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Fuel Cell Characteristics of the Membrane Electrode Assemblies using Phosphoric Acid-doped Poly[2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole] Membranes

Liang Fang, Li Sheng, Xiaoxia Guo, Jianhua Fang* and Zi-Feng Ma†

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

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Abstract: *The membrane electrode assemblies (MEAs) based on phosphoric acid (PA)-doped poly[2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI) membranes were prepared for the high temperature polymer electrolyte membrane fuel cells, and the moderate molecular weight poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (mPBI) with good solubility in aprotic solvents was synthesized and utilized as the binder in catalyst layers for the first time. The hot press and the components in catalyst layers that affected the performances of MEAs were studied. The cell performance evaluation and electrochemical impedance spectroscopy were carried out at temperatures ranging from 80 to 160 °C in a single cell setup. It was found that the prepared OPBI and the moderate molecular weight mPBI with high solubilities of polybenzimidazole could facilitate and simplify the preparation of MEAs. The novel MEAs using the PA-doped OPBI membranes and moderate molecular weight mPBI exhibited good performances in the polarization tests, constant current tests, and temperature cycle tests, which were comparable with those traditional MEAs using the PA-doped mPBI.*

Keywords: membrane electrode assembly; poly[2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole]; poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole]; moderate molecular weight; solubility.

1. INTRODUCTION

Recently there has been extensive research in the development of polymer electrolyte membrane fuel cells (PEMFCs) for transportation and portable power applications [1]. In PEMFCs, the perfluorosulfonic acid polymers, such as Nafion, have been utilized widely as electrolyte membranes and binders in the catalyst layers of gas diffusion electrodes [2, 3]. However the perfluorosulfonic acids are expensive, and their proton conductivity is strongly dependent upon their water content. Due to the requirement to maintain a high level of hydration, PEMFCs are limited to be operated below 100 °C under ambient pressure. In addition, at the low working temperatures obligatory platinum-based catalysts tend to be poisoned by impurities from the reforming processes. Thus intensive efforts have been devoted to the development of low-cost proton-conducting electrolytes used at elevated temperatures to reduce the impurities poisoning [4, 5, 6, 7, 8]. One kind of the promising candidates are the PA-doped polybenzimidazoles [6, 7, 8], which can function at higher temperatures and under non-humidification conditions to eliminate the water management [9, 10, 11], promote the fuel impurities tolerance [12, 13], increase the electrode kinetics [14], and facilitate the heat recovery [15, 16].

The most widely researched polybenzimidazole was the commercially available poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole](mPBI) due to its excellent thermal stability, high chemical durability, and mechanical strength [17, 18]. However, this polybenzimidazole with the rigid-rod structure and strong hydrogen bonding presents poor solubility and infusibility. For example, to cast membranes or prepare the catalyst layers of electrodes, mPBI has to be dissolved near the boiling point of aprotic solvents, preferably under an elevated pressure and oxygen-free atmosphere [12, 19, 20, 21]. For the long time storage, 1.5-2 wt% lithium salt needs to be added into the solution as stabilizer [21, 22]. At the end of preparation, the prepared membranes or electrodes need to be washed with hot water to remove the solvent and stabilizer [12, 21, 23, 24]. The aforesaid harsh dissolution and tedious washing processes motivate researchers to improve the solubility of the polybenzimidazole. Introduction of chemical groups on the benzimidazole N-H

To whom correspondence should be addressed:
Email: *jhfang@sjtu.edu.cn, †zfma@sjtu.edu.cn

positions [25, 26, 27]and reconstruction of the polymer from flexible monomer units [28, 29]have been proposed. In the latter approach, for example, poly[2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI) which contains flexible ether linkages between aromatic units in the main chain was synthesized [30, 31, 32, 33]. The designed polymer presented good solubility in aprotic solvents [30, 34, 35], high thermal stability [30, 31, 32, 33, 34, 35, 36, 37], and excellent mechanical properties [33, 34, 37, 38]. However, very few studies have been performed on an actual single cell setup using this PA-doped OPBI electrolyte yet [37, 39].

