

Effect of KOH Concentration in the Gel Polymer Electrolyte for Direct Borohydride Fuel Cell

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ABSTRACT: The performance of a direct borohydride fuel cell (DBFC) based on a polyacrylamide (PAAm) gel polymer electrolyte system is investigated at different electrolyte concentrations. The DBFC, constructed using 2M sodium borohydride (NaBH₄) as the fuel and potassium hydroxide (KOH) solution gelled with PAAm as the electrolytes yield the highest electrical conductivity of $2.73 \times 10^{-1} \text{ S cm}^{-1}$ at 6M KOH. The optimized composition, PAAm + 2M NaBH₄ + 6M KOH, and the selected composition, PAAm + 2M NaBH₄ + 3M KOH are then used in

preparing the cells. Open-circuit voltages for fuel cells is about 0.85–0.92 V, and the discharge characteristic produce discharge capacities of about 257.12–273.12 mAh cm⁻² for cells with PAAm-6M KOH. Current-voltage and current density-power density plots and internal resistance for both cells are almost the same. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2662–2666, 2012

Key words: sodium borohydride; gel polymer electrolyte; potassium hydroxide; alkaline fuel cell

INTRODUCTION

A fuel cell is an electrochemical energy conversion device that directly converts hydrogen and oxygen into water to produce electricity.^{1,2} High interest in fuel cell technology development is attributed by its capability to generate high power density, silently, and environmental friendly.^{3,4} There are several types of fuel cells classified by operating temperature and the type of electrolyte used. For the direct borohydride fuel cell (DBFC), the liquid electrolyte used consists of potassium hydroxide (KOH) and a fuel solution of borohydride-based salt, i.e., potassium borohydride (KBH₄)⁵ or sodium borohydride (NaBH₄).^{6–8} Meanwhile, the source of oxygen is obtained freely from the air through the gas diffusion layer. However, the leakage and evaporation of the liquid electrolyte caused by technical assembly of the components has been a critical factor for long-term practical operation and causes substantial problems for putting liquid electrolytes into practical use. To reduce leakage and evaporation problems of this conventional system, gel polymer electrolytes (GPEs)

can be introduced into DBFC systems. In fuel cells or other electrochemical device applications, the most important properties GPEs need to show are high ionic conductivity and the ability to sustain high electrochemical activities.

Polyacrylamide (PAAm) is a polymer formed from acrylamide subunits that can also be readily crosslinked. PAAm is a nontoxic polymer. Thus, it is suitable to be used in wide range of applications such as in contact lenses industry. PAAm dissolved in water and produce gel-like characteristic. It is highly water-absorbent, making it suitable to be employed as polymer host. The ability of PAAm to entrap water makes it a good candidate for forming the GPE in fuel cell applications. Studies on PAAm-based hydrogels with a phosphoric acid (H₃PO₄) and potassium carbonate (K₂CO₃) additives systems have already demonstrated the ability to be good proton conductors, with conductivities exhibited in the range of 10^{-3} to $10^{-1} \text{ S cm}^{-1}$ at ambient temperature.^{9,10}

Since PAAm behaves as a good polymer host for producing GPEs, optimum compositions of the PAAm + NaBH₄ + KOH electrolyte system are prepared in this study to obtain relatively high ionic conductivity. The effects of different KOH concentrations on fuel cell performance are investigated incorporating with NaBH₄. The electrochemical properties of the DBFCs are presented through open circuit voltage (OCV), discharge characteristics, current-voltage (*I-V*), and current density-power density (*J-P*) measurements.

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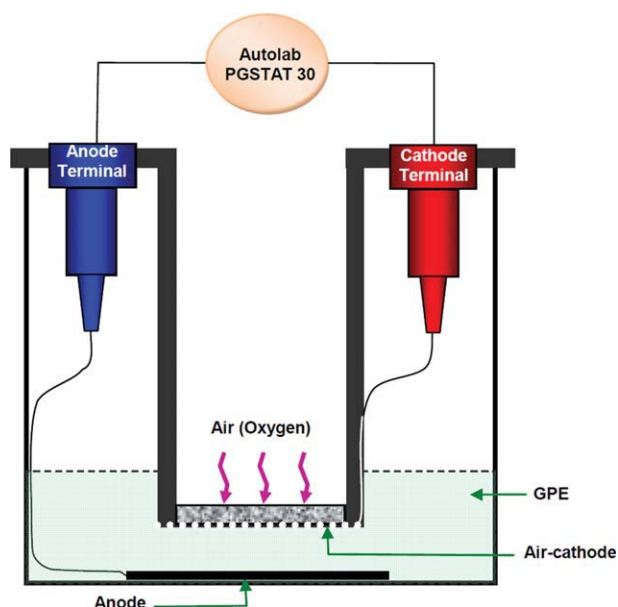


