Short communication

A direct borohydride fuel cell based on poly(vinyl alcohol)/hydroxyapatite composite polymer electrolyte membrane

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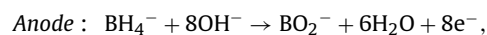
ABSTRACT

A new poly(vinyl alcohol)/hydroxyapatite (PVA/HAP) composite polymer membrane was synthesized using a solution casting method. Alkaline direct borohydride fuel cells (DBFCs), consisting of an air cathode based on MnO_2/C inks on Ni-foam, anodes based on PtRu black and Au catalysts on Ni-foam, and the PVA/HAP composite polymer membrane, were assembled and investigated for the first time. It was demonstrated that the alkaline direct borohydride fuel cell comprised of this low-cost PVA/HAP composite polymer membrane showed good electrochemical performance. As a result, the maximum power density of the alkaline DBFC based on the PtRu anode ($45\,mW\,cm^{-2}$) proved higher than that of the DBFC based on the Au anode ($33\,mW\,cm^{-2}$) in a 4 M KOH + 1 M KBH_4 solution at ambient conditions. This novel PVA/HAP composite polymer electrolyte membrane with high ionic conductivity at the order of $10^{-2}\,S\,cm^{-1}$ has great potential for alkaline DBFC applications.
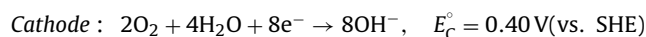
1. Introduction

Recently, direct borohydride fuel cells (DBFCs) [1–13] have gained a lot of attention in terms of their good electrochemical performances at room temperature. The advantages of the DBFC include: it can use non-noble metal catalysts for both the anode and the cathode, lower levels of toxicity, greater hydrogen capacity, as well as greater safety and energy density. However, three main issues concerning its development exist: (i) borohydride hydrolysis; (ii) BH_4^- crossover; (iii) materials cost related to use of the DBFC. A more detailed explanation can be found in review paper [1]. A great deal of research has focused on anode catalysts including Au/Pt [2], nano-Au [3], Pt black, Pt/C, and PtRu/C [4], Ni and Pd/C [5], metal hydride (MH) alloys [6], Pt black [7], and PtNi [8]. Also, non-platinum cathode catalysts, such as MnO_2 [9–11], Ag and Au/C [3], and Fe-phthalocyanine [12] have been extensively studied. More recently, Hong et al. [13] reported on the addition of sodium borohydride into the NaOH electrolyte to increase the discharge capacity of a DBFC/MH(or Zn)–MnO_2 hybrid power system. Currently, the polymer membranes for the DBFC are mainly Nafion perfluorinated polymer membranes (Du Pont) [5,6,11] and anion-exchange polymer m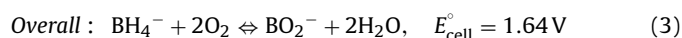embrane [8]; in particular, some authors also proposed a membraneless DBFC system [10]. Presently, a great need exists for a solid polymer electrolyte membrane with the properties of a low BH_4^- crossover rate and a low polymer cost for DBFC applications. Based on the above research, we prepared a novel alkaline polymer electrolyte membrane based on poly(vinyl alcohol) (PVA) and hydroxyapatite (HAP) use with the DBFC in order to reduce the BH_4^- crossover problem. The half-cell and cell reactions of the DBFC are as follows [1,6]:

$$Anode: \quad BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-,$$
$$E_A^\circ = -1.24\,V(vs.\ SHE) \tag{1}$$

$$Cathode: \quad 2O_2 + 4H_2O + 8e^- \rightarrow 8OH^-, \quad E_C^\circ = 0.40\,V(vs.\ SHE) \tag{2}$$

$$Overall: \quad BH_4^- + 2O_2 \Leftrightarrow BO_2^- + 2H_2O, \quad E_{cell}^\circ = 1.64\,V \tag{3}$$

where BH_4^- reacts with OH^- to form BO_2^- and H_2O, and releases eight electrons at the anode; meanwhile, oxygen reacts with H_2O to forms OH^- at the cathode. More importantly, the electrooxidation reaction of BH_4^- has been shown to be more favorable in an alkaline media as compared to an acidic media [1].