Besides the solubility, the viscosity of the binder in catalyst layers also affects the preparation and performances of MEAs, but has far less been studied. The fabrication process of the catalyst layers can be facilitated by using a well soluble and less viscous binder. It is well known that the solubility and viscosity of a polymer are related to its molecular weight. The lower molecular weight polymer tends to present higher solubility and lower viscosity, and vice versa [40]. Therefore, the *m*PBI with moderate molecular weight is expected to present good solubility and medium viscosity. Its utilization could overcome both the poor solubility of higher molecular weight *m*PBI and the inadequate binding capability of low molecular weight *m*PBI, and thus facilitate the preparation of catalyst layers in MEAs. However, Nafion [21, 39, 41] and high molecular weight *m*PBI [20, 21, 23] have dominantly been used as the binders in catalyst layers, and the preparation and the use of moderate molecular weight *m*PBI as the binder in catalyst layers and the performances of the prepared MEAs have not been reported yet.

In this paper, the novel PA-doped OPBI membrane was chosen as the electrolyte, and one moderate molecular weight *m*PBI was synthesized as the binder in catalyst layers. The preparation of MEAs was simplified. A detailed study of MEAs preparation and the performances of corresponding high-temperature single cells were reported.

2. EXPERIMENTAL

2.1. Materials

3,3'-Diaminobenzidine (DAB) was purchased from Acros Organics. 4,4'-Dicarboxydiphenyl ether (DCDPE) was purchased from Acros and vacuum dried at 80 °C prior to use. Polyvinylidene difluoride (PVDF) was purchased from 3M. Methanesulfonic acid (MSA), phosphorus pentoxide (P_2O_5), isophthalic acid (IPA), polyphosphoric acid (PPA), phosphoric acid (PA), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), sodium bicarbonate ($NaHCO_3$), ammonia solution and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC). DMSO was distilled under reduced pressure and dried by 4A molecular sieves before use. DAB, MSA, P_2O_5, IPA, PPA, PA, NMP, DMAc, $NaHCO_3$, ammonia solution, ethanol, and PVDF were used as received.

2.2. Polymerization

OPBI was synthesized by condensation polymerization of DAB and DCDPE in the PPMA solution (P_2O_5/MSA in a weight ratio of 1:10) at 140 °C with around 10 wt% total monomer concentration [31]. 2.0 g P_2O_5 and 20.0 g MSA were added into a 100 ml dry three-neck flask under N_2 atmosphere. The reaction mixture was magnetically stirred and heated at 100 °C under N_2 atmosphere until a homogeneous solution was formed. After cooling to room temperature, DCDPE (1.2912 g, 5.0 mmol) and DAB (1.0714 g, 5.0 mmol) were added into the solution, and the reaction mixture was stirred and heated at 140 °C for 160 min. Then the mixture was slowly transferred into ice water with stirring. The brown solid product was filtered and soaked in 5 wt% $NaHCO_3$ solution under 60 °C for 36 h, then filtered and thoroughly washed with the deionized water, and finally dried in a vacuum oven at 120 °C for 10 h. At room temperature, OPBI was easily dissolved in DMAc under sonication for 15 min to obtain a transparent solution up to 10 wt%, and the stabilizer is not needed for the long time storage.

The moderate molecular weight *m*PBI was synthesized as follows: 8.4 g P_2O_5 and 41.9 g PPA were added into a 100 ml dry three-neck flask under N_2 atmosphere. The reaction mixture was mechanically stirred and heated at 100 °C under N_2 atmosphere until a homogeneous solution was formed. After cooling to room temperature, IPA (2.4916 g, 15.0 mmol) and DAB (3.1030g, 14.5 mmol) were added into the solution and the reaction mixture was stirred and heated at 150 °C for 2 h and subsequently at 190 °C for 10 h. Then the mixture was slowly transferred into ice water with stirring. The yellow solid product was filtered and soaked in diluted ammonia solution (1:1 v/v ammonia solution and deionized water) under N_2 atmosphere at 40 °C for 48 h, then filtered and thoroughly washed with deionized water, and finally dried in a vacuum oven at 120 °C for 24 h.

2.3. Film casting and membrane doping

The 5-10 wt% OPBI solution in DMSO was cast onto a glass plate and dried in an oven at 80 °C for 10 h. The film was peeled off from the plate and further dried in a vacuum oven at 120 °C for 10 h to remove the residual solvent. The PA-doped membrane was prepared by immersing the cast film in an 85 wt% PA bath for 4 days at room temperature. Doping level acquired by the membrane was 6.5 molecules of PA per polymer repeating unit. The corresponding thickness of the doped membrane was 50-60 μm. These doped membranes were covered by the polyethylene film and stored in a desiccator.

