A H$_2$/O$_2$ FUEL CELL USING ACID DOPED POLYBENZIMIDAZOLE AS POLYMER ELECTROLYTE

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ABSTRACT

Phosphoric acid doped polybenzimidazole (PBI-poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole]) has been investigated for use in a H$_2$/O$_2$ fuel cell. The prototype fuel cell test results show that the PBI fuel cell worked quite well at 150°C with atmospheric pressure hydrogen and oxygen which were humidified at room temperature. No membrane dehydration was observed over 200 hours operating. The maximum power density of this prototype fuel cell was 0.25 W/cm$^2$ at current density of 700 mA/cm$^2$. Further improvement of the cell performance is to be anticipated by properly impregnating the electrode structure with the polymer electrolyte. The advantage of the H$_2$/O$_2$ fuel cell using PBI as polymer electrolyte is that the cell design and the routine maintenance can be significantly simplified because of the low electro-osmotic drag number and good proton conductivity of the PBI membrane at elevated temperature.

INTRODUCTION

Fuel cells employing a solid polymer electrolytes such as perfluorosulfonic acid polymer electrolyte (Nafion$^\circledast$) have been receiving more and more attention due to their promise for high energy density power plant for both stationary or mobile applications. The main features of the polymer electrolyte fuel cell (PEFC) are pollution free operation, less corrosion and high power density. During the last five years, many efforts were made to decrease the noble metal catalyst loading and improve the conductivity of the polymer electrolyte[1-4]. Gottesfeld et. al.[1,2] and Taylor et. al.[3] reported that the catalyst loading can be deceased to as low as 0.05-0.15mg/cm$^2$ with a fuel cell performance similar to that of a high loading PEFC (4mg/cm$^2$ Pt). Since the Nafion$^\circledast$ type of polymer electrolytes usually have a large electro-osmotic drag number, water is moved from the anode side to the cathode side when cell is operating, resulting a large cell voltage loss due

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to the dehydration of the membrane. In order to adequately hydrate the membrane, these cell must be operated under intensive gas humidification (reactant gas saturated at 100-105°C), though the cell operating temperature is 80°C. Therefore the water management is critical for these PEFC to achieve a high energy efficiency. There are several modeling and experimental studies published[5-9] that discuss the issues of the water and heat management of this kind of PEFC.

There is a motivation to increase the cell operating temperature in order to enhance the reaction kinetics and depress the electrode poisoning, for instance, when using impure reformed hydrogen or when the fuel is methanol. For such an application, a new polymer electrolyte which can be operated at elevated temperature is required. Savinell et. al.[10] proposed that the polybenzimidazole (PBI) can be used in PEFC as a polymer electrolyte when the PBI was doped with a strong acid such as phosphoric acid or sulfuric acid. PBI is a basic polymer (pKa=5.5) and it can be easily doped with a strong acid to form a single phase polymer electrolyte. The doping level, for instance, could be as high as five phosphoric acid molecules per polymer repeat unit. The results of the NMR spectroscopy show that phosphoric acid sorbed inside the PBI membrane is relatively immobilized as compared to free phosphoric acid. The solid-state NMR spectra reveals that there is an interaction between PBI and phosphoric acid[11]. The acid doped PBI membrane exhibits good proton conductivity, low gas permeability, excellent oxidative and thermal stability, and good mechanical flexibility at elevated temperature (200°C). The most interesting feature of the PBI is that it has an almost zero electro-osmotic drag number[12], compared to the drag number of 0.6-2 for Nafion® membrane[13,14]. This means that when the protons transport through the PBI membrane, they do not carry water with them. This unique feature of the PBI allows the PBI fuel cell to be operated under a high temperature and a low gas humidification without membrane and anode dehydration. Since a PBI fuel cell does not have the water management problem, the cell design and the routine maintenance can be significantly simplified. These properties of acid doped PBI polymer electrolyte are promising for applications of PEFC, including the hydrogen/oxygen fuel cell and the direct methanol fuel cell.

This paper presents the results of a H2/O2 fuel cell employing the acid doped PBI membrane as the polymer electrolyte. The PBI fuel cell was operated at 150°C using hydrogen and oxygen or air at atmospheric pressure. The effects of the gas humidification, and air on the cell performance were examined. The stability of the electrodes and the polymer electrolyte were examined in tests of several hundred hours duration. Different methods to prepare membrane/electrode assemblies were evaluated for the hydrogen electrode and the oxygen electrode, respectively.