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has long been used as an implant material owing to excellent biocompatibility, bioactivity

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and chemical stability. The addition of a hydrophilic hydroxyapatite ceramic filler into a polymer matrix not only facilitated a reduction in the glass transition temperature (T_g) and the crystallinity of the PVA polymer, as well as an increase of the amorphous phases of the polymer matrix, but also increased its ionic conductivity. Interestingly, Park and Yamazaki [14] recently prepared a Nafion/HAP composite membrane to suppress methanol crossover for direct methanol fuel cells. As we know, when an HAP filler, which is a stiffer material, is added into the PVA matrix, the swelling ratio of the PVA/HAP composite polymer membrane is effectively reduced. The characteristic properties of the crosslinked PVA/HAP polymer membranes with ionic conductivity of 10^{-2} S cm^{-1} at different amounts of HAP fillers (2.5–10 wt.%) have been investigated and discussed in detail [15].

In this study, the scheme of construction for the alkaline DBFC was similar to that used in the previous research [15]. The electrochemical characteristics of the DBFCs comprised of alkaline PVA/HAP composite polymer membranes were investigated by the linear polarization and the galvanostatic discharge methods for the first time. Further, the peak power density of the DBFC was also investigated.

2. Experimental

2.1. Preparation of PVA/HAP composite polymer membranes

PVA (Aldrich), HAP ceramic fillers (Aldrich), and KOH (Merck) were used as received without further purification. The degree of polymerization and saponification of the PVA was 1700 and 98–99%, respectively. The PVA/HAP composite polymer membranes were prepared using a solution casting method. The appropriate amounts of PVA:HAP = 1:2.5–15 wt.% were dissolved in distilled water by stirring. The resulting solution was stirred continuously until the solution mixture reached a homogeneous viscous appearance at 90 °C for 2 h. The addition sequence of powders and the time of blending in the vessel were well controlled. The resulting solution was poured out into a Teflon container or Petri dish. The thickness of the wet composite polymer membrane was between 0.020 cm and 0.040 cm. The container with the viscous PVA/HAP composite polymer solution was weighed again and then the excess water was allowed to evaporate slowly at 25 °C with a relative humidity of 30%. After the water solvent evaporation, the container with the composite solid polymer membrane was weighed again. The composition of the PVA/HAP composite polymer membrane was determined from the mass balance. The thickness of the composite polymer membrane was controlled within a range of 0.010–0.030 cm. The PVA/HAP composite polymer membrane was further crosslinked by immersing in a solution of 5 wt.% glutaraldehyde (GA, 25 wt.% content in distilled water, Merck), 1.0 vol.% HCl (HCl used as a catalyst) and acetone for the crosslinking reaction at 30–40 °C for 12 h. This composite polymer membrane preparation procedure has been described in detail elsewhere [15].

2.2. Preparation of the anode and the cathode

The catalyst ink for the anode was prepared by mixing 70 wt.% PtRu black inks (Alfa, HiSPEC 6000, PtRu black with Pt:Ru = 1:1 molar ratio), 30 wt.% PTFE binder solution (Du Pont, 60 wt.% base solution), and a suitable amount of distilled water and alcohol. The resulting PtRu black mixtures were ultrasonicated for 2 h. The PtRu black inks were loaded onto the Ni-foam using a paint-brush method to achieve a loading of 1.0 mg cm^{-2} PtRu black. The as-prepared PtRu anode was dried in a vacuum oven at 100 °C for 12 h.

The Au electrode with a loading of 1.0 mg cm^{-2} was also prepared by an Au sputter (Hitachi, Japan).

The catalyst layer of the air electrode was then prepared by spraying a mixture of a 15 wt.% of PTFE solution binder and 85 wt.% of mixed powders consisting of MnO$_2$ catalyst + BP2000 carbon black. The Ni-foam current collector was cut at 1 cm × 1 cm. The preparation method of the air cathode has been reported in detail elsewhere [16].