Figure 1 Schematic illustration of a gel polymer electrolyte-based alkaline fuel cell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Experiment

KOH (Merck) and PAAm (Polysciences, INC., $M_w = 5,000,000$) were used as the starting materials in the preparation of the gel electrolytes. The GPE solutions were prepared according to the following steps. PAAm (0.5 g) was first dissolved in 20 mL distilled water. After the polymer was completely dissolved, 20 mL of KOH solution at different concentrations (expressed as molarity values) was added, and the two solutions were mixed by stirring continuously at room temperature (25°C). When complete homogenization of the mixture was obtained, a fixed amount of NaBH_4 (2M) was then added to the resulting solution. The compositions of the samples were PAAm + 2M NaBH_4 + x M KOH, where $x = 0, 1, 2, 3, 4, 5, 6, 7,$ and 8.

For the conductivity measurement, samples of GPE with different concentrations were connected to a frequency response analyzer (FRA) module in an Autolab PGSTAT 30 system (Eco Chemie, B.V.). Stainless steel (SS) electrodes having a spacer for holding the GPE were used for conductivity cells. Ionic conductivity (σ) was calculated from the bulk resistance (R_b) obtained from the impedance spectrum in a frequency range of 0.1 Hz to 1 MHz with an amplitude of 0.01 V.

The commercial anode C/Ni (ECT, UK) with an active area of 16.0 cm^2 and an air-cathode made of $\text{MnO}_x/\text{C}/\text{Ni}$ (ECT, UK) with an active area of 16.0 cm^2 were used for testing the fuel cell performance. The experimental set-up of the GPE-based DBFC system for this work is shown schematically in Figure 1. A hollow cylinder with a cathode

attached to one of the open ends was placed inside a plastic beaker containing an anode at the bottom. Two wires connected to the anode and cathode acted as terminals for measuring the current and voltage of the fuel cell. The mixture of the gelled electrolyte and fuel solution was then introduced into the space between the anode and cathode. A combined volume of 60 mL for the fuel plus electrolyte medium was used in the experiments, and it was filled up to a certain level such that one side of the cathode was in contact with the fuel and electrolyte mixture while the other side was exposed to air. The oxygen present in the air acted as the oxidant.

An optimum concentration and intermediate conductivity values of the electrolytes were used in constructing DBFCs for comparison. The performances of the cells were evaluated according to their OCV by storing the cells in an open-circuit condition for 24 h at 25°C and with discharge profiles at a constant current of 1.0 mA cm^{-2} . The voltage and corresponding current were measured at different loads to get the I - V and J - P characteristic curves. Three cells were evaluated to obtain the average and standard deviation values for all the cell characteristics.

RESULTS AND DISCUSSION

Analysis of PAAm + 2M NaBH_4 + KOH electrolytes

Figure 2 shows the impedance spectrum of the GPE based on PAAm + 2M NaBH_4 at 0, 3, and 6M of KOH. The interception of the impedance spectrum on the real axis gives the bulk resistance (R_b) value. It can be seen that the GPE without KOH gave a R_b value of 2.625 Ω while the GPE with 6M KOH

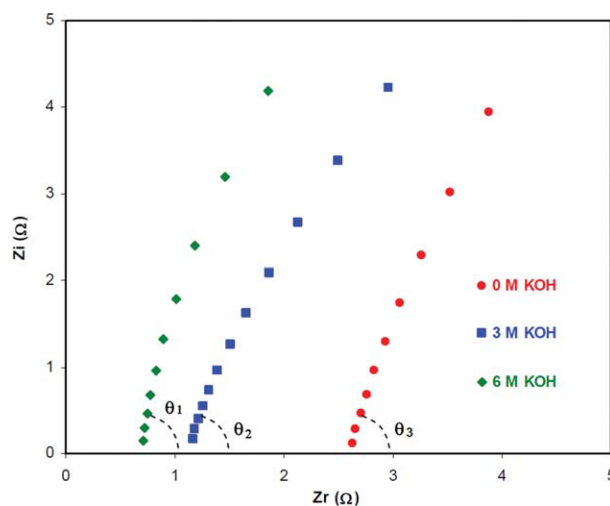


Figure 2 Impedance spectrum for the PAAm-2M NaBH_4 gel polymer electrolyte at different KOH concentrations at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

