EVALUATION OF AN ALKALINE FUEL CELL FOR MULTI-FUEL SYSTEM

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ABSTRACT

The performance of an alkaline fuel cell is investigated using three different fuels, e.g., methanol, ethanol and sodium borohydride. Pt/C/Ni was used as anode whereas Mn/C/Ni was used as standard (Electro-Chem-Technic, UK) cathode for all the fuels. Thus, the alkaline fuel cell is used for multi-fuel system. Fresh mixture of electrolyte, potassium hydroxide (5M), and fuel (2M) was fed to and withdrawn from the AFC at a rate of 1 ml/min. The anode was prepared by dispersing platinum and activated carbon in Nafion® (DuPont USA) dispersion and placing it onto a carbon paper (Lydall, USA). Finally prepared anode sheet was pressed onto Ni mesh and sintered to produce the required anode. The maximum power density of 16.5 mW/cm² is obtained at 28 mA/cm² of current density for sodium borohydride at 25 °C. Whereas, methanol produces 31.5 mW/cm² of maximum power density at 44 mA/cm² of current density at 60 °C.

INTRODUCTION

A fuel cell is an electrochemical device that converts the free energy of oxidation of fuel into electrical energy without combustion. This system works very efficiently and produces low pollution. Therefore, it is highly potential power source in the near future. The alkaline fuel cell (AFC) was the first fuel cell used in space operations. It uses potassium hydroxide solution as electrolyte, hydrogen gas as fuel and oxygen gas as oxidant. The AFC technology development reached its peak in the beginning of the 1980s (Schulze and Gülzous, in press) but further development was stopped due to many technical and commercial bottlenecks. Recently, the efforts have been directed towards low temperature fuel cell technology after the advent of polymer electrolyte membrane or proton exchange membrane (PEM). The fuel cell, which uses this membrane, is called polymer electrolyte membrane fuel cell (PEMFC) or direct methanol fuel cell (DMFC). Due to high cost, requirement of pure hydrogen as fuel and poisoning of anode catalyst by trace carbon monoxide, PEMFC and DMFC could not be successfully commercialized. The interest in the alkaline fuel cell rose again recently because of its simplicity, low cost and high efficiency compared to other fuel cells.

There are some problems associated with the use of hydrogen as fuel due to storage, explosion hazard, cost and low power output per unit weight of the fuel cell and fuel processor. The hydrogen gas generation using steam reforming, thermal decomposition, partial oxidation and gasification (Ledjef-hey et al., 1998) could not gain much popularity. In last ten years, investigators are working on direct feeding of hydrocarbons e.g., alcohols, ethers, and hydrogen rich compound, NaBH₄, into the fuel cells (Li et al., in press; Verma, 2000; Amendola et al., 1999; Wang et al., 2003). Methanol (Shobha et al., 2002; Verma, 2000; Arico et al., 1998; Ioannides and Neophytides, 2000) and ethanol (Arico et al., 1998; Ioannides and Neophytides, 2000) are the attractive liquid fuel because they are relatively cheaper, easily stored and handled, readily available from renewable sources. Moreover they are soluble in aqueous electrolytes. Comparative performance of such kind of fuel cells is given in table 1. In the present study, the use of methanol, ethanol, and sodium borohydride in alkaline fuel cell is tested. The electrodes used are same for all the fuels and thus the possibility of using AFC for multi-fuel system is checked.

The detailed reaction mechanisms for the three fuels in the presence of alkaline electrolyte and Pt/C/Ni anode (Carrette et al., 2001) are described below. The reaction at cathode is same irrespective of the fuel used. The reaction at cathode is given by,

\[
4e^- + O_2 + 2H_2O \rightarrow 4OH^- \quad (1)
\]

The reaction at anode for different fuels is given by,
Methanol

Step 1.

\[ \text{CH}_3\text{OH} + 2\text{OH}^- \rightarrow \text{HCHO} + 2\text{H}_2\text{O} + 2e^- \] (2)

Step 2.

\[ \text{HCHO} + 2\text{OH}^- \rightarrow \text{HCOOH} + \text{H}_2\text{O} + 2e^- \] (3)

Step 3.

\[ \text{HCOOH} + 2\text{OH}^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2e^- \] (4)

The major problem with methanol fuel, when using an alkaline electrolyte, is that the carbon dioxide produced reacts with the electrolyte, forming potassium carbonate, \( \text{CO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \). This gradually eats up the electrolyte. Further, it is documented in the literature (Kordesch et al., 1999) that if the cathode feed is contaminated by carbon dioxide, carbonate may form at the cathode and the performance of the AFC may decrease. Recently, Gülzow and Schulze (in press) investigated the long-term behavior of the alkaline fuel cell (AFC) electrodes supplied with \( \text{CO}_2 \) containing gases and it gives no evidence that \( \text{CO}_2 \) affects significantly the degradation process. Nevertheless, electrolyte can be recycled to remove the carbonate formed and also recharged with fresh KOH time to time.

Ethanol

\[ \text{C}_2\text{H}_5\text{OH} + 2\text{OH}^- \rightarrow \text{CH}_3\text{CHO} + 2\text{H}_2\text{O} + 2e^- \] (5)

In the case of ethanol, the reaction is not allowed to proceed further and thus \( \text{CO}_2 \) is not generated. The problem of carbonate formation does not arise. However, electrons generated are less than that for methanol.

