

Preparation of PBI/H₃PO₄-PTFE Composite Membranes for High Temperature Fuel Cells

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Abstract: The poly(benzimidazole) (PBI)/ poly(tetrafluoroethylene) (PTFE) composite membrane was prepared by impregnating a porous PTFE thin film in a PBI solution N,N'-dimethyl acetamide (DMAc) solution mixed with LiCl. LiCl was used as a stabilizer to avoid aggregations of PBI molecules in the DMAc solutions. In this paper, we report a 2 mg/ml PBI/ DMAc/ LiCl solution with a [LiCl]/[BI] molar ratio of ~8.0 (i.e. the LiCl/PBI is ~ 1.1 in wt ratio, where [BI] is the concentration of benzimidazole repeat unit in the solution) has a lowest PBI polymer aggregations and thus a lowest solutions viscosity. The PBI membrane and PBI/PTFE composite membrane prepared from the PBI/DMAc/LiCl solution with a [LiCl]/[BI] molar ratio of ~8.0 were used to dop H₃PO₄ and prepare membrane electrode assemblies (MEA). The unit cell performances of these MEAs were carried out at 150°C. Owing to the high mechanical strength of porous PTFE, the thickness of PBI/H₃PO₄-PTFE composite membrane is allowed to be lower than that of a PBI/H₃PO₄ membrane. The lower thickness of PBI/H₃PO₄-PTFE membrane than that of PBI/H₃PO₄ membrane results in a lower resistance of PBI/H₃PO₄-PTFE than PBI/H₃PO₄. Thus the MEA prepared from PBI/H₃PO₄-PTFE has a better fuel cell performance than that prepared from PBI.

Keywords: Poly(benzimidazole), PTFE, composite membrane, fuel cell.

1. INTRODUCTION

It is generally accepted that proton exchange membrane fuel cell (PEMFC) presents an attractive alternative to traditional power sources, due to its simplicity, high efficiency and non-pollution. The key component of a PEMFC is the membrane electrode assembly (MEA) which consists of a proton exchange membrane (PEM) located between two porous, electrically conductive electrodes [1-3]. The PEM is usually a polyelectrolyte or an ionomer. One of the most successful PEM for PEMFC is Nafion (a trade name of Du Pont Co). It is a perfluorosulfonated ionomer using water as proton conducting carriers and has an excellent proton conductivity and fuel cell performance at temperatures below 90°C with high humidity. However when working at temperatures above 100°C, Nafion loses its capability for proton transport due to the loose of humidity at high temperatures.

Instead of using Nafion as a PEM for PEMFC, the use of hydrocarbon polymers for polymer backbones had generally been accepted to be another route to high performance proton conducting PEMs [4]. One of the most promising hydrocarbon polymer PEMs is phosphoric acid doped polybenzimidazole (PBI/ H₃PO₄) membrane. It was first successfully used in high temperature (140~180°C) PEMFC by Savinell and Litt group in early 1990 [5-9]. The chemical structure of PBI is shown in Fig. (1). In PBI/ H₃PO₄ membrane, phosphoric acid acts as protons conducting

carrier and no water is needed for protons conduction. Thus PEMFCs using PBI/ H₃PO₄ membranes as proton-conducting separators are available to work at high temperatures (100°C < Temp < 200°C) and low humidity environment [9,10].

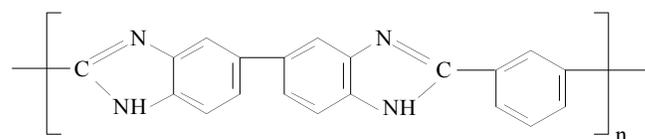


Fig. (1). The chemical structure of a repeat unit BI of PBI.

The advantages of high temperature working PEMFCs are [11]: (1) lower CO adsorption of catalysts leading to lower CO poison of catalysts, thus higher efficiency of catalysts; (2) lower heat exchange area needed to dissipate excess heat; and (3) the electrochemical reaction product, i.e. water, is easier to be evaporated at higher temperatures, thus easier water management. The lower CO adsorption of catalyst at higher temperatures leads the fuel cell easier to be operated with a liquid fuel reformer, which for kinetic reasons is run at a high temperature, yielding a significant amount of CO. The lower heat exchange area and easy water management results in a simple design of fuel cells systems.

