Short communication

Direct use of alcohols and sodium borohydride as fuel in an alkaline fuel cell

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Abstract

The performance of an alkaline fuel cell (AFC) was studied at different electrolyte concentrations and temperatures for the direct feeding of methanol, ethanol and sodium borohydride as fuels. Potassium hydroxide is used as the electrolyte in the alkaline fuel cell. The anode was prepared by using Pt black, carbon paper and Nafion dispersion. Nickel mesh was used as the current collector. A standard cathode made of manganese dioxide/carbon paper/Ni-mesh/Teflon dispersion (Electro-Chem-Technic, UK) was used for testing the fuel cell performance. The experimental results showed that the current density increases with increase in KOH concentration. Maximum current densities of 300, 270 and 360 A m^{-2} were obtained for methanol, ethanol and sodium borohydride as fuel respectively with 3 M KOH electrolyte at 25 °C. The cell performance decreases with further increase in the KOH concentration. The current density of the alkaline fuel cell increases with increase in temperature for all the three fuels. The increase in current density with temperature is not as high as expected for sodium borohydride. These results are explained based on an electrochemical phenomenon and different associated losses.

1. Introduction

Interest in the alkaline fuel cell rose again recently because of its simplicity, low cost and comparable efficiency compared to other types of fuel cell [1]. The use of alkaline electrolyte in fuel cell has many advantages such as higher efficiency [2], and a wider selection of possible electrode catalysts and fuels. The electrocatalysts used in the alkaline fuel cell are Platinum [3,4], Nickel [5,2], Fe(III) [6], Al(III) [6], Pt/Ru [7], and fuels used are hydrogen [3], methanol [4,8], ethanol [8] and sodium borohydride [9,10]. Koscher and Kordesch [4] reported experimental work of Vieltich, in which 10 M KOH and 4.5 M methanol were used as an electrolyte and fuel, respectively. Platinum (2–5 mg cm^{-2}) and electrocatalytically active carbon were used as anode and cathode catalyst. The open circuit voltage was found to

be 0.9 V and current density was 2 mA cm^{-2} at 0.6–0.75 V. They also reported the use of a third electrode as grid to minimize the methanol cross-over to the cathode side. The anode consisted of an un-sintered Ag/PbO catalyst for the methanol oxidation, the cathode consisted of a platinized carbon/PTFE bonded structure and platinum catalyzed nickel as grid electrode. A mixture of 6 M methanol and 9 M KOH solution was used as anolyte and 9 M KOH solution as catholyte, which were separated by an anion exchange membrane. The best performance achieved with a single cell ranged from 0.6–0.7 V at 6 mA cm^{-2}. Prabhuram and Manoharan [11] investigated methanol oxidation on platinum electrodes in KOH solution using half-cell analysis. They have recorded cyclic voltammograms in different electrolyte concentrations in the presence and absence of different methanol concentration. The Methanol oxidation reaction was carried out in different electrolyte/methanol mixtures and it was highest for a 6 M KOH/6 M CH$_3$OH mixture.

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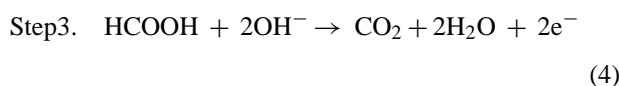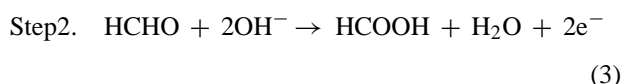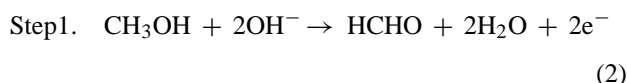 *E-mail address:* sbasu@chemical.iitd.ac.in (S. Basu).

Although different electrode catalysts, and electrolyte-fuel concentrations were used in the direct alcohol alkaline fuel cell, there was no systematic study conducted on the effect of electrolyte concentration alone and of temperature on the performance of the fuel cell. In the present investigation, experiments were performed with an alkaline fuel cell to study the effect of electrolyte concentration and temperature on the performance of the cell for three different fuels, e.g., methanol, ethanol and sodium borohydride.

