions taking place in the microfluidic fuel cell. It is defined as the ratio of negative of Gibb's energy ($-\Delta G$) and enthalpy change (ΔH). The lowering of the efficiency by the losses due to electrode overpotentials is expressed by electrochemical efficiency (η_V) and it is the ratio of operating cell potential to ideal cell potential. Faradic efficiency, η_F is defined as the ratio of the experimental current and theoretical maximum current of the microfluidic fuel cell. It is assumed that fuel utilization, η_U is typically about 0.95, which is used for the cell efficiency calculation (Larminie and Dicks 2003).

The heating value efficiency is defined as the ratio of the fuel that is converted electrochemically to the heating value of all fuel present in the fuel stream (Carrette et al. 2001). Heating value efficiency is neglected in the present work because the fuel is in pure form. Thus, equation (5.10) is written in the following final form as:

$$\eta_{FC} = \eta_r^{cell} \times \eta_V \times \eta_F \times \eta_U \quad (5.11)$$

Using equation (5.11) the efficiencies calculated in terms of operating cell-voltage, V_{cell} , for methanol, ethanol, and sodium borohydride fuel cell are 0.465 V, 0.43 V and 0.66 V,

respectively. Table (5.1) shows the individual efficiencies for methanol, ethanol and sodium borohydride, used in the microfluidic fuel cell.

Table 5.1 Individual efficiencies, thermodynamic, η_r^{cell} , electrochemical, η_v , Faradic, η_F , fuel utilization, η_U of the microfluidic fuel cell at room temperature and atmospheric pressure (1 atm):

Fuel	η_r^{cell}	η_v	$\times \eta_F$	$\times \eta_U$
Methanol (34 °C)	0.96	0.39	1	0.95
Ethanol (34 °C)	0.97	0.38	0.67	0.95
Sodium borohydride (40 °C)	0.64	0.41	0.50	0.95

Table (5.1) shows individual efficiencies for methanol, ethanol and sodium borohydride as fuel in the microfluidic fuel cell. The maximum efficiency values at maximum power density of 1.3 mW/cm², 4.18 mW/cm² and 8.4 mW/cm² for methanol, ethanol, and sodium borohydride microfluidic fuel cells are 0.36, 0.24 and 0.13, when optimum concentration of methanol (0.5 M), ethanol (0.5 M) and NaBH₄ (0.1 M) mixed with optimum KOH (1 M) as electrolyte at room temperature were used of Pt-Ru (30 %:15 % by wt.)/C_{HSA} as anode and Pt (40 % by wt.)/C_{HSA} as cathode electrocatalyst for methanol and ethanol, respectively. The anode and cathode electrocatalyst for NaBH₄ were Pt/C_{HSA}.

5.6 Model Prediction

In this section, model predictions and experimental data on current density vs. cell voltage (j-v) characteristics for the variation fuel and electrolyte concentration and temperature are compared. The model uses simple numerical tools as MS excel, for calculation allowing the rapid prediction of the air breathing microfluidic fuel cell performance, i.e., j-v characteristics.

5.6.1 Fuel Concentration

Fig (5.20a) to (5.20c) shows the experimental data and model prediction on current density vs. cell voltage characteristics at different fuel concentrations for methanol, ethanol and sodium borohydride. The experimental data are shown by the symbols, and the model predictions are shown by lines for different concentrations of the fuels. It is seen in the fig (5.20a) to (5.20c) that the cell voltage increases with the increase in fuel concentration for a particular value of current density. The current density vs. cell voltage data is well reflected by the model prediction for different fuel concentrations. The model proved to predict the correct trends of the different concentration of the fuel presented in experimental data, especially for low current densities. However, the model shows some divergence in experimental data in the region of higher current density in the range of ohmic and concentration overpotential as both the polarizations further increase. Fig (5.20a) to (5.20c) show standard deviation ranging between 4-8 %. The model parameters used in the prediction are shown in the table (5.2).