2.4. Preparation of MEAs

In order to test the PA-doped OPBI membrane in an actual fuel cell setup, MEAs were prepared with moderate molecular weight *m*PBI in the catalyst layer by the typical optimized procedures [42]. The Pt/C catalyst and the binder solution (4 wt% in DMAc) were added into DMAc. The weight ratio of catalyst/binder (dry weight)/DMAc was 78/22/7800 for the 20 wt% Pt/C catalyst (BASF fuel cell, Inc.) and 95/5/9500 for the 40 wt% Pt/C catalyst (Johnson Matthey, Inc.). The mixture was stirred for 24 h, and was treated in an ultrasonic bath for 5 min. And then the homogeneous slurry was sprayed (using airbrush) onto 2.5 cm×2.5 cm carbon cloth-based gas diffusion layers (LT 1200-W, 370 μm thickness, 27wt % polytetrafluoroethylene, BASF fuel cell, Inc.) to obtain gas diffusion electrodes. Both gas diffusion electrodes with 0.5 $mg \cdot cm^{-2}$ Pt loading were dried at 190 °C in a vacuum oven for 3 h to remove the remaining DMAc. Afterwards they were soaked with a 15 wt% PA/ethanol solution for 10 min at room temperature in order to soften the ionic contact between the membrane and the electrodes, and then dried at 60 °C for 1 h. The PA-doped OPBI membrane was wiped off with filter papers to remove the bled acid, and was sandwiched between two pieces of dry gas diffusion electrodes. The electrodes and the membrane were hot-pressed under a pressure of 1.2 MPa at 150 °C for 10 min.

2.5. Single cell test and electrochemical characterization

The MEAs were installed in the standard testing fixture (FC05-MP, the active geometrical area of 5 cm^2, ElectroChem, Inc.). The assembly torque was 5N·m. The performances of single cells were tested at different temperatures using a homemade fuel cell test system. Gases without humidification were fed to the single cell at the flow rates of 100, 150, and 750 $ml \cdot min^{-1}$ for H_2, O_2, and air, respectively (the oxygen stoichometry was 8 at a current density of 1 $A \cdot cm^{-2}$). The working pressure of the single cell was atmospheric pressure. Current-voltage curves were measured using a DC electronic load (IT8514F) and recorded by the constant current mode at a scan rate of 400 $mA \cdot min^{-1}$.

Electrochemical impedance measurements were performed at the open circuit. The frequency ranged from 100 KHz to 100 mHz, with a potential amplitude of 10 mV. Data were collected using a computer controlled CHI 604B electrochemical analyzer (Chenhua, Shanghai).

3. RESULTS AND DISCUSSION

As reported, the high molecular weight *m*PBI membranes containing massive amounts of PA presented high proton conductivity and acceptable mechanical properties [43]. Thus, high molecular weight OPBI with good solubility and mechanical property was synthesized and used to dope PA. The obtained OPBI displayed high inherent viscosity (η=4.7 $dL \cdot g^{-1}$ which was measured at 0.5 $g \cdot dL^{-1}$ OPBI solution in DMSO at 30 °C) due to the high molecule weight [34].

3.1. Mechanical analysis and proton conductivity of PA-doped OPBI membranes

At first, the study was focused on the mechanical analysis of PA-doped OPBI membranes, because the stability of membranes against mechanical stresses plays an important role in both their short- and long-term performance for the real PEMFCs application. Mechanical properties of the OPBI membrane and the corresponding PA-doped OPBI membrane were evaluated by the tensile tests. The tensile tests were performed with a universal electromechanical tester Instron 4465 (Instron Corporation) at a crosshead speed of 5 $mm \cdot min^{-1}$ at 25 and 150 °C, respectively (Table 1). The tensile strength at break for the undoped OPBI membrane was 116 MPa at 25 °C at 32 % relative humidity. The doping of PA led to a significant reduction in tensile strength at break of the membrane, and the PA-doped OPBI membrane exhibited a tensile strength at break of 44 MPa. However the elongation at break was enhanced from 27% to 57%. This was attributed to the plasticization effect of PA in the membrane. When the temperature was raised to 150 °C (the corresponding relative humidity was 0.2 %), the tensile strength decreased and the elongation at break increased for both the undoped OPBI membrane and the PA-doped OPBI membrane, and the changes were more significant for the PA-doped OPBI membrane. It was shown that the doped OPBI membranes with the same doping level displayed higher tensile strength at break than the doped *m*PBI membranes reported in the literature [6, 43], and this property could facilitate the preparation of MEAs and the operation of fuel cells using doped OPBI membranes.