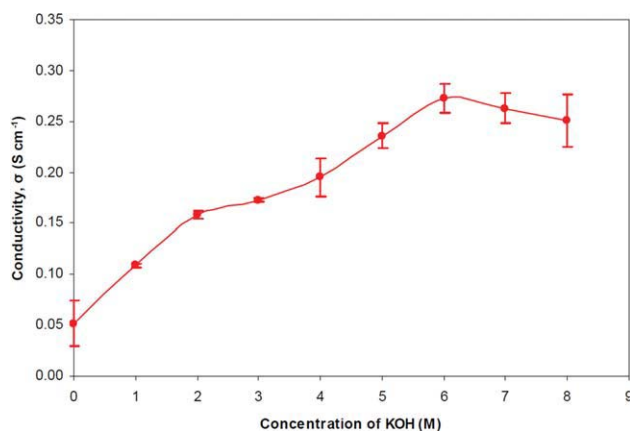


Figure 3 Effect of the KOH concentration on the conductivity of gel polymer electrolytes containing 2M NaBH₄ at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

yielded lower results than the GPE with 3M KOH, at 0.713 and 1.168 Ω , respectively. This decreasing pattern of R_b is due to the increasing of the charge carrier, hydroxyl ions (OH⁻) with the addition of KOH. These mobile ions reduce the ionic resistance and increase the conductivity of the GPE. Moreover, the inhomogeneous of electrode–electrolyte surface contacts is the reason why the Nyquist plot shown in Figure 2 is nonvertical. The interface between electrode and electrolyte can be regarded as a capacitance where the blocking electrode is used to analyze the impedance spectrum. An ideal capacitance should possess a vertical line with an angle of 90°. However, the angles of θ_1 , θ_2 , and θ_3 are slightly lower, at 70, 70, and 80°, respectively, but they are better than those of solid state KOH-based electrolytes.¹¹

The variation of the conductivity of PAAm + 2M NaBH₄ as a function of KOH concentration is given in Figure 3. It is apparent that the conductivity of GPE increases with increasing KOH concentration. The conductivity of PAAm + 2M NaBH₄ without any addition of KOH is $(0.52 \pm 0.22) \times 10^{-1}$ S cm⁻¹. With 3M KOH added, the conductivity value is $(1.73 \pm 0.02) \times 10^{-1}$ S cm⁻¹. The highest GPE conductivity value is $(2.73 \pm 0.14) \times 10^{-1}$ S cm⁻¹ at 6M KOH concentration added. This conductivity value is comparable with other PAAm gels giving conductivity values in the range of 10^{-3} to 10^{-2} S cm⁻¹.⁹ These results are also in agreement with other polymer-KOH-based GPEs.¹² However, beyond a 6M KOH concentration, the conductivity values are slightly decreased. It is a common understanding that the formation of ion multiples between high concentration free ions can occur, and this contributes to decreasing charge carrier. Decreases in ion mobility affect the conductivity of KOH based electrolytes at high concentrations.¹³

In DBFC applications, hydrogen (H₂) must be supplied to the electrolytes with the addition of fuel solution. H₂ is produced when NaBH₄ is dissolved in distilled water according to the reaction:



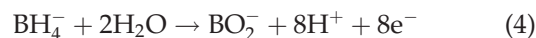
Or else, eq. (1) also can be explained in detail to eq. (4) through eq. (2) and (3):



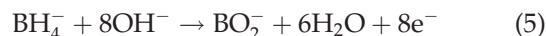
Then, the hydrogen will react to release electrons



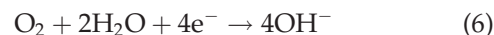
Therefore, eq. (1) also can be written as:



After the addition of KOH into the system, the reaction take place at the anode is as shown in eq. (5):



Spontaneously, cathodic reaction also occurs between oxygen from ambient air with water shown in eq. (6):



From eq. (5), it can be explained that the hydrogen supplied by the fuel reacts with the OH⁻ supplied by KOH to produce water and release the electrons. OH⁻ is the main ionic conductor in the GPE that diffuses continuously between the electrodes. Therefore, even the PAAm + NaBH₄ GPE without the addition of KOH give a conductivity value $[(0.52 \pm 0.22) \times 10^{-1}$ S cm⁻¹]; however, it is critical to supply OH⁻ to the GPE to complete the chemical reaction.