The detailed reaction mechanisms for the three fuels in the presence of an alkaline electrolyte and a Pt/Ni anode [12] are described below. The reaction at $MnO_2/C/Ni$ cathode is the same irrespective of the fuel used. The reaction at the cathode is given by:

$$4e^- + O_2 + 2H_2O \rightarrow 4OH^- \tag{1}$$

The reaction at the anode for different fuels is given by:

- Methanol

  Step1. $CH_3OH + 2OH^- \rightarrow HCHO + 2H_2O + 2e^-$ (2)

  Step2. $HCHO + 2OH^- \rightarrow HCOOH + H_2O + 2e^-$ (3)

  Step3. $HCOOH + 2OH^- \rightarrow CO_2 + 2H_2O + 2e^-$ (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, $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$. This gradually eats up the electrolyte. Further, it is documented in the literature [13] that if the cathode feed is contaminated by carbon dioxide, carbonate may form at the cathode and the performance of the cell may decrease. Recently, Gülzow and Schulze [14] investigated the long-term behavior of alkaline fuel cell electrodes supplied with CO_2-containing gases and gave no evidence that CO_2 affects significantly the degradation process. Nevertheless, electrolyte can be recycled to remove the carbonate formed and also recharged with fresh KOH from time to time.

- Ethanol

  $$C_2H_5OH + 2OH^- \rightarrow CH_3CHO + 2H_2O + 2e^- \tag{5}$$
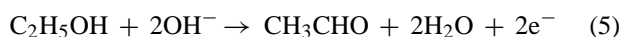
In the case of ethanol, the reaction is not allowed to proceed further and thus CO_2 is not generated. The problem of carbonate formation does not arise. However, the number of electrons generated is less than for methanol for per mole of fuel.

- Sodium borohydride

  There are two possible routes for oxidation of $NaBH_4$. In the first route $NaBH_4$ is directly oxidized [9,10]:

  $$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^- \tag{6}$$
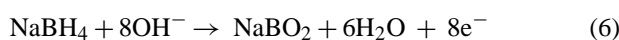
In the second route, hydrogen is liberated at high temperature or pH less than 7.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{7}$$

$$4H_2 + 8OH^- \rightarrow 8H_2O + 8e^- \tag{8}$$
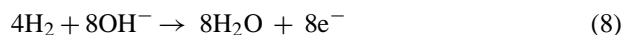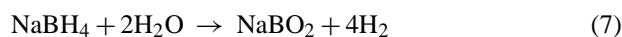
The hydrogen produced by this route may escape from the system thus the fuel may not be fully utilized.

2. Experimental

2.1. Set-up and method

The experiments were carried out in a plastic beaker containing an anode at the bottom. The cathode is attached to the bottom of a hollow plastic cylinder, which fits into the plastic beaker. A schematic diagram of the alkaline fuel cell is shown in Fig. 1. The anode was prepared in the lab whereas a standard cathode made of $MnO_2/C/Ni$ (Electro-Chem-Technic, UK) was used. Two leads from the anode and the cathode are used as terminals for measuring current and voltage of the alkaline fuel cell. The space between the anode and the cathode was filled with a mixture of electrolyte and fuel (2 M). The fuel and electrolyte mixture was filled up to a certain level such that one side of the cathode was in contact with the fuel and the other side was exposed to air. Oxygen present in the air acts as oxidant. The three fuels tested were methanol, ethanol and sodium borohydride. Fresh fuel and electrolyte mixture was fed to the AFC and withdrawn with the help of a peristaltic pump at the rate of 1 ml min^{-1}. The fuel-electrolyte mixture in the beaker was continuously stirred by a magnetic stirrer to maintain a uniform concentration and temperature in the beaker and to reduce any concentration polarization near the electrodes. The voltage and current were measured after a steady state is reached. There was no significant change in performance of the cell after 1 h of operation, whereas the
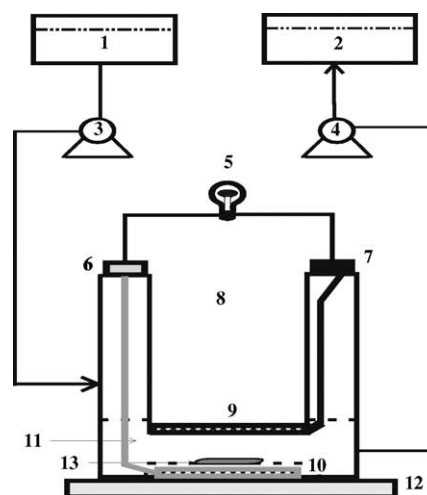