2.3. Electrochemical measurements

The linear polarization curves for the air cathode wrapped with the PVA/HAP composite polymer membrane (A = 1 cm^2) were carried out on a three-electrode system in 4 M KOH and 4 M KOH + 1 M KBH$_4$ solutions. A large section (10 cm × 10 cm) of Pt sheet was used as a counter electrode and a Hg/HgO electrode was used as a reference electrode. All electrode potentials were recorded here vs. reversible hydrogen electrode (RHE). The chronoamperomtric curves for the anode based on PtRu black and nano-sized Au were carried out on a three-electrode system in a 4 M KOH + 1 M KBH$_4$ solution at room temperature.

The electrochemical measurements for the DBFC were carried out in a two-electrode system. The chronopotentiometric curve ($E–t$), $I–V$ and the power density curves of the DEFC comprised of the alkaline PVA/HAP composite polymer membrane were recorded at the current density of 20 mA cm^{-2} and a scan rate of 1 mV s^{-1}, respectively. All electrochemical measurements were performed on an Autolab PGSTAT-30 electrochemical system with GPES 4.8 package software (Eco Chemie, The Netherlands). The detailed construction of the alkaline DBFC for measurement has been described in detail elsewhere [15].

3. Results and discussion

The polarization curves for the air cathode covered with a PVA/10 wt.% HAP composite polymer membrane (with σ ca. 0.0442 S cm^{-1} at 30 °C or with area resistance of 0.31–0.366 Ω cm^2) [15] in 4 M KOH and 4 M KOH + 1 M KBH$_4$ aqueous solutions, respectively, at 1 mV s^{-1} are shown in Fig. 1. It illustrates that the current density of the air electrode in the 4 M KOH solution was similar to that of the air electrode in the 4 M KOH + 1 M KBH$_4$ solution. It was clearly observed that the degree of the borohydride crossover in the PVA/HAP composite polymer membrane is insignificant. Interestingly, the electrochemical activity of the air (MnO$_2$) electrode with PVA/HAP SPE was not strongly affected by the borohydride crossover. In fact, it was observed that the decay of the current
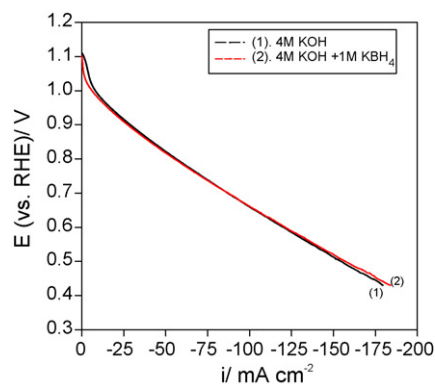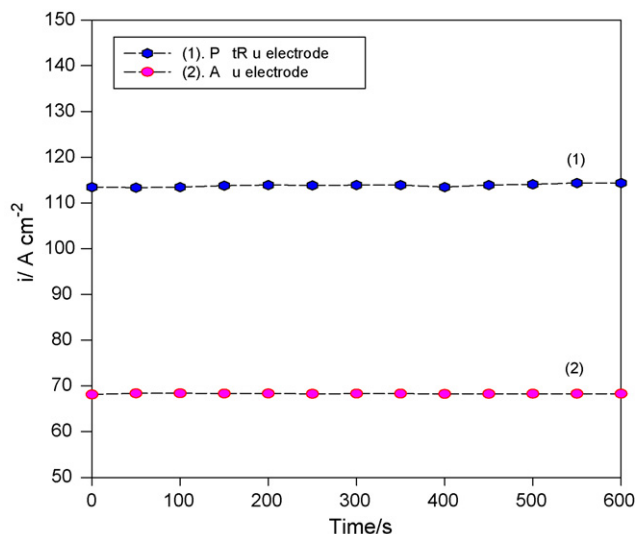

Fig. 1. The $I–V$ curve for the air cathode covered with the PVA/10 wt.% HAP composite polymer membrane in 4 M KOH and 4 M KOH + 1 M KBH$_4$ solutions at room temperature and ambient pressure.

Fig. 2. The *I–t* curves for the anodes loading with PtRu black and Au catalysts in 4 M KOH and 4 M KOH + 1 M KBH$_4$ solution (at −0.40 V vs. Hg/HgO).