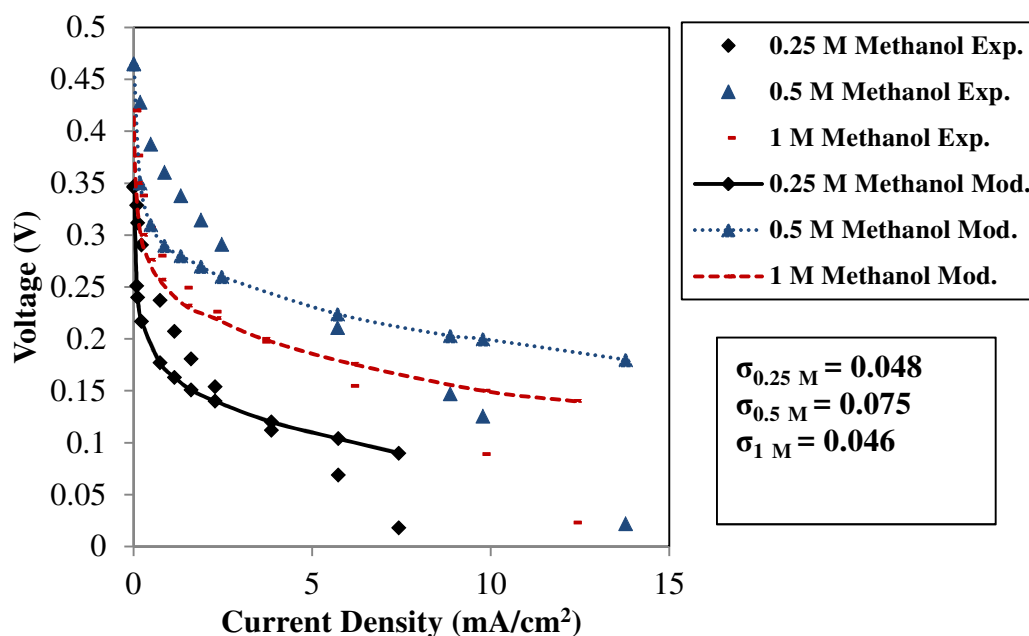


Figure 5.20a Current density vs. cell voltage characteristic for different methanol concentration; Temperature 34 °C

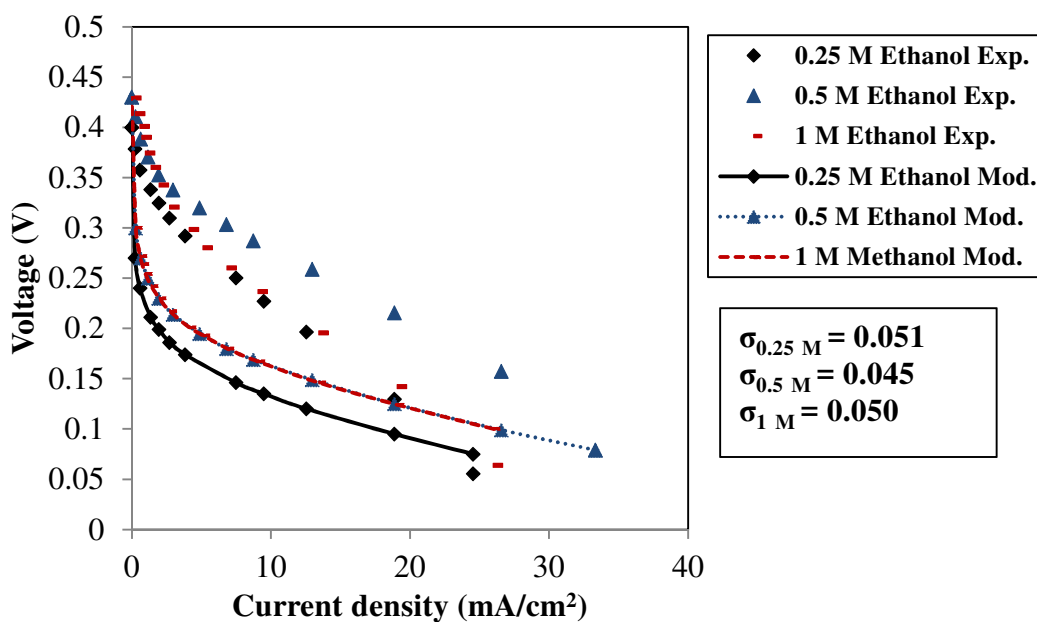


Figure 5.20b Current density vs. cell voltage characteristic for different ethanol concentration; Temperature 34 °C.