Table 1. Tensile strength and elongation at break of OPBI and PA-doped OPBI membranes.

Membrane	Temperature (°C)	Stress (MPa)	Strain (%)
OPBI	25	116	27
	150	101	31
PA-doped OPBI	25	44	57
	150	17	84

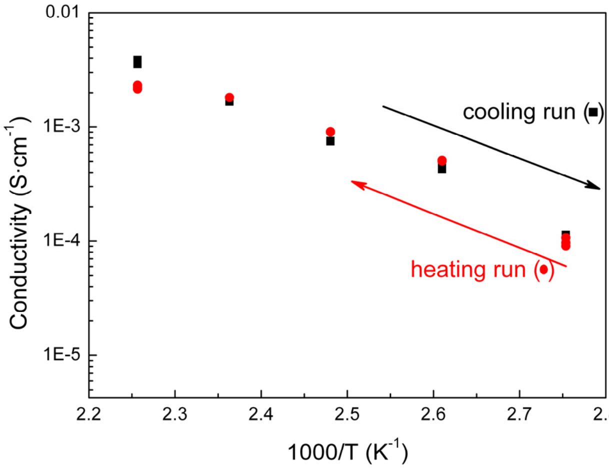

Figure 1. Proton conductivity of the PA-doped OPBI membrane as a function of temperature at 0% relative humidity measured in the cooling run and in the subsequent heating run.

Proton conductivity was measured using a two-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 kHz. A strip of PA-doped OPBI membrane and two platinum electrodes were set in a Teflon cell. The cell was placed in a thermo-controlled chamber, which had an inlet and an outlet for the continuous dry N_2 flow. The chamber was heated at 150 °C for 10 h to remove water vapor thoroughly (the 0% relative humidity). And then, the temperature of chamber was kept constant for 1 h at each desired temperature point from 90 to 170 °C. The resistance (R) was determined from the impedance at the high frequency intercept. The in-plane proton conductivity (σ) was calculated by $\sigma = d/(twR)$, where d means the distance between platinum electrodes, t and w are the thickness and width of the strip of PA-doped membrane. It was found that the in-plane proton conductivity increased with temperature (Fig. 1). At 170 °C, PA-doped OPBI showed the highest in-plane proton conductivity of 0.004 $S \cdot cm^{-1}$. To check if there was the hysteresis of the in-plane conductivity, the corresponding proton conductivities in both the cooling run (from 170 to 90 °C) and the subsequent heating run (from 90 to 170 °C) were measured and compared (Fig. 1). The proton conductivities obtained at reverse runs were quite similar at each temperature point, indicating that the hysteresis phenomenon was negligible.

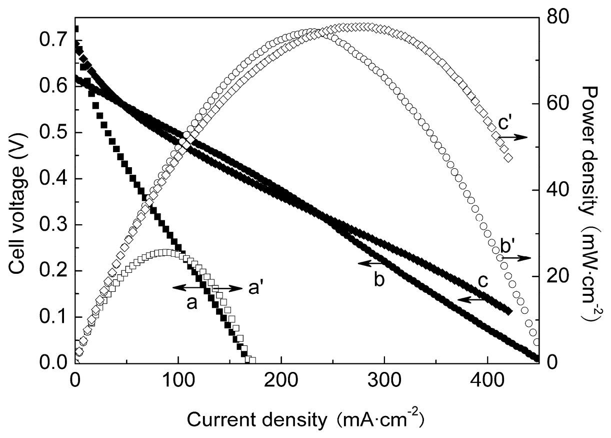

Figure 2. Effect of hot press on the performances of H_2-O_2 single cells based on PA-doped OPBI membranes. PA-doped Nafion electrodes were used as gas diffusion electrodes. Gases were fed with the humidification at room temperature to restrain rapid dehydration of Nafion. Cell temperature: 150 °C. (a, a’) Hot press at 130 °C and 4.2 MPa for 5 min; (b, b’) hot press at 150 °C and 3.0 MPa for 2 min; (c, c’) hot press at 150 °C and 1.2 MPa for 10 min.