Fig. 1. Schematic diagram of an alkaline fuel.

performance of the cell is reduced by 3% after about 10 h of operation.

2.2. Preparation of electrode

Platinum-black (Johnson Matthey) powder was first dispersed in the required quantity of Nafion® dispersion (SE-5112, DuPont) for 30 min using an ultrasonic water bath to produce an anodic slurry. The anodic slurry was spread on C-paper (Lydall 486C-1) in the form of a continuous wet film. It was then dried in an oven for 30 min at 80 °C. A nickel mesh was used as current collector. The catalyzed carbon paper was pressed on to the nickel mesh using Teflon® (DuPont) dispersion. The prepared electrode was pressed at 60 kg cm^{-2} and 120 °C for 10 min. Finally, the electrode was sintered at 250 °C for 2 h. The size of the prepared anode was 10 cm^2 with 1 mg cm^{-2} of Pt-black loading.

3. Results and discussion

3.1. Effect of electrolyte concentration

Figs. 2–4 show the current–voltage relationship (25 °C) at four different KOH concentrations for methanol, ethanol and sodium borohydride, respectively. Fig. 2 shows that the cell voltage increases with the increase in KOH concentration from 1 to 3 M for a particular load and then it decreases with further increase in KOH concentration. The reason for the
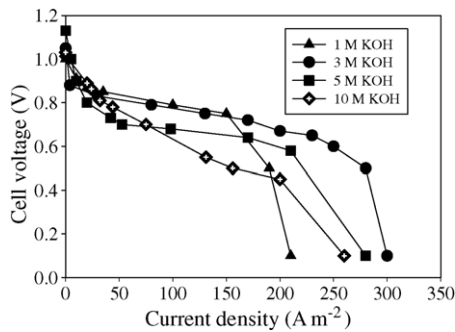

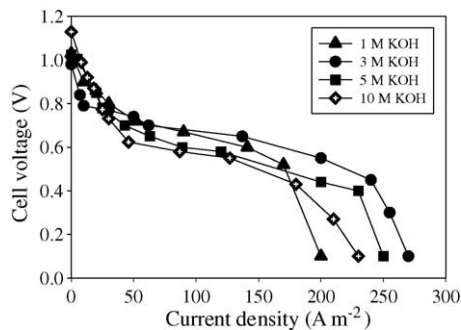Fig. 2. Polarization curve for methanol (2 M) in different KOH concentration.

Fig. 3. Polarization curve for ethanol (2 M) in different KOH concentration.
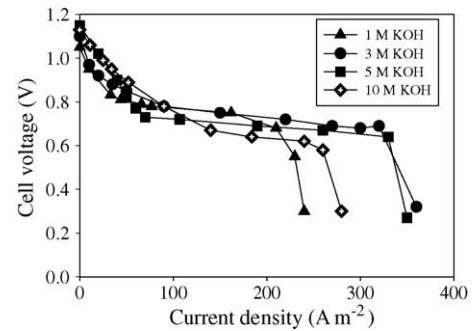

Fig. 4. Polarization curve for sodium borohydride (2 M) in different KOH concentration.