It had been shown that porous poly(tetrafluoro ethylene) (PTFE) thin film reinforced Nafion composite membranes could be prepared by impregnating a microporous thin film support with a Nafion solution [11-18]. It is important to note that the Nafion/PTFE (thickness around ~20 μm) composite membranes contain much less of the expensive Nafion resin than the traditional Nafion membranes such as Nafion-117 (thickness 175 μm) and Nafion-212 (thickness 50 μm). Thus the cost of composite membranes is much

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lower than that of the traditional Nafion membranes. Besides the cheap cost, other advantages of the composite membranes are: good mechanical strength in both swollen and unswollen state, good thermo-stability, and thinner thickness (thickness $\sim 20 \mu\text{m}$). Although the room-temperature conductivity of a 1100 EW Gore-Select Nafion/PTFE membranes is lower than that of a Nafion membrane, the resistance of the whole membrane of a Nafion/PTFE composite membrane is significantly lower than that of a Nafion membrane due to the thinness of the Nafion/PTFE composite membrane.

Following the preparation of Nafion/PTFE composite membranes, Lin and Yu *et al.* [19-20] reported the preparation and application of PBI/PTFE composite membrane (thickness 25~30 μm) to high temperature (140~180°C) PEMFC. The reinforcement of PBI membranes with high mechanic strength porous PTFE thin film (thickness 16~20 μm) allows one to reduce the membrane thickness without losing mechanic strength. The low thickness of a PEM causes a reduction in the resistance of PEM and an improvement of fuel cells performance.

The PBI/PTFE composite membranes are prepared by impregnation porous PTFE support thin films in PBI solutions. Thus the properties of the impregnated membranes are strongly influenced by the properties of PBI solutions. In this paper, we reported the PBI solutions properties, the preparation of PBI/PTFE composite membranes, and the application of composite membranes to PEMFC.

2. EXPERIMENTAL

2.1. Synthesis of PBI

PBI was synthesized from 3,3'-diamino benzidine (Aldrich Chemical Co) and isophthalic acid (Aldrich Chemical Co) using polyphosphoric acid (Aldrich Chemical Co) as a solvent. The detailed polymerization procedures were same as those reported by Ueda *et al.* [21]. The inherent viscosity (I.V.) was determined by dissolving 0.5 wt% of PBI in 98 wt% sulfuric acid solution using an Ubbelohde viscometer (with a water flow time of 98 sec) and an I.V. of 1.58 dL/g was obtained, which corresponded to $M_v = 1.03 \times 10^5 \text{ g/mol}$ calculated using an equation derived by Choe *et al.* [22].

2.2. Preparation of PBI/DMAc/LiCl Solutions

PBI/DMAc/LiCl solutions with a PBI concentration of 2 mg/ml and various concentrations of LiCl (Riedel-deHaën Co, Germany) were prepared by mixing PBI with N,N'-dimethyl acetamide (DMAc, Fluka Chemical Co, Japan) and LiCl. Wherein the molar ratios of [LiCl]/[BI] were 3.63, 5.00, 6.00, 7.26, 8.00, 9.07, 10.88, and 14.51 (BI is the repeat unit of PBI), i.e. the wt. ratios of [LiCl]/ [PBI] were 0.50, 0.69, 0.83, 1.00, 1.10, 1.25, 1.50, 2.00, respectively.

2.3. Characterizations of 2 mg/ml PBI/DMAc/LiCl Solutions

The characterizations of 2.0 mg/ml PBI in DMAc solutions with various concentrations of LiCl were performed at 25°C. (1) The dynamic shear viscosities of solutions were measured using a capillary VE viscoelastic analyzer (Vilastic Co, Inc, Austin, TX) with a capillary inner diameter of 0.0513 cm and a capillary length of 6.115 cm;

(2) The hydrodynamic radii (R_G) of 2 mg/ml PBI in DMAc solutions mixed with various concentrations of LiCl were obtained from dynamic light scattering (DLS) measurements at a scattering angle of $\theta = 60^\circ$ using a BI-9000 correlator (Brookhaven Co., Inc, USA). The incident light source was a He-Ne ion laser (Spectra Physics Inc) with a wavelength of $\lambda = 633 \text{ nm}$ and was operated at 20 mW. The PBI solutions were filtered through a Millipore filter (FHL P 02500, pore size 1.0 μm) before DLS measurements were carried out; (3) The Zeta-potential of 2 mg/ml PBI in DMAc solutions mixed with various concentrations of LiCl were analyzed using a Zeta-potential analyzer (Brookhaven Co).