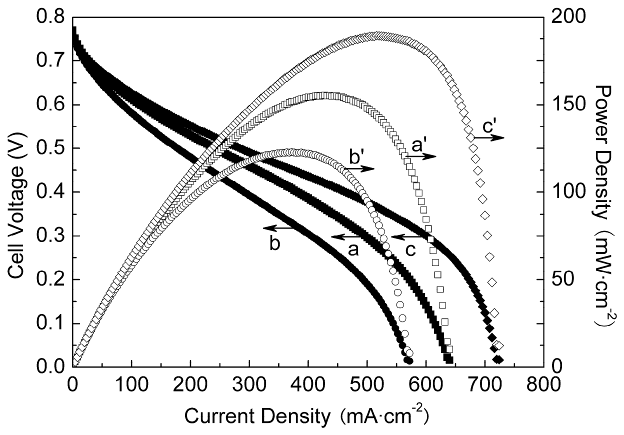

Figure 3. Performances of H_2-O_2 single cells based on PA-doped OPBI membranes. Gases were fed without humidification. Cell temperature: 160 °C. Hot press at 150 °C and 1.2 MPa for 10 min (a, a’) PA-doped electrodes containing moderate molecular weight *m*PBI; (b, b’) PA-doped electrodes containing moderate molecular weight *m*PBI, without sufficient drying; (c, c’) PA-doped electrodes containing OPBI.

3.2. Hot press process of MEAs

In the preparation of MEAs using the aforesaid PA-doped OPBI membranes, parameters of the hot press process (temperature, time, and pressure) and the components (moderate molecular weight *m*PBI and PVDF) in the catalyst layers were optimized.

In the optimization of hot press, commercial Nafion-based gas diffusion electrodes (LT 120E-W, BASF fuel cell, Inc.) were used. It was found that the lower maximum power density 26 mW·cm^{-2} was obtained at the hot press temperature of 130 °C (Fig. 2 a’) and the maximum power densities 76-77 mW·cm^{-2} could be achieved at the high hot press temperature of 150 °C (Fig. 2 b’ and c’). These performances of MEAs using the PA-doped OPBI membranes were comparable with those of reported MEAs using the PA-doped *m*PBI membranes as electrolytes in the single cells when Nafion was used as the catalyst binder [21, 41]. In our experiments, when the high compaction load and short press time at 150 °C were applied, the open circuit voltage was reduced obviously (Fig. 2 b and c). It was speculated that high pressure at 150 °C could affect the mechanical stability of membrane and squeeze PA out of the electrolyte concomitantly. Thus, the optimized hot press conditions using the PA-doped OPBI membranes were considered as 150 °C and 1.2 MPa for 10 min. These hot press temperature and time were the same to those reported hot press conditions using the PA-doped *m*PBI membranes, but the pressure was much lower [23, 24, 44]. In our study, the commercial carbon cloth-based gas diffusion electrodes were used rather than the carbon paper-based gas diffusion electrodes in the literature. It was speculated that different gas diffusion electrodes resulted in the different hot pressure.

3.3. Components in the catalyst layers of MEAs

At room temperature, the synthesized moderate molecular weight *m*PBI was easily dissolved in DMAc and a clear solution up to 4.0 wt% was obtained in the absence of any stabilizer. Moreover, it could be dissolved up to 18.9 wt% in DMAc (0.20 g·ml^{-1} DMAc solution) at 80 °C without any stabilizer, which indicated good solubility of the synthesized *m*PBI. The inherent viscosity of the moderate molecular weight *m*PBI was 0.55 dL·g^{-1}, which was measured in DMAc at a concentration of 0.5 g·dL^{-1} with an Ubbelohde viscometer at 30 °C. According to the determined standard of solubility and viscosity [40], it was also confirmed by the good solubility and medium viscosity of our sample that the synthesized polymer possessed moderate molecular weight. The good solubility and medium viscosity of moderate molecular weight *m*PBI could facilitate the preparation of MEAs.

Depending on the aforementioned optimized hot press conditions and moderate molecular weight *m*PBI, components in the catalyst layers were optimized. Firstly the 20 wt% Pt/C catalyst ink which contained 78 wt% catalyst and 22 wt% moderate molecular weight *m*PBI (dry weight) was selected as reported [12, 22, 24]. It was found that without external humidification the maximum power output 155 mW·cm^{-2} was achieved at 160 °C when the PA-doped electrodes containing moderate molecular weight *m*PBI were used as gas diffusion electrodes.(Fig. 3a’). This performance was comparable with those reported results using the PA-doped *m*PBI as the catalyst binder in the H_2-O_2 fuel cell [21, 22, 23], confirming that the moderate molecular weight *m*PBI could be used as the catalyst binder in the single cell.

