Short communication

Iron phthalocyanine as a cathode catalyst for a direct borohydride fuel cell

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Abstract

A direct borohydride fuel cell (DBFC) is constructed using a cathode based on iron phthalocyanine (FePc) catalyst supported on active carbon (AC), and a AB_5-type hydrogen storage alloy ($MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$) was used as the anode catalyst. The electrochemical properties are investigated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), etc. methods. The electrochemical experiments show that FePc-catalyzed cathode not only exhibits considerable electrocatalytic activity for oxygen reduction in the BH_4^- solutions, but also the existence of BH_4^- ions has almost no negative influences on the discharge performances of the air-breathing cathode. At the optimum conditions of 6 M KOH + 0.8 M KBH_4 and room temperature, the maximal power density of 92 mW cm^{-2} is obtained for this cell with a discharge current density of 175 mA cm^{-2} at a cell voltage of 0.53 V. The new type alkaline fuel cell overcomes the problem of the conventional fuel cell in which both noble metal catalysts and expensive ion exchange membrane were used.
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Keywords: Borohydride; Fuel cell; Iron phthalocyanine; Oxygen reduction

1. Introduction

Fuel cells convert chemical flows to electrical power, they are the strongest candidates for alternative power generators of future. They can be used in diverse ways, from as small portable models to constant power generators. 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.

Recently, direct borohydride fuel cell (DBFC) [1–9] has become an interesting alternative as an electricity generator for fuel cell due to its many advantageous features: DBFC demonstrates high theoretical open cell voltage (OCV) of 1.64 V which is about 0.43 V higher than that of the direct methanol fuel cell (DMFC); DBFC system has more attraction for application in portable power supplies due to its high H-capacity and more compact structure than the DMFC system; DBFC has no harm to environment because its by-product borate can be recycled by reductant; Furthermore, DBFC has good cell performances at low temperatures compared with the DMFC. Research into

catalysts for the anode of the DBFCs has been well documented [10–12], however, the cathode has been less investigated. Platinum or platinum-based catalysts are the best electrocatalyst for oxygen reduction reaction (ORR) both in acid and alkaline fuel cells because of their high electrocatalytic activity and chemical stability, but it is too expensive and the ion exchange membrane must be used simultaneity to avoid crossover of BH_4^-. Ponce Deleon et al. [13,14] reviewed and compared DBFCs depended on different catalyst, and most of the fuel cells reported were divided by expensive ion exchange membrane with noble metal catalyst. Non-platinum cathode catalysts such as MnO_2 [1,3,15], Co-porphyrin [14,16–18], perovskite oxides [19–21], etc. cathode catalysts for ORR have been studied extensively. Metal phthalocyanines, which have been widely researched as an ORR catalyst in Ni-MH batteries [22], microbial fuel cells [16,23], direct methanol fuel cells [24,25], are expected to be alternative non-noble metal catalysts for ORR in the DBFC in this work.

Here we demonstrate a high efficient output direct borohydride fuel cell in which iron phthalocyanine (FePc) is used as a cathodic catalyst for ORR. Hydrogen storage alloy (HAS) can be used as an anodic catalyst in DBFCs because it can alleviate the problem of the low utilization of BH_4^- ions arising from the

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BH_4^- decomposition reaction on anode [1]. The electrochemical properties of half-cell and cell indicate that iron phthalocyanine (FePc) is capable of combining high oxygen reduction activity with good durability. As a result, this DBFC shows an acceptable stability and output power density which is higher than those of other reported DBFCs without using platinum catalyst and ion exchange membrane at the same test conditions.

2. Experiment

2.1. Materials

$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (where Mm denotes Ce-rich mixed mischmetal composed of 50 wt%Ce, 30 wt%La, 5 wt%Pr and 15 wt%Nd) alloy was prepared by inductive melting under argon atmosphere and the purity of all the additive elements was over 99.9 wt%. Iron phthalocyanine, analytical grade, was purchased from J&K Chemical Ltd. Activated carbon (YiHuan Carbon Co., Ltd. Fuzhou, China) was used as catalyst support. All other chemicals were analytical grade and were also used as received.