At higher concentrations of added KOH, there are more OH⁻ ions available for conduction since most solutions have conductivity proportional to the ion concentration. Since GPE was used, the ionic conduction is related with the polymer host. For a polymer to be an optimum ionic conductor, it should possess the presence of fixed charge sites.¹⁴ PAAm as the polymer host has accommodated the fixed charge sites with H⁺, where the moving OH⁻ can be temporarily accepted and released. PAAm exhibits better properties as a polymer host since it yields higher conductivity as compared with the chitosan used in the direct methanol fuel cell by Cui et al.¹⁵ However, when a certain concentration is reached, the conductivity will decrease because of the restricted ion mobility. At concentrations greater than

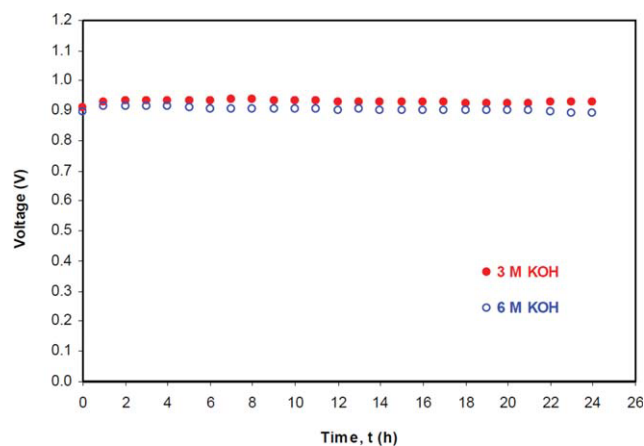


Figure 4 The open circuit measurement of direct borohydride fuel cells with PAAM-2M NaBH₄-KOH gel polymer electrolyte for 24 h of storage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

6M, the conductivity of KOH decreases due to the solvation of the K⁺ ions significantly impacting the amount of unbound H₂O molecules in the GPE.¹⁶ Consequently, the GPE resistance will increase and will reduce the conductivity.

Cell characterization

Figure 4 presents the OCV characteristic of the 2M NaBH₄ DBFC based on PAAM-3M KOH and PAAM-6M KOH electrolytes. The OCV values of the cells were at 0.92 and 0.90 V for the PAAM-3M KOH and PAAM-6M KOH, respectively. The results for the OCV of both cells with different KOH concentrations remained steady during 24 h of storage without any significant drops. The range of this OCV result is comparable with the values of other reported DBFCs, at about 0.9 V.⁵

Figure 5 shows the discharge characteristic at a constant current of 1.0 mA cm⁻² as a function of time for the cells. It is clearly seen that the discharge time of the cell using the PAAM-3M KOH electrolyte is 17 h, slightly longer than that of the cell employing PAAM-6M KOH electrolyte at 16 h. The average nominal voltages at the flat plateau region range from 0.70 to 0.90 V for both the fabricated cells with 3M and 6M KOH concentrations before hitting cutoff voltages of 0.80 and 0.70 V, respectively. It was also observed that the voltages decrease slightly in the plateau region, which may be due to the concentration polarization caused by reactant depletion or product accumulation within the cell.¹⁴ The voltage abruptly decreased after the cutoff voltage where the cell is completely discharged. The calculated discharge capacities obtained were 273.12 and 257.12 mAh cm⁻² for 3M and 6M concentration of KOH, respectively. Such low discharge efficiency is prob-

ably due to the crossover of reactants resulting because fresh fuel and electrolyte were not continuously fed to the DBFC, as demonstrated by Verma and Basu.⁶ Efficient delivery of fuel and electrolyte can be accomplished by feeding them continuously to the DBFC. However, in this work, since the experiment was set up to study the abilities of a fixed amount of PAAM- NaBH₄-KOH, the system did not include tanks for the fuel and electrolyte.

Figure 6 gives the *I-V* and *J-P* curves for the PAAM-based gel electrolyte DBFCs with 3M and 6M of KOH. It was observed that the increase in KOH concentration from 3 to 6M results in slightly higher *I-V* and *J-P* characteristics, and this means that the performance of the cell with a 6M concentration of KOH system improves slightly compared with the cell employing 3M KOH as the electrolyte. From Figure 6 it is expected that the internal resistance (*r*) of the cell using the optimum composition of electrolyte (6M KOH) was slightly lower than that of the cell using 3M KOH, with values of 3.02 and 3.05 Ω, respectively. The small difference in the *r* values of both cells shows that different KOH concentrations do not produce significant affects in the ionic resistance of the cells. Once again, this proves that PAAM is a good polymer host as it provides large free volumes for the OH⁻ to move across and therefore decreases the intrinsic resistance in the electrolyte. Furthermore, the highest power densities shown by the cells with 3 and 6M KOH as electrolytes are almost the same, namely, 4.27 and 4.92 mW cm⁻², respectively, as shown in Figure 6. However, at highest current density of 16.25 mA cm⁻², cell with 6M KOH performed higher power density of 3.45 mW cm⁻². As compared to cell with 3M KOH which gave 1.96 mW cm⁻² at same current density, cell with 6M KOH is more suitable for application that needs higher current. The works by Haijun et al.¹⁷ and Verma and Basu⁶ also found that the addition

