Studies on PEM Fuel Cells Using Various Alcohols for Low Power Applications

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The Direct Alcohol Fuel Cell (DAFC) appears to be the most promising replacement for batteries in portable applications such as cellular phones, personal Digital Assistants (PDAs), digital cameras and laptop computers. The necessity, along with related consumer demand has been an impetus to incorporate direct alcohol fuel cells (DAFCs) to power these smart electronic devices. The present study deals with the investigation of various aliphatic alcohols such as ethanol, 1-propanol, 2-propanol and butanol with respect to methanol as fuels in polymer electrolyte membrane fuel cell (PEMFC). 2-Propanol emerges the prospective fuel candidate as the study shows.

Keywords: Methanol, 2-propanol, PEMFC, DAFC, D2PFC and DMFC

1. INTRODUCTION

The worldwide demand for energy in the 21st century is growing at an alarming rate resulting in stringent energy concerns. The European “World Energy Technology and Climate Policy Outlook” (WETO) predicts an average growth rate of 1.8% per annum for the period 2000-2030 for primary energy worldwide. The increased demand is being met largely by reserves of fossil fuel that emit both greenhouse gases and other pollutants. Those reserves are diminishing and they will become increasingly expensive. Fuel cell systems are one of the vital, reliable and renewable green power packs to circumvent the conventional fossil based energy systems that are actually noxious for human survival. Fuel cells can deliver power from micro to mega-watt applications. However the types of fuel cell systems to be applied for specific use will depend on economic considerations and the field of application. Among the diverse fuel cells, PEMFC offers advantages of high power density, low operating temperature (60–90°C), with consequent rapid start up and dynamic response. The major barriers with PEM fuel cells using hydrogen as a fuel are production, distribution, storage, and humidification. The lower flash point of hydrogen (i.e. ~423 ºF) also raises concerns about the safety...
issues of hydrogen. These limitations of hydrogen have necessitated researchers to try other fuels that are directly oxidizable. Direct oxidation fuel cells using liquid methanol as a fuel has already attracted intensive research worldwide [1-4]. Furthermore, the ever-increasing number of portable electronic devices which presently use batteries will inevitably lead to troubles in the recycling process and also batteries run out too fast and recharging seems to be inconvenient and time consuming from the user’s point of view. On contrary alcohol based fuel cell systems can be designed comparatively simple, also the operating times are extensive and the fuels can be easily produced, stored and transported without any risk of explosion. In recent years research activities in direct methanol fuel cell (DMFC) technology has increased remarkably because of potential advantages such as high-energy density, low operating temperature and the potential to eliminate moving parts. The most imminent commercial application of DMFC is as a power sources for portable electronic devices [5]. The challenges associated with the development of them includes poisoning of anode electro catalyst by CO or related species of methanol and crossover of methanol from the anode to cathode. The methanol, which enters the cathode directly through the membrane reacts with oxygen and reduces the efficiency of DMFC [6]. The above limitations of DMFC have prompted us to carryout studies using other alcohols such as ethanol, 1-propanol, 2-propanol and n-butanol and compare the performance with that of methanol. Only few studies have been reported so far on Direct Alcohol Fuel Cells, using fuels other than methanol.

2. EXPERIMENTAL PART

Single cells having an electroactive area of 25cm$^2$ were invariably employed in our studies. Unsupported Pt-Ru (1:1 a/o) and unsupported Pt purchased from M/s. Arora Matthey Limited (India) were used as the anode and cathode electro catalysts, respectively. Catalyst loading of about 3 mg/cm$^2$ was given to the cathode and the anode. By decal method Membrane and Electrode Assemblies were prepared by hot pressing the electrodes onto a Nafion-117 membrane at 130$^0$C for 4 min.

Various alcohols were diluted to 1 M and fed by a peristaltic pump at the anode side of the cells at 25 ml/min rate and $O_2$ (or air) at 1 LPM at the cathode side. Since our earlier studies with the similar cell configuration, design and catalyst loading etc demonstrated better cell performance with DMFC (the results of which are communicated elsewhere), the same flow rate of about 25 ml/min for the alcohol fuel solutions and 1LPM for $O_2$ (or air) was fixed in the present studies also. Experiments were conducted at ambient temperature(28$^0$C) and 60$^0$C and at ambient pressure. Polarization profiles (current density vs. voltage) of the fuel cells fed with alcohol fuel solutions and $O_2$ (or air) were obtained by incorporating a current load using a DC electronic load bank.