EXPERIMENTAL

Polybenzimidazole (Hoechst Celanese) films were cast from a solution of the high molecular weight (HMW) PBI (25,000 amu) in dimethylacetamide (DMAc). The films...
were then doped by immersion in a 11M phosphoric acid solution for at least 24 hours. The resulting doping level is approximately five phosphoric acid molecules per polymer repeat unit. The film thickness after doping were about 0.008 cm.

E-TEK electrodes (The Electrosynthesis Co., Inc.) with a Pt loading of 0.5mg/cm² on carbon and homemade Pt black electrodes with Pt loading of 2mg/cm² were used. The membrane/electrode (M&E) assemblies were formed by hot pressing the electrodes on an acid doped PBI membrane at 150°C, 2.2×10⁴ kPa for 10 min. The M&E assemblies were then impregnated with phosphoric acid by adding few micro-liters of 5M H₃PO₄ solution on the gas backing side, and letting the acid solution penetrate into the electrode structure. The function of added acid is to soften the PBI/electrode interface to make ionic contact when the electrode is heated to 150°C. Since the ionic conductivity of the electrode is important to the electrode performance, several other methods to form M&E assembly were tested to investigate the effect of the polymer loading within the electrode structure on the electrode performance.

One method to add electrolyte to the electrode structure is to impregnate the electrode with 10% PBI solution (HMW PBI in DMAc with 2% LiCl). To help the PBI solution penetrate into the electrode structure, the electrodes were placed in 10% PBI solution under vacuum at room temperature, and then repressurized to 1 atm. They then were dried under vacuum at room temperature. Electrodes impregnated with 10% PBI solution increased in weight by 12%. Two impregnated electrodes were attached to an undoped PBI membrane with a small amount of solvent DMAc and pressed at 100°C and 8.8×10⁴ kPa for 2 min to form M&E assembly. Finally the M&E assembly was immersed in DI water for four days to extract LiCl, and then whole M&E assembly was doped with H₃PO₄.

In a second method, instead of impregnating electrodes first, the electrodes were directly glued on a undoped PBI membrane with 12% PBI solution (HMW PBI in DMAc with 2% CH₃COOLi) at 100°C and 8.8×10⁴ kPa for 2 min to form the M&E assembly. It is expected that when the electrodes are glued directly onto the PBI membrane, some of PBI solution will penetrate into the electrode structure. Like the first method, the salt was then extracted with DI water for four days and then the M&E assembly was doped with H₃PO₄. In both the first method and the second method, the PBI membranes are doped after forming M&E assembly. While doping the M&E assembly with H₃PO₄, the PBI membrane formed wrinkles due to its expansion upon adsorbing acid and water. Therefore these methods may not be suitable to prepare large M&E assemblies.

The third method eliminates membrane expansion. The electrodes were first brushed by a dilute PBI solution (HMW PBI in DMAc with 2% CH₃COOLi). After the electrodes were impregnated with PBI solution, they were dried at 80°C for 2 hours and then the lithium salt was washed out by boiling the electrodes in DI water. The electrodes
were kept in clean DI water four days. Before the electrodes were hot pressed onto a PBI membrane, they were doped with 5M H₃PO₄. Then the electrodes were hot pressed on an acid doped PBI membrane at 150°C, 2.2x10⁴ kPa for 10 min. Since this method uses doped PBI membrane to form the M&E assembly, it significantly reduces the stress between electrodes and membrane. This method appears to be more suitable for preparing large size electrodes.

All the electrochemical experiments were carried out in a single cell test station. A drawing of the single cell is shown in Fig. 1. The fuel cell hardware consisted of two PTFE blocks supported by two stainless steel plates at the outside. The gas distribution channels and feed-throughs were machined into the PTFE blocks. The whole construction was held together by four threaded studs with nuts at each end. At the anode side, a small hydrogen fed gas diffusion electrode (E-TEK electrode 0.5 mg/cm² Pt on carbon) was used as the reference electrode and was found to operate satisfactorily. The potential of this reference electrode was assumed to be equivalent to the reversible hydrogen electrode (RHE), and all potentials reported are with respect to this reference electrode. The whole fuel cell hardware was placed in an oven and heated to 150°C. The reactant gases were humidified by bubbling through distilled water at room temperature or the temperature as specified. The pressures of the reactant gases were one atmosphere. The cell resistance was measured by a current interrupt method. All of the electrode polarization curves reported in this paper are iR corrected.