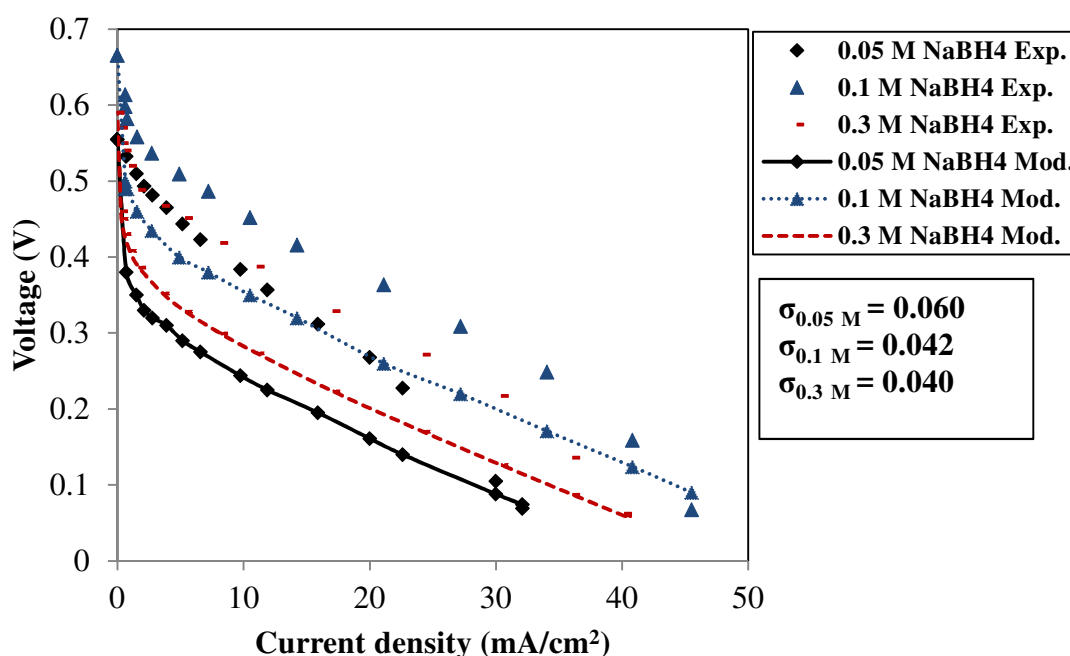


Figure 5.20c Current density vs. cell voltage characteristic for different NaBH₄ concentration; Temperature 40 °C.

5.6.2 Temperature

Fig (5.21a) to (5.21c) show the experimental data and model prediction on current density vs. cell voltage characteristics at different operating temperatures for methanol, ethanol and sodium borohydride. It is seen in the fig (5.21a) to (5.21c) that the cell voltage increases with the increase in temperature for a particular value of current density. The experimental data are, shown by the symbols which reasonably well reflected by the model as shown by the lines except at higher current densities. The reason for over-prediction of experimental data at a higher temperature by the model may be due to higher concentration overpotential at the anode. Fig (5.21a) to (5.21c) shows standard deviation ranging between 7-8.5 %.