Fig. 3. The *E–t* curves for DBFC with different catalysts (PtRu black vs. Au) in 4 M KOH + 1 M KBH$_4$ solution (at 20 mA cm^{-2} at 25 °C and 1 atm).

density for the ORR at different electrode potentials was approximately 1–2%. As we know, the crossover borohydride tends to block some active surface areas of the cathode (Pt) catalysts [1]. It was found that the MnO$_2$ cathode exhibited much more tolerance for the BH$_4^-$ crossover than the Pt electrode [9,10]. The higher the current density was, the higher the BH$_4^-$ crossover that occurred. The polarization results demonstrated that the BH$_4^-$ crossover affected the electrochemical performance of the air electrode based on the MnO$_2$ catalyst. The degree of degradation of the air electrode was completely dependent on the types of composite polymer membranes such as Nafion or PVA/HAP SPEs, and the cathode catalysts, such as Pt/C or MnO$_2$.

The chronoampometric curves for the anodes containing 1 mg cm^{-2} PtRu black and Au catalysts in a 4 M KOH + 1 M KBH$_4$ aqueous solution at 25 °C at −0.40 V (vs. Hg/HgO) are shown in Fig. 2. The borohydride oxidation current density for the PtRu anode was ca. 113.8 mA cm^{-2}; however, it was only 69.3 mA cm^{-2} for the Au anode. This result indicates that the electrochemical performance of the PtRu anode was better than that of the Au anode. Thus, the PtRu black catalyst appeared to be more electroactive than the Au catalyst according to their electrochemical oxidation abilities.

Fig. 3 shows the *E–t* curves of alkaline DBFCs consisting of the PtRu anode and the Au anode, the air cathode and the PVA/10 wt.% HAP composite polymer membrane in a 4 M KOH + 1 M KBH$_4$ solution, respectively, at 20 mA cm^{-2} at 25 °C and ambient air. The average cell potentials of the DBFCs containing the PtRu anode and the Au anode were 0.82 V and 0.76 V, respectively. These results show that the DBFC performance with the PtRu anode was superior to that of the DBFC with the Au anode.

Fig. 4 shows the potential–current density and the power density–current density curves for alkaline DBFCs containing the PtRu anode and the Au anode in a 4 M KOH + 1 M KBH$_4$ solution at room temperature, respectively. As a result, the maximum power density of 45 mW cm^{-2} for alkaline DBFC with the PtRu anode was achieved at $E_{p,max} = 0.418$ V with a peak current density ($i_{p,max}$) of 107.0 mA cm^{-2}. On the other hand, the maximum power density of alkaline DBFC with the Au anode was 33 mW cm^{-2} at $E_{p,max} = 0.399$ V with a peak current density of 82.9 mA cm^{-2} at 25 °C. The utilization of the KBH$_4$ reactants for the PtRu black electrode was around 58% (i.e., $n = 8 \times 0.58 = 4.62e^-$), in contrast, for the Au electrode about 70.1% (i.e., $n = 8 \times 0.701 = 5.6e^-$). Clearly, it was
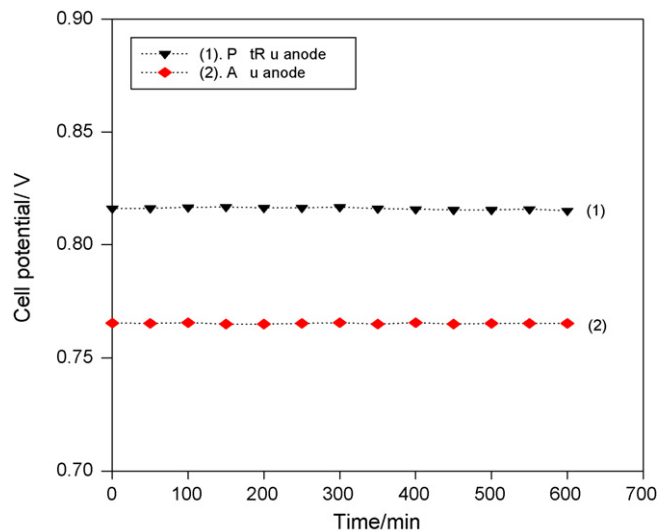
revealed that the utilization of the KBH$_4$ reactants for the Au electrode was higher than that for the PtRu black electrode. It may be due to much less hydrolysis reaction (less H$_2$ produced) on the Au electrode.