2.2. Electrodes preparation

The cathode used in the cell was a three-layer electrode consisting of a gas diffusion layer, an active layer, and a current accumulating matrix. The gas diffusion layer was prepared by mixing 60 wt% acetylene black (with surface area $2500 \, m^2 \, g^{-1}$) and 40 wt% polytetrafluoroethylene (PTFE) with ethanol into 0.2 mm thick film. The active layer was prepared by a slurry of 30 wt% FePc catalyst, 45 wt% activated carbon and 25 wt% PTFE emulsion and then coated onto a Ni-foam (thickness = 1.7 mm, porosity > 95%), the three-layer gas electrode was finished by pressing the coated Ni-foam and the gas diffusion layer at $120 \, kgf \, cm^{-2}$ into a 0.6 mm thick sheet.

To prepare anode, $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ alloy power (95 wt%) was mixed together with acetylene black (3 wt%), and cobalt monoxide (2 wt%) was also added to improve the electrochemical activity and high-rate discharge ability of alloy electrodes [26], then the mixture was smeared onto a Ni-foam (thickness = 1.7 mm, porosity > 95%), the mass loading of alloy in anode was $0.15 \, g \, cm^{-2}$. After drying at 80 °C in vacuum for 2 h, the catalyst layer was pressed at $120 \, kgf \, cm^{-2}$. Before cell testing, the anode was pretreated in the 6 M KOH and 0.2 M KBH_4 aqueous solution for 24 h to activate.

2.3. Experimental set-up and procedure

The cyclic voltammetry (CV) and line sweep voltammetry (LSV) were employed to characterize the electrochemical performance of cathode by using a computer controlled CHI650C Electrochemistry Workstation (CH Instrument, Inc., USA) with a conventional three-electrode configuration. The air-breathing cathode made in the above mentioned procedure served as the working electrode, a Hg/HgO/6 M KOH electrode as a reference electrode, and a Pt mesh as a counter electrode. The reference electrode was connected to the main body of the cell through a
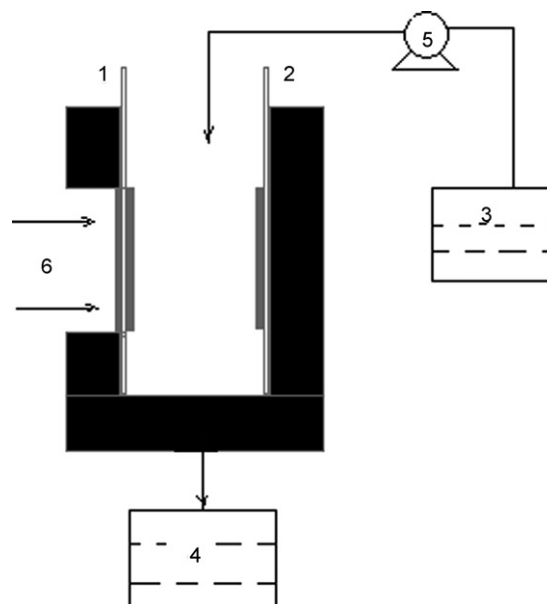

Fig. 1. Schematic diagram of air-breathing DBFC: (1) cathode; (2) anode; (3) fresh fuel–electrolyte mixture storage; (4) exhausted fuel–electrolyte mixture storage; (5) pump; (6) air.

Luggin capillary, whose end was centered on the working electrode and positioned closed to the electrode surface. The CV and LSV were plotted within a potential region of 0.2 to −1.1 V and 0 to −0.6 V at a scanning rate of $5 \, mV \, s^{-1}$, respectively. All potential values measured and reported in this work were versus Hg/HgO electrode.

The steady-state cell voltage–current density and discharging curves of this DBFC were performed by using a battery testing system (from Neware Technology Limited, Shenzhen, China). Fig. 1 shows a two electrode cell system, a cathode was placed on one side of the square container, the gas diffusion layer was exposed to air and the active layer was contacted with the electrolyte, an anode was placed on the other side with a gap of 1 cm between the two electrodes. The space of the two electrodes was used to feed with the fresh mixture of electrolyte (KOH) and fuel (KBH_4) through a pump.

All the electrochemical experiments were carried out at ambient atmosphere.