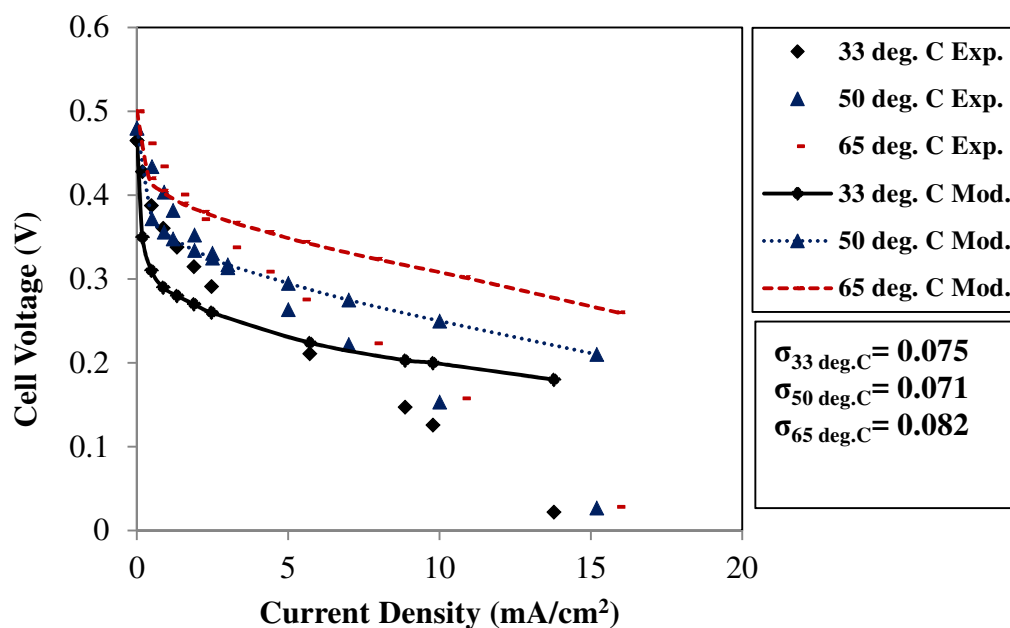


Figure 5.21a Current density vs. cell voltage characteristic at different cell temperatures for 0.5 M methanol concentration.

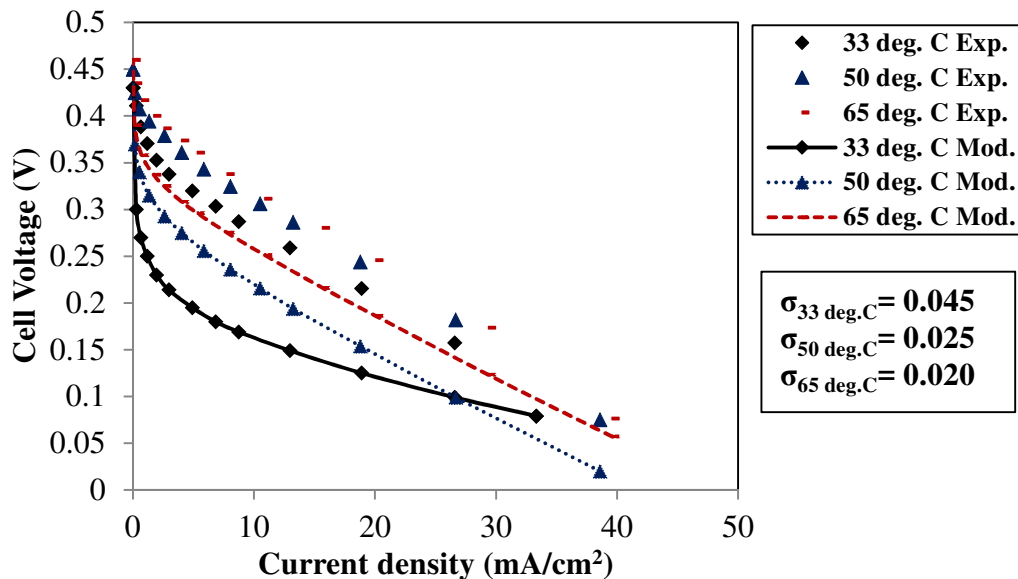


Figure 5.21b Current density vs. cell voltage characteristic at different cell temperatures for 0.5 M ethanol concentration.