3. RESULTS AND DISCUSSION

Polarization and power density curves of various alcohols @ ambient temperature (28$^0$C) with air as the oxidant are presented in Figs. 1 & 2. In addition to the polarization curves, power density vs.
current density plots are also provided since it would give a comparative picture on the electrochemical activity of the alcohols taken for the study.

Figure 1. Polarization curves of alcohol fuel cells

![Figure 1. Polarization curves of alcohol fuel cells](image)

Figure 2. Power Density curve of alcohol fuel cells.

![Figure 2. Power Density curve of alcohol fuel cells](image)

The OCP is 0.709 V and 0.588 V for 2-propanol and methanol respectively. The maximum power density achieved is 8.42 mW/cm² and 3.08 mW/cm² at a current density of 20 mA/cm² for 2-
propanol and methanol respectively. The performance of the remaining alcohols is out of comparison due to poor kinetics of the anode reactions. From Fig.1, of all, the performance of 2-propanol is better as it has the highest cell voltage at the current of 20 mA/cm$^2$. Performance of the fuel cells at 60$^\circ$C is illustrated in Figs.3 & 4. From the plots we infer that the performance of all the alcohols has improved when compared with that observed at ambient temperature due to the enhanced catalytic activity and reduced polarization effects. The OCP is 0.757 V for 2-propanol and 0.611 V for methanol.

The maximum power density attained by the cell is 9.82 mW/cm$^2$ at a current density of 20 mA/cm$^2$ for 2-propanol and 9.24 mW/cm$^2$ at a current density of 44 mA/cm$^2$ for methanol.
The experiment is then continued with oxygen as the oxidant.

![Figure 5](image1.png)

**Figure 5.** Polarization curve at ambient temperature and Oxygen flow rate of 1 LPM

![Figure 6](image2.png)

**Figure 6.** Power Density curve at ambient temperature and Oxygen flow rate of 1 LPM.

It is understood from the polarization curve (Fig. 5) that the performance of all the alcohols improve when using oxygen as the oxidant. Typically, the OCP is 0.798 V and 0.608 V for 2-propanol and methanol respectively. The maximum power density obtained by the cell is 15.932 mW/cm² at a current density of 28 mA/cm² for 2-propanol and 10.032 mW/cm² at a current density of 44 mA/cm² for methanol. The performance of butanol, 1-propanol and ethanol has improved considerably by using oxygen as oxidant but still relatively less compared to 2-propanol and methanol as shown in Fig. 6.

As evidenced from Figs.7 & 8 improvement in performance with 2-propanol is observed to be much better at 60°C than at ambient condition, followed by methanol, which is more stable than 2-propanol. The OCP is 0.828 V and 0.662 V for 2-propanol and methanol respectively. The improved performance accompanied with the increasing temperature can be attributed to the combined effects of
reduction of Ohmic and activation polarization [7]. The experiments best data show a performance of 0.648V at a current density of 52 mA/cm$^2$, which corresponds to a power density of about 34 mW/cm$^2$ for 2-propanol as fuel and 0.41V at a current density of 68 mA/cm$^2$, which corresponds to a power density of about 28 mW/cm$^2$ for methanol as fuel. The cathode appears less susceptible to poisoning by CO from 2-propanol at higher oxygen pressures [8].

**Figure 7.** Polarization curve at T=60$^0$C and Oxygen flow rate = 1 LPM

**Figure 8.** Power Density curve at T=60$^0$C and Oxygen flow rate = 1 LPM
From all the above performance curves it is well understood that the performance of 2-propanol is better for lower values of current density and it is also inferred that though the cell voltage of methanol is less compared to 2-propanol its value is more stable at higher current densities. The empirical equation that governs the oxidation reactions of alcohols is given by.

$$C_nH_{2n+1}OH + (2n-1) H_2O \rightarrow nCO_2 + 6nH^+ + 6ne^-$$  \hspace{1cm} (1)

Equations (2) and (3) are the oxidation reactions of 2-propanol and methanol which are in-line with equation (1).

$$CH_3CHOHC_3 + 5H_2O \rightarrow 3CO_2 + 18H^+ + 18e^-$$  \hspace{1cm} (2)

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$  \hspace{1cm} (3)

For each methanol molecule, 6 electrons are produced, while for each 2-propanol molecule, 18 electrons are produced. In other words, for a complete oxidation of each 2-propanol molecule, three times as large a current should be observed compared to a complete oxidation of each methanol molecule. Therefore, the amount of 2-propanol crossing through the membrane is less than 1/7 of that of methanol based on the cross over currents [9]. This reduced 2-propanol crossover should greatly increase fuel cell efficiency.