3. Results and discussion

3.1. Catalyst activity of cathode

The catalytic activity of the FePc for the oxygen reduction reaction was first characterized by using the catalytic electrode as the working electrode in air and argon-saturated 6 M KOH solutions, respectively. Fig. 2 presents cyclic voltammograms with a scan rate of $5 \, mV \, s^{-1}$ of ORR on the $10 \, mg \, cm^{-2}$ of FePc, as indicated by comparing the data observed in the air and argon-saturated 6 M KOH solutions, the great cathodic current of air electrode appeared at about 0.1 V (versus Hg/HgO) and rapidly increased with the negative shifting of potential, which is due to the reduction of oxygen. However, it did not happen
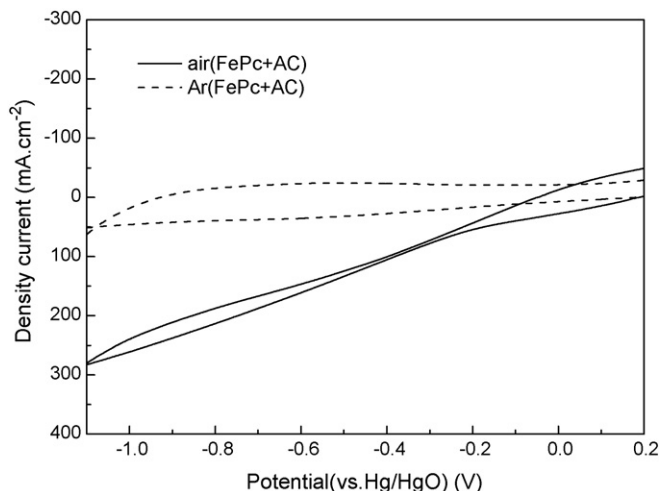
Fig. 2. Cyclic voltammograms on the FePc/C electrodes in the 6 M KOH solution saturated with Ar and air-saturated at ambient atmosphere. Catalyst loading: $10\,mg\,cm^{-2}$, scan rate: $5\,mV\,s^{-1}$.

in the argon-saturated electrolyte. As a result, the irreversible oxidation current displays a high activity of FePc for ORR.

3.2. Borohydride tolerance of cathode

Borohydride tolerance is an important criterion for selection of cathode materials for the DBFC, which can be determined by comparing the data obtained from the solutions with and without borohydride. Fig. 3 shows the LSV of air cathode catalyzed by $10\,mg\,cm^{-2}$ of FePc in 6 M KOH solutions with and without presence of $1\,M\,BH_4^-$ ions at the potential region of 0 to $-0.6\,V$, with a scan rate of $5\,mV\,s^{-1}$. As shown in Fig. 3, the polarization curve of the FePc-catalyzed cathode in the presence of BH_4^- ions is almost identical to that obtained from the blank alkaline solution ranging from 0 V to $-0.5\,V$, indicating that the existence of BH_4^- ions has almost no negative influences on the air-breathing cathodes. The result of Fig. 2 suggests
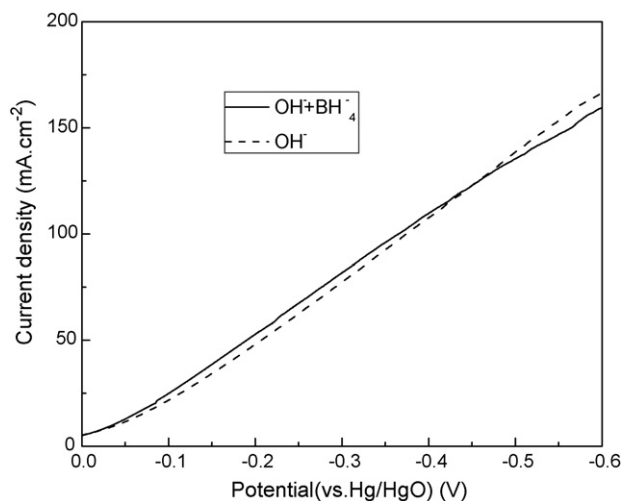