At the initial stage of our experiments, different batches of PA-doped OPBI membranes and electrodes were used. The lower maximum power densities were always obtained (Fig. 3b’) although the electrodes were prepared following the same protocol. In controlled experiments, a significant effect of drying on the resulting membrane electrode assemblies was observed, and sufficient drying was essential in order to obtain repeatable and reliable results. It was proposed that the PA on the surface of doped OPBI membranes and the PA in electrodes could absorb water rapidly from the ambient moisture before the hot press. Thus the PA-doped

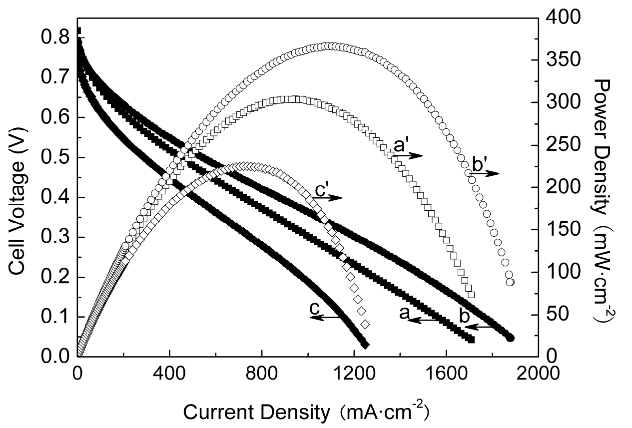

Figure 4. Performances of single cells based on PA-doped OPBI membranes. Gases were fed without humidification. Cell temperature: 160 °C. Hot press at 150 °C and 1.2 MPa for 10 min. (a, a') H_2-O_2 single cell using the PA-doped electrodes containing moderate molecular weight *m*PBI; (b, b') H_2-O_2 single cell using the PA-doped electrodes containing moderate molecular weight *m*PBI and PVDF; (c, c') H_2-air single cell of MEA in (b, b').

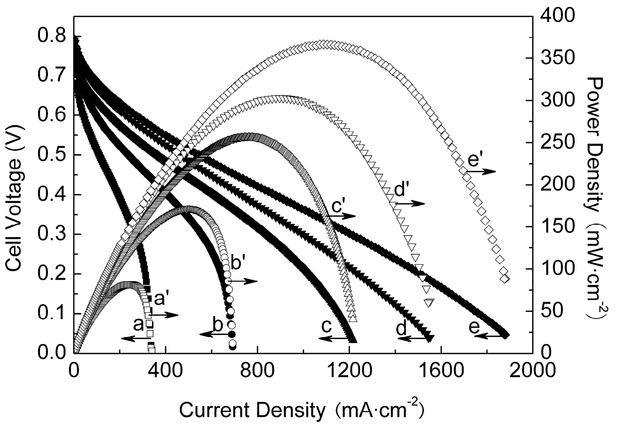

Figure 5. Effect of temperature on the performances of H_2-O_2 single cells based on PA-doped OPBI membranes. Electrodes contained moderate molecular weight *m*PBI and PVDF. Gases were fed without humidification. Hot press at 150 °C and 1.2 MPa for 10 min. Cell temperature was: (a, a') 80 °C; (b, b') 100 °C; (c, c') 120 °C; (d, d') 140 °C; (e, e') 160 °C.

OPBI membranes needed to be wiped off with filter papers. At the same time, the hot air needed to be blown onto the catalyst layers if the acid droplets were visible on the catalyst layers before the hot press. OPBI was also used as the catalyst binder in gas diffusion electrodes, and the 189 mW·cm^{-2} maximum power density was achieved (Fig. 3c'). PA-doped electrodes containing OPBI displayed higher power density, but OPBI as the binder presented high viscosity, and accurate measurement of the catalyst ink components was inconvenient. Thus the PA-doped electrodes containing moderate molecular weight *m*PBI were mainly studied in this report.