RESULTS AND DISCUSSION

1. Gas humidification effect

A typical cell polarization curve and iR free polarization curve for a one atmosphere pressure hydrogen/oxygen fuel cell are shown in Fig. 2. This PBI fuel cell demonstrates quite good performance even at a high operating temperature and a low gas humidification. It shows a maximum power density of 0.25 W/cm² at 700 mA/cm². The cell resistance of this fuel cell was about 0.45 ohm cm², corresponding to a membrane conductivity about 0.0167 ohm⁻¹ cm⁻¹. This value is consistent with the conductivity of PBI membrane measured by the four probe AC technique[10]. The cell resistance of the PBI fuel cell is large if compared to the cell resistance of a well hydrated Nafion membrane fuel cell at 80°C (0.1-0.2 ohm cm²)[8]. However, on consideration of the high operating temperature and low humidification, the performance of the membrane is quite significant. Moreover, the cell resistance could be further reduced by decreasing the membrane thickness because of the good mechanical properties of the PBI polymer film. The experiment demonstrates that the cell resistance is independent of gas humidification. According to electro-osmotic drag measurements[12], the water drag number is nearly zero. This unique feature of the PBI membrane allows the fuel cell to be operated at a very low humidification level. Under most conditions, the water produced at an operating cathode is sufficient to maintain the conductivity of the PBI membrane. One fuel cell was
operated with dry hydrogen and oxygen at a current density of 200 mA/cm² for over 20 hours with no performance decay observed. However, it was found that upon a slight increase of the humidification temperature of the hydrogen from room temperature to 48°C, the performance of the anode and cathode improved at high current density (see Fig. 3). This result indicates that increased humidification level of the electrode improves the ionic conductivity of the electrode. Thus, more active catalyst surface of the electrode is utilized for reaction.

2. Stability of the cell performance

Multi-hour discharge tests were conducted on PBI/electrode assemblies to investigate the stability of the PBI membrane and electrodes. In these tests, the cell voltage was kept constant, and the current density and the cell resistance were measured. A typical cell performance is shown in Fig. 4. Except for the first few hours, the cell performance is quite stable over 200 hours. The polarization curves of hydrogen and oxygen electrodes before the test and after 200 hours test are shown in Fig. 5. These curves show that the performance of oxygen electrode became better after 200 hours, and the performance of the hydrogen electrode was slightly degraded. In the first few hours, the cell performance slowly improved probably due to the water produced at the cathode which enhanced the membrane conductivity and the ionic conductivity of the electrodes. The cell resistance for this fuel cell was between 0.4-0.55 ohm cm² during the 200 hour test.

3. Air effect

Since air is a more realistic oxygen source, a PBI fuel cell was tested using air instead of oxygen. The cell performance is shown in Fig. 6. The open circuit potential of the cell decreases from 1.015V with oxygen to 0.970V with air. The cell voltages of this PBI fuel cell with oxygen or air are about 0.54V and 0.41V at a current density of 250 mA/cm², respectively. The cathode polarization curve with air parallels that with oxygen. An approximately 80 mV potential loss when using air instead of oxygen was observed because of the lower partial pressure of the oxygen in air.

4. The effect of the polymer electrode impregnating method on electrode performance

For a good gas diffusion electrode, it not only needs high catalytic activity and high electronic conductivity, but also requires high ionic conductivity. The latter may become more important in high temperature operation due to the decrease of the ionic conductivity of polymer electrolyte. In the conventional method of preparing the PBI M&E assembly, a small amount of phosphoric acid was added to the electrode structure to increase the ionic contact of the electrode/membrane. It was expected that the electrodes loaded with PBI polymer will have more stable performance and longer life time. Our simulation results[15,16] also show that for an agglomerated gas diffusion electrode there...
is an optimal polymer loading for best electrode performance. Therefore, several methods to making M&E assembly were developed as described in the experimental section. These M&E assemblies were evaluated electrochemically as a hydrogen electrode and an oxygen electrode.

Figure 7 and Figure 8 show the electrode performance of these different assemblies for hydrogen oxidation and oxygen reduction, respectively. The performance of the electrode prepared by the first method (impregnated 10% PBI solution) was not as good as the electrode only impregnated with H₃PO₄ for both oxygen reduction and hydrogen oxidation. Since in this electrode PBI solution is added under a vacuum, the amount of the PBI in the electrode structure may be too much so that the electrode performance is limited by the mass transport of the reactant gases. The electrode prepared by the second method shows improved performance for hydrogen oxidation at high current density, but only slightly improved for oxygen reduction. It can be expected that when electrodes are glued by PBI solution, a small amount of PBI solution will penetrate into the electrode structure dependent on the viscosity of the PBI solution. The improved electrode performance is believe to be due to improved ionic conductivity within the electrode structure. The only disadvantage of this method is that the polymer loading is not reproducible and that the stress between the membrane/electrode interface is introduced due to acid doping after making the M&E assembly.