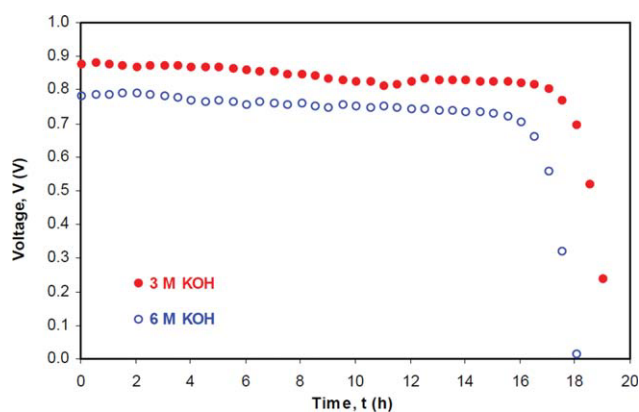


Figure 5 Discharge characteristic of direct borohydride fuel cells with PAAM-2M NaBH₄-KOH gel polymer electrolyte. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

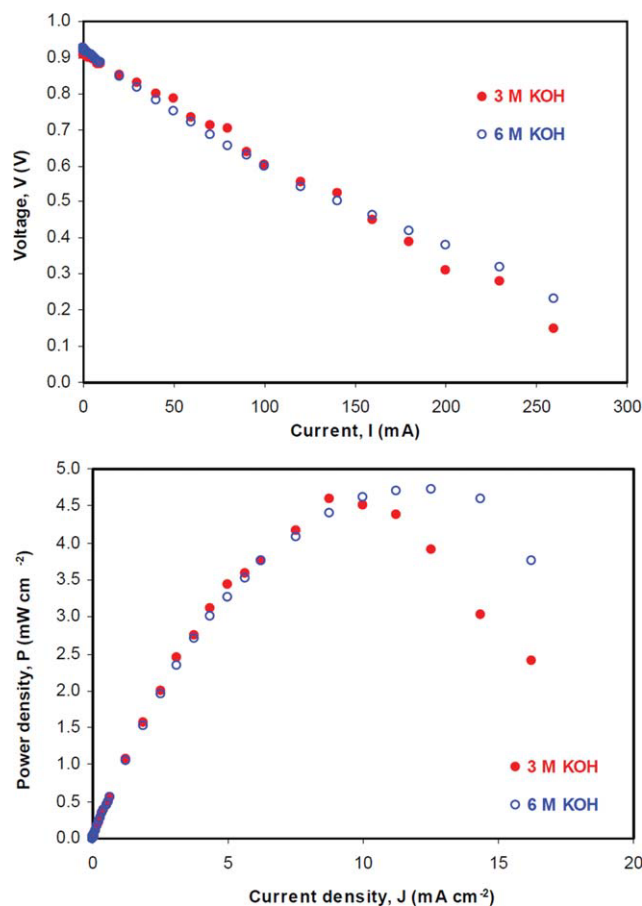


Figure 6 Plot of I - V and J - P for direct borohydride fuel cells with PAAm-2M NaBH₄-KOH gel polymer electrolyte. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of NaOH and KOH have their certain optimum values, but those are not at the highest points of conductivity.

CONCLUSIONS

PAAm-based gel polymer electrolytes containing 2M NaBH₄ and different concentrations of KOH have been prepared and gave the highest conductivity

value at 6M of KOH addition. For further comparisons, the intermediate conductivity value of 3M KOH was also studied. On the basis of cell characterizations, the performances of DBFCs with 3 and 6M KOH were just slightly different. With regards to power density performance, cell with 6M KOH has an advantage over cell with 3M KOH since it produced more than 50% power density at highest current density. From an economics point of view, the cost of NaBH₄ which matter most, so fixed amount of NaBH₄ was used in this work. At low and higher currents, the significant differences of power densities of the DBFCs with different KOH concentrations recovered had much more economic interest than the more affordable KOH used.

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