Then, the 40 wt% Pt/C catalyst ink which contained 95 wt% catalyst and 5 wt% moderate molecular weight *m*PBI (dry weight) was selected. A much enhanced cell performance was obtained when the 40 wt% Pt/C catalyst was used, and the maximum power density was 303 mW·cm^{-2} (Fig. 4a'). The quantity of the catalyst ink was decreased when the content of platinum in catalysts increased. Thus, the differences of performances in single cells were derived from the reduction of catalyst layer thickness and the concomitant enhancement of mass transfer rate.

In the controlled experiments, the polymer PVDF was added into the catalyst ink to replace part of the moderate molecular weight *m*PBI. The hydrophobicity of PVDF resulted in the lower water uptake in the electrodes and the enhancement of mass transfer rate. The weight ratio of PVDF/moderate molecular weight *m*PBI was chosen as 1/2 [9, 45]. Consequently the 40 wt% Pt/C catalyst ink contained 95 wt% catalyst, 1.7 wt% PVDF (dry weight) and 3.3 wt% moderate molecular weight *m*PBI (dry weight). It was found that the highest peak power density 366 mW·cm^{-2} was obtained by the addition of PVDF (Fig. 4b'). When H_2 and air were introduced into the single cell using this MEA, the open circuit voltage was reduced from 0.79 V to 0.75 V due to the reduction of oxygen partial pressure. The corresponding maximum power density was 225 mW·cm^{-2} (Fig. 4c').

3.4. Effect of temperature on the performances of MEAs

The effect of temperature on the performances of single cells was also investigated. When the temperature was raised from room temperature to 160 °C, the potential was scanned by the constant voltage mode at a rate of 100 mV·s^{-1}. At preset temperatures, polarization curves and impedance spectra were consecutively recorded. When the temperature was raised from 80 to 160 °C, the performance was increased significantly (Fig. 5). At the same time, the corresponding electrochemical impedance measurements showed that the ohmic resistance (the impedance at the high frequency intercept) and the charge transfer resistance (the impedance difference between the low frequency intercept and the high frequency intercept) were decreased with the increase of temperature (Fig. 6). Furthermore, the reduction extent of impedance with temperature was gradually diminished. These electrochemical impedance results suggested that the conductivity of PA-doped OPBI membrane and moderate molecular weight *m*PBI increased as a function of increasing temperature. At the same time, it was indicated that the electrode kinetics was enhanced as temperature increased. Thus, main beneficial effects of high temperature membranes were indicated. The water management was not needed, and the enhanced electrode reaction rates with temperature were observed. Moreover, the temperature played an important role in the performance of PA-doped OPBI-based PEMFC, and the increased performance with temperature was contributed to the increased conductivity and the enhanced electrode kinetics.

When the temperature was 160 °C, the ohmic resistance was about 0.07 Ω (Fig. 6e), and the corresponding through-plane conductivity of PA-doped OPBI membrane in the real single cell was estimated as 0.016 S·cm^{-1} (the membrane thickness was 55 μm). This through-plane conductivity was consistent with the through-plane conductivity (0.025-0.04 S·cm^{-1}) of PA-doped OPBI membranes reported in the literature [35, 38], and was close to those

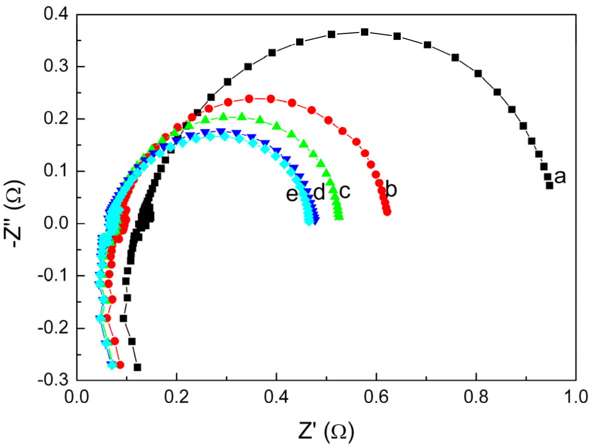

Figure 6. Effect of temperature on the electrochemical impedance spectrometry of H_2-O_2 single cells based on PA-doped OPBI membranes. Electrodes contained moderate molecular weight *m*PBI and PVDF. Gases were fed without humidification. Hot press at 150 °C and 1.2 MPa for 10 min. Cell temperature was: (a) 80 °C; (b) 100 °C; (c) 120 °C; (d) 140 °C; (e) 160 °C.