decrease in voltage may be because of the relative decrease in the concentration of methanol in the presence of a high concentration of KOH. It is well known that the initial and final voltage losses with an increase in current consumption are attributed to activation and concentration over-potentials, whereas the over-potential in the flattened portion of the curve is due to ohmic loss. It is apparent from Figs. 2–4 that the increase in KOH concentration has minimum effect on activation over-potential while the concentration over-potential first decreases and then increases with the increase in KOH concentration. The concentration polarization increases at a higher KOH concentration because of less availability of methanol at the anode. On the other hand, the lowering of the KOH concentration increases the ionic conductivity of the medium or decreases the ohmic loss. It is seen in Figs. 2–4 that the cell performance is highest in the ohmic loss region for all the three fuels, e.g., methanol, ethanol and sodium borohydride, when 3 M KOH was used with 2 M fuels. The sharp fall in the performance in the case of sodium borohydride in the range of concentration polarization may be because of a decrease in solubility of sodium borohydride at a high KOH concentration (10 M).

3.2. Effect of temperature

Figs. 5–7 show the current–voltage relationship for methanol, ethanol and sodium borohydride fuel when 2 M fuel and 3 M KOH solution was fed to the alkaline fuel cell at
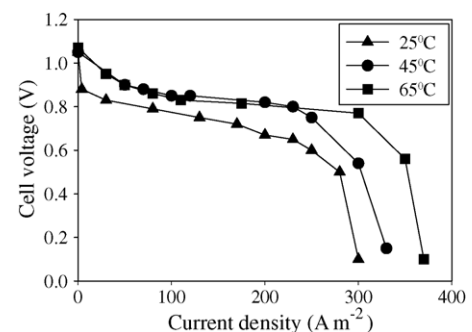

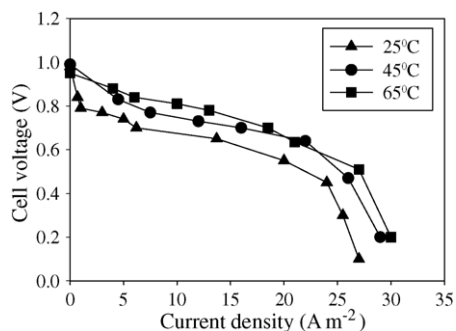Fig. 5. Polarization curve for 3 M KOH/methanol (2 M) at different temperatures.

Fig. 6. Polarization curve for 3 M KOH/ethanol (2 M) at different temperatures.
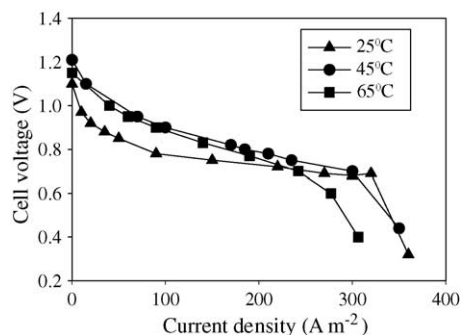

Fig. 7. Polarization curve for 3 M KOH/sodium borohydride (2 M) at different temperatures.

different temperatures. It is seen that the cell performance increases with the increase in temperature because of decrease in the activation and concentration over-potentials. Fig. 7 indicates that the performance for a sodium borohydride/KOH fuel cell does not increase appreciably with increase in temperature and in fact it decreases at 65 °C. This may be because of the hydrogen gas generation from sodium borohydride at a higher temperature and its subsequent release from the fuel cell without taking part in the reaction.

Although the direct methanol alkaline fuel cell performed well its performance is lower than that for direct methanol fuel cell based on PEM technology in the given process conditions. The lower performance of the direct alcohol fuel cell may due to cross over of alcohol to the cathode side since the fuel-electrolyte mixture was in contact with both the anode and cathode. Further, carbonate formation due to the presence of CO_2 might have affected the electrodes and the electrolyte. This may handled by recycling and recharging the cell with fresh KOH, as mentioned earlier.

4. Conclusion

A systematic study was conducted of the effect of electrolyte concentration and temperature on the performance of an alkaline fuel cell in which methanol, ethanol or sodium borohydride were directly fed as fuel. The cell performance was highest when 3 M KOH was used with 2 M fuel. The cell performance decreases with further increase in KOH concentration. This is attributed to the activation and concentration over-potentials at high KOH concentration. In general, the alkaline fuel cell performance increases with the increase in temperature for all the three fuels.

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