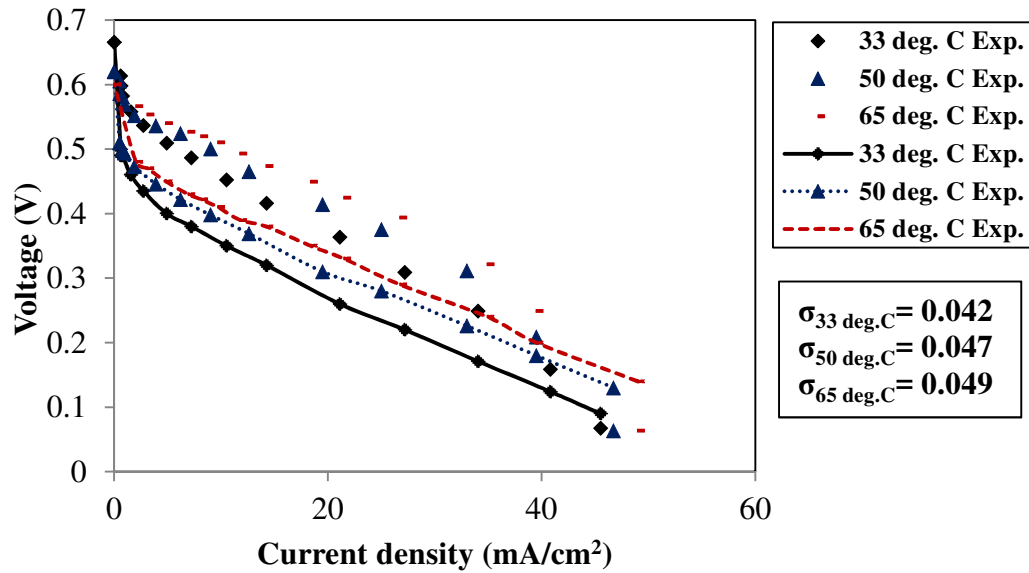


Figure 5.21c Current density vs. cell voltage characteristic at different cell temperatures for 0.1 M NaBH₄ concentration.

5.6.3 Model Parameters

The parameters used in the model equation (4.70), (4.73) and (4.76) for methanol, ethanol and sodium borohydride at different temperatures are presented in table (5.2). The lumped constant, (K_{MeOH} , K_{EtOH} and K_{NaBH_4}) as listed in the table (5.2) is taken as the same order that of methanol, ethanol and sodium borohydride which were determined by Sundmacher et al., (2001) and Tripkovic et al., (1996). The charge transfer coefficients α for different fuels were within the comparable range as quoted in the literature (Larminie and Dicks 2003). The value of exchange current density, j_0 at different temperatures were used same as was proposed by Andreadis et al., (2006) for the model development. The bulk diffusion coefficient of oxygen in the air, D_{O_2} is calculated using equation (4.64). The ionic conductivity of the solution, σ was measured by the conductivity meter. The external resistance of cell interconnects, $R_{\text{ext.}}$ was measured by the multimeter.

Table 5.2 Model parameters

Parameter	Temp. (°C)	Unit	Present model value	Literature value	Reference
$C_{F,EtOH}$	34	mol/ml	0.00025 0.0005 0.001	Known	
$C_{F,MeOH}$	34	mol/ml	0.00025 0.0005 0.001	Known	
C_{NaBH_4}	40	mol/ml	0.00005 0.0001 0.0003	Known	
C_{OH}	34	mol/ml	0.001	Known	
C_{ob}	34	mol/ml	9.4×10^{-6}	Calculated	
K_{MeOH} K_{EtOH} K_{NaBH_4}	34	Coulomb(mol. cm) $^{-0.5}$ s	1 1 1	1(70°C)	Sundmacher et al. (2001)
α	34 50 65	Dimensionless	0.5 0.7 0.9	(0 - 1.0)	Larminie and dicks (2003)
j_o at anode and cathode	34	$mAcm^{-1}$	0.136	0.136 (at 75 °C)	Andreadis et al. (2006)
l_d		cm	0.02	Measured	
ε^d		Dimensionless	0.78	Given	
d_{ct}		cm	0.1	Measured	
A_{ct}		cm^2	0.90	Calculated	
σ		scm^{-1}	2206.67	Measured	
$R_{ext.}$		Ωcm^2	0.006	Measured	
D_{O_2}	34 50 65	$cm^2 s^{-1}$	2.29×10^{-6} 3.75×10^{-6} 5.5×10^{-6}	Calculated	