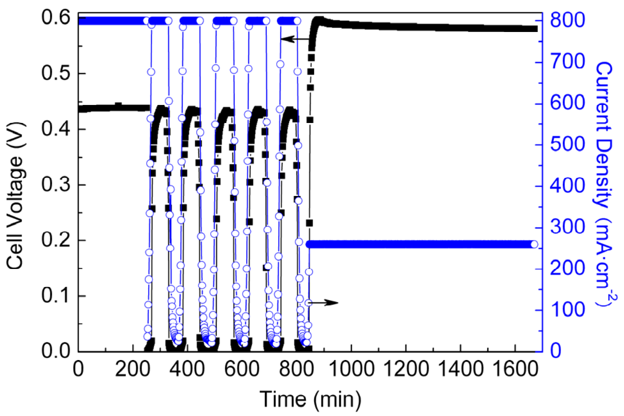

Figure 7. Performances of single cells based on PA-doped OPBI membranes at the constant current test (800 mA·cm^{-2}), five temperature cycle tests between 30 and 160 °C, and another constant current test (260 mA·cm^{-2}). Electrodes contained moderate molecular weight *m*PBI and PVDF. Gases were fed without humidification. Cell temperature: 160 °C. Hot press at 150 °C and 1.2 MPa for 10 min.

through-plane conductivities (0.02-0.05 S·cm^{-1}) of typical PA-doped *m*PBI membranes with the similar doping level in the literature [7, 46]. These abovementioned results indicated that the conductivities of PA-doped polybenzimidazole membranes which were prepared by the casting-doping method were usually lower than that of Nafion which was operated at full hydration (0.09 S·cm^{-1}). Thus, the lower proton conductivity resulted in the lower performances of fuel cells using this kind of membranes compared with those of cells using Nafion.

3.5. Constant current tests and temperature cycle tests of MEAs

At last, based on the optimized MEA, a constant current test (800 mA·cm^{-2}), a temperature cycle test between 30 and 160 °C, and another subsequent constant current test (260 mA·cm^{-2}) were performed successively (Fig. 7).

The first constant current test (800 mA·cm^{-2}) at 160 °C continued for 250 min, and the voltage was around 0.439 V and very stable.

In the subsequent stage of the five temperature cycle tests, the single cell was started from 30 °C. The single cell was heated from 30 °C to 160 °C and held at 160 °C for 15 min, and then it was cooled down to 30 °C and held at 30 °C for 15 min. The discharge current density was set as 800 mA·cm^{-2}, but when the temperature was lower than the critical temperature, the current density was less than 800 mA·cm^{-2}. This test condition was set in order to investigate the cold start under preset high current condition.

In every temperature cycle test, the current density increased from ~35 mA·cm^{-2} (the temperature was 30 °C) to the preset value 800 mA·cm^{-2} at the first stage, and the preset value was reached when the temperature was between 104 and 114 °C (the critical temperature) according to the corresponding cycle test. At this stage, the voltage increased very slowly and kept below 0.02 V. At the second stage, the current density was held at 800 mA·cm^{-2}, and the voltage rose sharply with temperature, and reached 0.4 V at the temperature between 138 and 142 °C. At the third stage, the voltage rose slowly again and the single cell was run at the constant current mode steadily. During the five temperature cycle tests, the constant voltage value at the third stage degraded from 0.435 to 0.428 V, and presented a degradation rate of 1.6% power loss. The degradation rate in five temperature cycle tests could be estimated to be about 0.75mV·h^{-1}, assuming the test was performed at a constant current density of 800 mA·cm^{-2}.

During the last constant current test (260 mA·cm^{-2}) at 160 °C, the constant voltage value degraded from 0.595 to 0.581 V, and the degradation rate could be estimated to be about 1 mV·h^{-1}.

Although subsequent efforts are still needed to improve the performances and durability of MEAs, the aforementioned tests suggest that the PA-doped OPBI membranes and moderate molecular weight *m*PBI binders could be the promising candidates used in fuel cell systems.

4. CONCLUSION

Compared with the traditional utilization of *m*PBI, the preparation of MEAs using the novel PA-doped OPBI membranes and one moderate molecular weight *m*PBI binders in the catalyst layers was facilitated and simplified due to the improved solubility of polybenzimidazole. This optimized MEAs exhibited desirable performances in the electrochemical tests up to 160 °C. This investigation opened up a new way to develop the practical proton-conducting fuel cell systems working at elevated temperatures.

5. ACKNOWLEDGEMENTS

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