Sodium Borohydride

There are two possible routes for oxidation of \( \text{NaBH}_4 \). In the first route \( \text{NaBH}_4 \) is directly oxidized (Li et al., in press; Amendola et al., 1999).

\[ \text{NaBH}_4 + 8\text{OH}^- \rightarrow \text{NaBO}_2 + 6\text{H}_2\text{O} + 8e^- \] (6)

In the second route, hydrogen is liberated at high temperature or pH less than 7.

\[ \text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 \] (7)

\[ 4\text{H}_2 + 8 \text{OH}^- \rightarrow 8\text{H}_2\text{O} + 8e^- \] (8)

The hydrogen produced by this route may escape from the system thus the fuel may not be fully utilized.

EXPERIMENTAL

Set-up and Method

The experiments were carried out in a plastic beaker-containing anode at the bottom. The cathode is attached to bottom of a hollow plastic cylinder, which fits into the plastic beaker. Anode was prepared in the lab whereas standard cathode made of Mn/C/Ni (Electro-Chem-Technic, UK) was used. Two leads from anode and cathode are used as terminals for measuring current and voltage of the alkaline fuel cell. The space between anode and cathode was filled with the mixture of electrolyte (5M KOH) and fuel (2M). The fuel and electrolyte mixture was filled up to a certain level such that one side of the cathode was in contact with fuel and the other side with was exposed to air. Oxygen present in air acts as oxidant. The three fuels tested are methanol, ethanol and sodium borohydride. Fresh fuel and electrolyte mixture was fed to the AFC and withdrawn with the help of peristaltic pump at a rate of 1 ml/min. The fuel-electrolyte mixture in the beaker was continuously stirred by magnetic stirrer to maintain uniform concentration and temperature in the beaker and to reduce any concentration polarization near the electrodes.

Preparation of electrode

Activated carbon, used as the support for the platinum catalyst, was first dispersed in required quantity of Nafion® (SE-5112, DuPont, USA) solution for 30 min. using an ultrasonic water bath. platinum powder was added to this
dispersion and it was thoroughly dispersed in the ultrasonic water bath to obtain anodic slurry. Anodic slurry was spread on C-paper (Lydall 486C-1, USA) in the form of continuous wet film. It is then dried in an oven for 30 min. at 80°C. Nickel mesh was used as current collector. The catalyzed carbon paper was pressed on to the nickel mesh using Teflon® (DuPont, USA) dispersion. The prepared electrode was pressed at 60 kg/cm² and 120°C for 10 min. Finally, the electrode was sintered at 250°C for 2 hours. The size of the prepared anode was 9 cm² with 0.8 mg/cm² of Pt loading.

RESULTS AND DISCUSSION

I-V Characteristics

Figures 2 and 3 show the current-voltage relationship at two different temperatures for methanol, ethanol and sodium borohydride. It is seen that the cell voltage decreases with the increase in load. Figure 2 shows that sodium borohydride produces higher voltage at 25°C than that for methanol and ethanol in the region of high and low applied load. In the intermediate range of load the ohmic losses are higher for sodium borohydride compared to methanol and ethanol. At higher temperature (65°C), methanol showed slightly better i-v characteristics compared to ethanol and sodium borohydride (Fig. 3). Sodium borohydride produces hydrogen at higher temperature, which escapes from the cell causing unexpected low value of i-v characteristics. Formation of gas bubbles and release of such gas bubbles from electrode area was observed in the case of sodium borohydride at 65°C.
Power Density

Figures 4 and 5 show the plot for power density versus current density at two different temperatures, 25 °C and 65 °C. It is seen that the power density increases with increase in current density and finally it become steady. Although not shown, the power density decreases with the further increase in current density.

The short circuit current density (SCCD), open circuit voltage (OCV) and maximum power density for methanol, ethanol and sodium borohydride are shown in table 2. From table 2, it is seen that the performance of sodium borohydride at 25 °C is better than that for methanol. The maximum power density of 16.5 mW/cm² is obtained at 28 mA/cm² of current density for sodium borohydride. Whereas, methanol produces 31.5 mW/cm² of maximum power density at 44 mA/cm² of current density at 60 °C. Due to the hydrolysis of NaBH₄ and loss of H₂ gas at 60 °C, the performance of sodium borohydride is slightly less than methanol.

CONCLUSION

An alkaline fuel cell was tested with three different fuels, e.g., methanol, ethanol and NaBH₄. Anode used, Pt/C/Ni, was prepared in the lab. A standard cathode made of Mn/C/Ni (Electro-Chem-Technic, UK) was used. The maximum power density of 16.5 mW/cm² is obtained at 28 mA/cm² of current density for sodium borohydride at 25 °C. Whereas, methanol produces 31.5 mW/cm² of maximum power density at 44 mA/cm² of current density at 60 °C. Due to the hydrolysis of NaBH₄ and loss of H₂ gas at 60 °C, the performance of sodium borohydride is slightly less than methanol.

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REFERENCES


Table 2. Comparison of cell performance for different fuel at different temperatures

<table>
<thead>
<tr>
<th>Fuel</th>
<th>OCV(V)</th>
<th>SCCD (mA/cm²)</th>
<th>MPD (mW/cm²)</th>
<th>OCV (V)</th>
<th>SCCD (mA/cm²)</th>
<th>MPD (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.93</td>
<td>22.00</td>
<td>13.86</td>
<td>1.15</td>
<td>45.0</td>
<td>31.50</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.00</td>
<td>20.75</td>
<td>11.42</td>
<td>1.19</td>
<td>30.0</td>
<td>18.00</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>1.20</td>
<td>30.00</td>
<td>16.50</td>
<td>1.36</td>
<td>35.3</td>
<td>24.14</td>
</tr>
</tbody>
</table>

Fig. 5 Plot for power density versus current density for different fuels at in AFC at 60 °C