Fig. 9 shows the cell voltage change with time when constant current densities of 20, 40 and 60 mA/cm$^2$ were generated, respectively at 60$^0$C. This curve gives details about the application of D2PFC for charging various low power electronic devices. Better operating time results in the better utilization of them to incorporate in various portable electronic applications. From Fig. 9 it is perspicuous that 2-propanol can deliver a power density of about 15 mW/cm$^2$ for 30 minutes and 27 mW/cm$^2$ for around 15min which are approaching the target performance required to charge low power electronic devices such as cell phones. The rate of decline of cell voltage at 60mA/cm$^2$ is greater than that of 20 and 40mA/cm$^2$. The quicker decline at higher current densities is normally due to increased mass transport limitation. Such a speedy decline is normally not observed in a direct methanol fuel cell (DMFC). Based on this observation, it has been concluded that reaction intermediates or products continuously poisoned the cell anode, and that a higher current led to a faster poisoning due to a quicker formation and accumulation of the poisoning species [9]. As the current was increased, the poisoning not only accumulated, but also proceeded faster; and finally, there were not enough active surfaces for the reaction to proceed, resulting in a quicker decline at current densities higher than 60mA/cm$^2$. Therefore, in addition to an increased mass transport limitation, accumulated anode poisoning has been presumed to be another justifiable factor to cause the cell voltage to decline quickly in the higher current density region. These observations are in-line with the experiments conducted by Zhigang Qi et al. [9].
Figure 9. Performance of 2-propanol with time at current densities of 20, 40 and 60mA/cm$^2$ for $T=60^\circ$C and Oxygen flow rate = 1 LPM.

Table 1. Comparison of power density at 20, 40 and 60mA/cm$^2$ for 2-propanol and methanol at $T=60^\circ$C and Oxygen flow rate = 1 LPM.

<table>
<thead>
<tr>
<th>Current Density (mA/cm$^2$)</th>
<th>Power Density (mW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For 2-propanol</td>
</tr>
<tr>
<td>20</td>
<td>14.86</td>
</tr>
<tr>
<td>40</td>
<td>27.52</td>
</tr>
<tr>
<td>60</td>
<td>24.6</td>
</tr>
</tbody>
</table>

It is evident from Table.1 that at 60mA/cm$^2$ 2-propanol couldn’t exhibit comparatively reasonable voltage compared to that at 20 and 40mA/cm$^2$ whereas methanol gives relatively better cell voltage and power density. Thus it is observed that for lower current density (up to 40mA/cm$^2$) 2-propanol is a much better candidate than methanol.
The major challenges of this approach are anode poisoning by deep oxidation and by acetone buildup, and 2-propanol crossover. The development of anode catalysts and anode structures that are immune to these deficiencies is the more consequential of these challenges. These issues presented in this article are under further investigation. As a result of these strengths and problems, D2PFCs (Direct 2-propanol Fuel Cells) are limited in the power they can produce, but can still store a lot of energy in a small space. Moreover, the toxicity level of 2-propanol is far less compared to its counterpart methanol and any leakage of the fuel can be easily identified by its characteristic smell.

4. CONCLUSIONS

The performance of various alcohols as fuel solutions is studied in polymer electrolyte membrane fuel cell and the results strongly imply that 2-propanol is a much better candidate than butanol, 1-propanol, ethanol and even methanol at lower current densities. It is also inferred that the performance of DMFC is better when compared to other alcohols including 2-propanol even at higher current densities. The paper also suggests that direct alcohol fuel cells utilizing 2-propanol and other alcohols as a fuel will be a versatile power source to energize mobile and other portable electronic kits in near future with a considerable improvement in the economic viability of the catalysts, membrane and graphite plates.

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References


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