Fig. 3. Polarization curves of a FePc-catalyzed air cathode in 6 M KOH solution with or without addition of $1\,M\,KBH_4$ at ambient atmosphere. Catalyst loading: $10\,mg\,cm^{-2}$, scan rate: $5\,mV\,s^{-1}$.
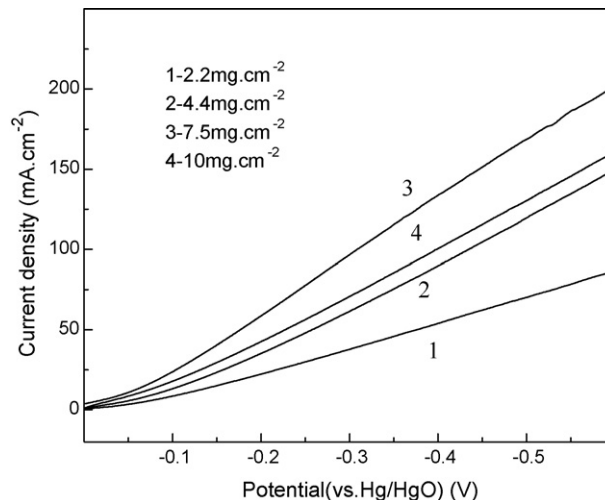

Fig. 4. Effect of catalyst loading on the performance of the air-breathing cathode at ambient atmosphere, scan rate: $5\,mV\,s^{-1}$.

that the FePc-catalyzed air-breathing cathode not only exhibits considerable electrocatalytic activity for ORR, but also shows catalytic inactivity for electrooxidation and chemical hydrolysis of BH_4^- ions. When the overpotential is more negative than $-0.5\,V$, the BH_4^- has a slight effect on this air-breathing electrode, which probably due to the ion migration velocity was restricted by the BH_4^-, but as generally considered, the practical value will be lost in this negative potential of oxygen reduction electrodes, so the authors think that the FePc-catalyzed cathode has an acceptable borohydride tolerance.

3.3. Influence of catalyst loading on performance of cathode

As an important region for oxygen reduction, the catalyst loading or thickness of the activate layer has an influence on the performance. With the increase of catalyst loading, the performance of cathode can be enhanced. However, if the loading is too high, it becomes very difficult for the O_2 to transport through the activated layer and also causes an increase in the resistance. So it is important to maintain an optimum loading of catalyst for the gas diffusion electrode. Shown in Fig. 4 is polarization curves of gas diffusion electrode dependence on various loading of FePc catalyst with a fixed proportion of FePc:AC:PTFE (30 wt%:45 wt%:25 wt%) in 6 M KOH solutions at ambient conditions. Fig. 4 indicates that with the increase of loading of FePc range from $2.2\,mg\,cm^{-2}$ to $10\,mg\,cm^{-2}$, the polarization current density of the air-breathing electrode with $7.5\,mg\,cm^{-2}$ FePc is much higher than that of other electrodes under the same overpotential, so the catalyst loading of $7.5\,mg\,cm^{-2}$ is selected in this research.

3.4. Influence of borohydride concentration on performance of DBFCs

In DBFC systems, the performance of DBFC greatly depends on the KBH_4 concentration in the fed anolyte. Fig. 5 shows the
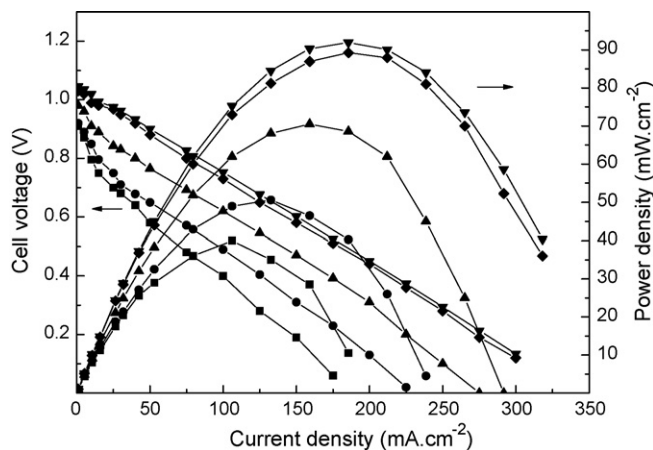
Fig. 5. Cell voltage vs. current density and power density vs. current density of borohydride fuel cells at different KBH_4 concentration in 6 M KOH solutions at ambient atmosphere: (■) 0.2 M; (●) 0.4 M; (▲) 0.6 M; (▼) 0.8 M; (♦) 1.0 M.