The third method was developed to eliminate the problem of membrane/electrode stress. Two different PBI solutions were used to impregnate the M&E assembly. For low polymer loading (0.3mg/cm²), 1% PBI solution was used and for high polymer loading (0.9 mg/cm²), 2% PBI solution was used. From Figures 7 and 8, it can be seen that the performance of the electrode impregnated with 1% PBI solution is not as good as that of the electrode impregnated only with H₃PO₄. However, the performance of the electrode impregnated with 2% PBI solution (0.9 mg/cm²) is better than any other electrodes for both hydrogen oxidation and oxygen reduction. The overpotential of this electrode decreases about 60-100 mV for hydrogen and oxygen in comparison to the electrode impregnated only with H₃PO₄. The lower performance of the electrode impregnated with 1%PBI solution could be caused by strong adsorption of PBI on catalyst surface. Since 1% PBI solution has a low viscosity, it can be easily penetrated into the electrode and be adsorbed on the active catalyst sites thus causing poor performance. Cyclic voltammetry of these electrodes indicate that the PBI polymer strongly adsors onto active surface sites and thus blocks the reaction. These results suggest that the electrode structure should be impregnated with only a small amount of PBI so that the electrode will have good ionic contact with the PBI membrane and will stabilize the phosphoric acid in the electrode structure, but will not block too many active catalyst sites. Using a PBI solution with proper viscosity to impregnate the electrode appears to be critical.
SUMMARY

Phosphoric acid doped polybenzimidazole has been investigated for use in a H₂/O₂ fuel cell. Prototype fuel cell test results show that a PBI fuel cell works quite well at 150°C and with low gas humidification without membrane dehydration occurring for over 200 hours. Impregnating the M&E assembly with polymer electrolyte is critical to improving electrode performance. Since these results obtained from the non-optimal electrode structures, it can be expected that the cell performance could be further improved by optimizing the electrode structures and operating conditions. These preliminary results clearly demonstrate the new opportunity offered by acid doped PBI membranes and the potential benefits in the simplification of the cell design and the cell maintenance when an acid doped PBI membrane is used as the polymer electrolyte.

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Fig. 1. Schematic of single cell with an electrode area of 1 cm$^2$.

Fig. 2. Cell polarization curve and iR free polarization curve from a PBI fuel cell. E-TEK electrodes (0.5 mg/cm$^2$ Pt on carbon). Hydrogen: 1 atm, humidified at 48°C and oxygen: 1 atm, humidified at 28°C. Cell resistance: 0.45 ohm. Cell operating temperature: 150°C.
Fig. 3. Polarization curves from a PBI fuel cell. E-TEK electrodes (0.5 mg/cm² Pt on carbon). Oxygen: 1 atm, humidified at 28°C. Hydrogen: 1 atm, humidified at 28°C and 48°C, respectively. Cell operated at 150°C.

Fig. 4. Cell performance of PBI H₂/O₂ fuel cell at constant cell voltage 0.55V and 150°C. Anode: E-TEK electrode (0.5 mg/cm² Pt on carbon); Cathode: homemade electrode (2 mg/cm² Pt); all gases humidified at room temperature, 1 atm.
Fig. 5. Polarization curves of a PBI fuel cell before and after 200 hours of operation. Anode: E-TEK electrode (0.5 mg/cm² Pt on carbon); Cathode: homemade electrode (2 mg/cm² Pt); all gases humidified at room temperature, 1 atm. Cell operated at 150°C.

Fig. 6. Cell performance of a PBI H₂/O₂ fuel cell with oxygen or air. Anode: E-TEK electrode (0.5 mg/cm² Pt on carbon); Cathode: homemade electrode (2 mg/cm² Pt); all gases humidified at room temperature, 1 atm. Cell operated at 150°C.
Fig. 7. Polarization curves of hydrogen oxidation from electrodes impregnated with polymer electrolyte using different methods. E-TEK electrodes (0.5 mg/cm$^2$ Pt on carbon), hydrogen humidified at room temperature, 1 atm. Cell temperature 150°C.

Fig. 8. Polarization curves from oxygen reduction for electrodes impregnated with polymer electrolyte using different methods. E-TEK electrodes (0.5 mg/cm$^2$ Pt on carbon), oxygen humidified at room temperature, 1 atm. Cell temperature 150°C.