Verma and Basu [4] also reported on the performances of DBFCs based on different types of anode catalysts, such as Pt black, PtRu/C and Pt/C. It was found that the best DBFC performance occurred using a PtRu/C anode catalyst with an optimal loading at 1.5 mg cm^{-2} in a 3 M KOH + 2 M NaBH$_4$ solution at 25 °C. However, it was also discovered that the maximum power density of the DBFC with Pt black was about 20 mW cm^{-2} at a current density of 30 mA cm^{-2}. Verma et al. [9] studied alkaline DBFCs comprised of the MnO$_2$ cathode (with a load of 3 mg cm^{-2}), the Pt/Ni anode and Nafion polymer membrane. The maximum power density of 19 mW cm^{-2} was obtained at 39 mA cm^{-2} in a 3 M KOH + 1 M NaBH$_4$ solution. This clearly indicates that the performance of the alkaline DBFC system based on the PVA/HAP composite polymer membrane performs better than that of the DBFC based on the Nafion polymer membrane.
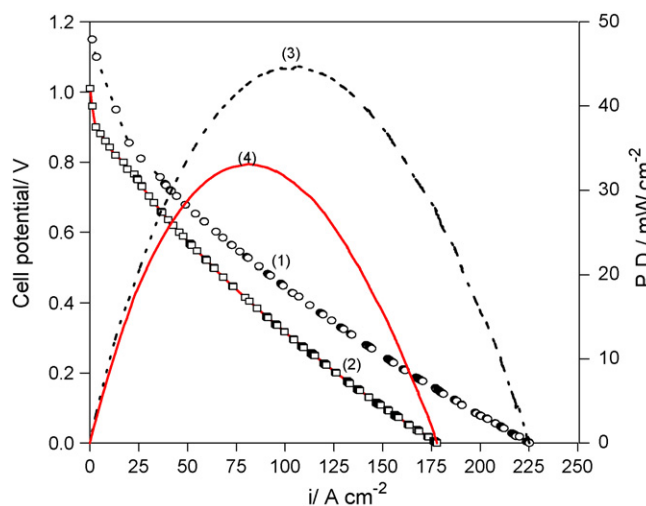
Fig. 4. The *I–V* polarization and the power density curves of the DBFC. Symbol: (1) IV curve by PtRu black; (2) IV curve by Au catalyst; (3) P.D. curve by PtRu black; (4) P.D. curve by Au catalyst.

Accordingly, the alkaline DBFC with the PtRu anode exhibited higher performance than the alkaline DBFC with the Au anode using the identical amount catalyst, i.e., $1\,mg\,cm^{-2}$. More importantly, the alkaline DBFC consists of an air cathode based on MnO_2, i.e., a non-precious metal oxide catalyst. The metal oxide MnO_2 catalyst is not only inexpensive but also more tolerant towards crossover, and is active for the reduction of O_2 to OH^- in the alkaline media. Another advantage is that the alkaline PVA/HAP composite polymer membrane is a cheap (non-perfluorosulfonated) polymer membrane, as compared with the Nafion (perfluorosulfonated) polymer membrane.

4. Conclusions

The composite polymer membrane based on the PVA polymer and HAP ceramic fillers was prepared using a solution casting method. Alkaline direct borohydride fuel cells (DBFCs) comprised of the PVA/HAP composite polymer membrane were assembled and tested for the first time. The electrochemical performances of the DBFCs containing the PtRu anode and the Au anode were studied and compared. The result demonstrated that the DBFC with the PtRu anode exhibited higher electrochemical performances. The maximum peak power density of the DBFC with the PtRu anode in a 4 M KOH + 1 M KBH_4 solution is ca. $45\,mW\,cm^{-2}$. A free-standing PVA/HAP composite polymer membrane can easily be prepared. The PVA/HAP composite polymer membrane is a good candidate for alkaline DBFC system applications.

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