Fig. 6. Comparison of durability test of the DBFCs with the discharging of $50 \, mA \, cm^{-2}$ in this work and reference [14].

DBFCs voltage–current and power density curves are relative to the KBH_4 concentration range from 0.2 M to 1.0 M in the 6 M KOH solutions at ambient atmosphere. As it can be seen from Fig. 5, the cell performances are enhanced with increasing of KBH_4 concentration from 0.2 M to 0.8 M, and the open cell voltage (OCV) reaches 1.1 V, but it no longer increases when the KBH_4 concentration is more than 0.8 M. Fig. 5 also displays that there is a linear relationship between cell voltage and current density at high concentrations (0.8 M and 1.0 M). In other words, there is only an ohmic polarization in this cell reaction without obvious activation polarization and concentration polarization. This may attributes to that the presence of ion balance in the electrode/electrolyte at high concentration and elimination of the activation polarization and concentration polarization. The result also indicates that the electrode in this cell has high activity and stability. At this optimum KBH_4 concentration of 0.8 M, a maximal power density of $92 \, mW \, cm^{-2}$ at the discharge current density of $175 \, mA \, cm^{-2}$, with a work voltage of about 0.53 V, is attained.

3.5. Stability of DBFC

Furthermore, under the chosen conditions, the short-term stability of DBFC is tested by monitoring the cell voltage change during the galvanostatic discharging of $50 \, mA \, cm^{-2}$ of the DBFC in a period of 50 h at ambient atmosphere. The comparison of the cell voltage–time curves of this work and that of reference [14] are presented in Fig. 6. As it can be seen in Fig. 6, the OCV of this work is 1.1 V (0.72 V in reference), and rapidly to reaches and maintains a cell voltage of 0.82 V (0.63 V in reference) for about 32 h. Comparative results show that both the open circuit potential and steady cell potential in this work are higher than that of literature reported with Pt-catalyzed cathode at 70 °C. However, there is a gradual decay of cell voltage about 5% of this platform cell voltage, this mainly attributes to the carbonate and water reduced effective porosity of the gas diffusion electrode, which cause cathode flooding and therefore hinder the reactant transport and led to less oxygen supply.
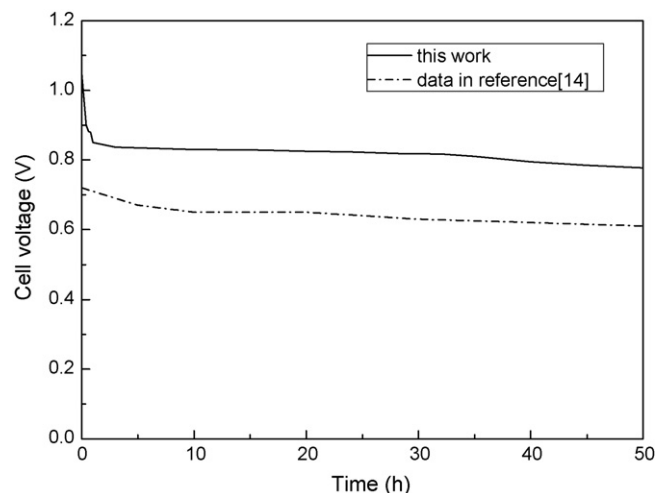
4. Conclusion

In this paper, a simple direct borohydride fuel cell based on the FePc-catalyzed cathode and the hydrogen storage alloy anode was constructed. In this fuel cell, electrochemical experiments reveal that FePc is a promising cathodic catalyst without expensive ion exchange membrane used for the direct borohydride fuel cell due to its acceptable activity, borohydride tolerance, and stability in alkaline media. The results suggest that the FePc-catalyzed air-breathing cathode not only exhibits considerable electrocatalytic activity for oxygen reduction, but also shows catalytic inactivity for electrooxidation and chemical hydrolysis of BH_4^- ions. Furthermore, under 0.53 V of cell voltage, a maximal power density $92 \, mW \, cm^{-2}$ is obtained for this cell at a discharge current density of $175 \, mA \, cm^{-2}$ at ambient condition. Although the DBFCs have higher output voltage and power density, there are many other parameters which influence the cell performance such as operating temperature, air pressure, etc. should be further explored in our continuous works.

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