2.4. Preparations of PBI/H₃PO₄ Membranes

A 2 wt% of PBI/LiCl/DMAc solution with [LiCl]/[BI] molar ratios of 8.0 (LiCl/PBI= 1.10 in wt. ratio) was prepared under nitrogen atmosphere at 150°C. The DMAc solvent was then evaporated from the solution at 80°C under vacuum to obtain a solution with a PBI content of around 5 wt%. The PBI solution was coated on a glass plate using a film applicator with a gate thickness of 140 μm . The glass plate with a thin film of PBI solution was heated at 80°C for 1 h and then 120°C for 5 h under vacuum to remove DMAc solvent. The PBI membrane was then immersed in distilled water for 3 days and the water was changed each day to remove LiCl. Finally, the PBI membrane was immersed in 85 wt% phosphoric acid solution for 3 days. The final thickness of PBI/H₃PO₄ membranes were around 94~98 μm .

2.5. Preparations of PBI/H₃PO₄-PTFE Composite Membranes

Before porous PTFE thin film was impregnated in a PBI solution, PTFE thin film was treated with a 0.7 wt% Nafion solution. And, then the PTFE thin film coated with a thin layer of Nafion on the surfaces of PTFE fibers was impregnated in a PBI solution to prepare a PBI/H₃PO₄-PTFE composite membrane. Herein Nafion is used as a coupling agent between PTFE and PBI, the perfluorocarbon backbone of Nafion is compatible with PTFE and the vinyl ether sulfonic acid side chain of Nafion is compatible with PBI. The procedures for preparing a PBI/PTFE composite membrane are as following:

(2.5-a) The solvent of as received 5 wt% Nafion solution (EW=1100, Du Pont Co) was evaporated under vacuum at 60°C and the residual solid Nafion resin was mixed with 2-propanol/ water (4/1 wt ratio) mixture solvent to a solution containing 0.7 wt% of Nafion. Porous PTFE film (thickness $16 \pm 2 \mu\text{m}$, pore sizes $0.5 \pm 0.1 \mu\text{m}$, and porosity $85 \pm 5\%$, Yu-Ming-Tai Chem Co, Taiwan) was mounted on a 12 x 12 cm^2 steel frames and boiled in acetone at 55°C for 1 hr. This pretreated PTFE membrane was then impregnated with a 0.7 wt% Nafion solution for 24 hr. These impregnated membranes were then annealed at 130°C for 1 hr. After annealing, the membrane was then swollen with distilled water for 24 hr. Thus the porous PTFE membrane was coated with a thin film of Nafion. (2.5-b) The porous PTFE membrane coated with a thin film of Nafion was impregnated in a PBI/LiCl/DMAc (4.5/5.0/100 in wt ratio, [LiCl]/[BI]= 1.1/1.0 in mol ratio) solution for 5 min, the membrane was then heated at 80°C for 30 min and then 120°C for 30 min under vacuum. The process of membrane impregnation in PBI/LiCl/DMAc solution and annealing was

repeated for 3~5 times to obtain a composite membrane with a desired film thickness. The PBI/PTFE composite membrane was then immersed in distilled water for 3 days and the water was changed each day to remove *LiCl*. Finally, the PBI/PTFE composite membrane was immersed in 85 wt% phosphoric acid for 3 days to obtain PBI/H₃PO₄-PTFE composite membrane.

2.6. Characterizations of PBI/H₃PO₄-PTFE Composite Membranes

The morphology of membranes was investigated using a scanning electron microscope (SEM, model JSM-5600, Jeol Co., Japan). The sample surface was coated with gold powder under vacuum before SEM observation was performed. The membrane acid-doping contents were determined by weighing the membranes before and after doping phosphoric acid. In order to avoid the deviation from moisture contents, before weighing, the membranes were dried by evaporating the water at 110°C under vacuum for more than 10 h until an unchanged weight was obtained. The ionic conductivities (σ) of membranes were measured by using a four-probe cell. The measurements were performed at temperatures of 150°C with a relative humidity of 18±2% by ac impedance spectroscopy using a Solartron 1260 gain phase analyzer interfaced to a Solartron 1480 multi-meter.

2.7. PEMFC Single Cell Test

A PBI membrane and a PBI/H₃PO₄-PTFE composite membrane prepared according to the procedure described in sec. 2.4 were used to prepare MEAs. The catalyst was Pt-C (carbon supported platinum, E-TEK, 40 wt% Pt) and the Pt loadings of anode and cathode were 0.5 mg/cm². Pt-C/ PBI/ LiCl/ DMAc (3.5/1/0.5/49 by wt) catalyst solution was prepared by ultrasonic disturbing for 5 hr. In catalyst ink solution, *LiCl* was a stabilizer of PBI/ DMAc solution. The catalyst ink was brushed onto a carbon cloth (E-TEK, HT 2500-W), dried at 110°C in a conventional oven to calculate catalyst loading. The catalyst coated carbon cloths were immersed in deionized water for 24 h to remove *LiCl*. They were then doped with phosphoric acids by dipping in 10% H₃PO₄ solution for 24 h and dried in oven at 110°C. The membrane was sandwiched between two carbon cloths coated with a catalyst layer and pressed at 150°C with a pressure of 50 kg/cm² for 5 min to obtain a MEA. The unit cell performances were tested at 150°C using a FC5100 fuel cell testing system (CHINO Inc., Japan). The area of testing fixture was 5x5 cm² and the anode *H*₂ cathode *O*₂ input flow rates were 300 ml/min. Both *H*₂ and *O*₂ flows were unhumidified.

3. RESULTS AND DISCUSSION

In general, PBI membranes are not dissolved in most of solvents, due to its strong inter-polymer hydrogen bonding between -NH and -N=C- groups (see the chemical structure of PBI shown in Fig. 1). PBI can be dissolved in DMAc mixed with LiCl. By mixing LiCl into PBI/DMAc solution, the hydrogen bonds formed from -NH ... -N=C- groups can be dissociated. Thus the mobility, zeta potential and particle sizes (i.e. hydrodynamic radius *R*_h) of PBI in DMAc/ LiCl solutions and viscosities of PBI/ DMAc/ LiCl solutions vary with LiCl concentration in the solutions.

3.1. Zeta Potential for Dilute PBI/DMAc/LiCl Solutions

Zeta potential measurement is a reliable method to investigate particles stability of the colloidal system. Table 1 shows the mobility and Zeta potential of PBI in 2 mg/ml PBI/LiCl/DMAc solutions with various molar ratios of [LiCl]/[BI]. The data showed the mobility and Zeta potential of PBI in the solution increased with increasing LiCl concentration and reached a maximum mobility and a maximum Zeta potential as the molar ratio of [LiCl]/[BI] was at 8.0. When the molar ratio of [LiCl]/[BI] was increased above 8.00, the mobility and Zeta potential of PBI solution decreased with increasing molar ratio of [LiCl]/[BI].

Table 1. Mobility and Zeta Potential Values of PBI/DMAc/ LiCl Solutions with Various [LiCl]/[BI] Molar Ratios

[LiCl]/[BI] Molar Ratio	Mobility*10 ⁻⁸ (m ² V ⁻¹ s ⁻¹)	Zeta Potential (mV)
3.62	0.75	-22.97
5.00	0.96	-29.25
7.26	1.06	-32.20
8.00	1.24	-37.66
9.07	1.15	-35.10
10.88	1.12	-34.17
14.51	1.09	-33.28

3.2. Dynamic Shear Viscosities of PBI/DMAc/LiCl Solutions

The dynamic shear viscosities of 2.0 mg/ml PBI in DMAc solutions mixed with various concentrations of LiCl were measured using a Vilastic VE viscoelastic analyzer. The dynamic shear viscosity $\eta(\omega)$ data of PBI solutions were plotted against shear frequency ω and are shown in Fig. (2). All the $\eta(\omega)$ data, except the solution with [LiCl]/[BI]= 8/1 mol ratio, show a shear thinning behavior at $\omega < \omega_{onset}$ (i.e. $\eta(\omega)$ decreases with increasing ω) and a shear thickening behavior at $\omega > \omega_{onset}$ (i.e. $\eta(\omega)$ increases with increasing ω). The PBI solution with [LiCl]/[BI]= 8/1 mol ratio shows a Newtonian solution at $\omega < \omega_{onset}$ (i.e. $\eta(\omega)$ does not change with increasing ω) and a shear thickening behavior at $\omega > \omega_{onset}$ (i.e. $\eta(\omega)$ increases with increasing ω). Where ω_{onset} is the critical ω at which the solution viscosity starts to increase as the ω is increased from a low frequency to a high frequency. The shear thinning and thickening behavior of polymer solutions had been reported in literatures [23-25]. Most of researchers attributed the shear thinning of a polymer solution to the dissociation of polymer aggregates by the shear force. At high shear frequencies ($\omega > \omega_{onset} = 10 \sim 30$ rad/sec in Fig. 2), the polymer chains were highly extended by the shear force. The extension of polymer chains increases the inter-polymer contact frequency. The shear thickening behavior of a solution at a high shear frequency can be attributed to the inter-polymer association of these extended polymer chains [23-25]. The $\eta(\omega)$ data at $\omega = 1.0$ rad/sec (the frequency in the shear thinning region) and the ω_{onset} data for PBI/DMAc/LiCl solutions with various molar ratios of [LiCl]/[BI] are listed in Table 2.

Table 2 shows that $\eta(\omega=1.0 \text{ rad/sec})$ and ω_{onset} decrease when the $[\text{LiCl}]/[\text{BI}]$ molar ratio decreases from 3.63 to 8.00. Then, $\eta(\omega=1.0 \text{ rad/sec})$ and ω_{onset} increase when the $[\text{LiCl}]/[\text{BI}]$ molar ratio increases from 8.00 to 14.51. The data of Table 2 reveal that there is a lowest viscosity and a lowest ω_{onset} as the $[\text{LiCl}]/[\text{BI}]$ molar ratio in PBI/DMAc/LiCl solutions is around 8.00. The $\eta(\omega=1.0 \text{ rad/sec})$ data suggest there are aggregations of PBI molecules in DMAc solutions at low shear frequencies when LiCl is not mixed into the solution. The mixing of LiCl into PBI/DMAc solution causes dissociation of PBI aggregates via the $[\text{>N}\dots\text{H}^{\delta+}\dots\text{Cl}^{\delta-}\dots\text{N}<]$ interactions among the imidazole groups of PBI polymers as molar ratio of $[\text{LiCl}]/[\text{BI}]$ was increased from 0.0 to 8.00. As molar ratio of $[\text{LiCl}]/[\text{BI}]$ was increased from 8.00 to 10.88, the excess contents of Li^+ and Cl^- ions results in hydrophobicity of PBI molecules in the DMAc solutions. Thus inter-polymer hydrophobic aggregations increased with increasing LiCl concentration as molar ratio of $[\text{LiCl}]/[\text{BI}]$ was increased from 8.00 to 10.88. Table 2 also shows the ω_{onset} strongly depends on the aggregation behavior PBI molecules in the solution. The higher degree of PBI aggregations in a solution (i.e. the higher viscosity of a PBI solution) leads to a higher shear frequency (i.e. ω_{onset}) or shear force to dissociate the PBI molecular chains from the aggregates and to form extended polymer chains. Further discussion of the influence of LiCl concentration on PBI aggregations in DMAc will be shown in section 3.4.

Table 2. $\eta(\omega=1.0 \text{ rad/sec})$ and ω_{onset} Data of 2 mg/ml PBI/DMAc/LiCl Solutions

$[\text{LiCl}]/[\text{BI}]$ (Mole Ratio)	$\eta(\omega=1.0 \text{ rad/sec})$	ω_{onset} (rad/sec)
3.62	0.033	34.0
5.00	0.016	11.5
7.26	0.015	10.3
8.00	0.014	9.0
9.07	0.018	9.7
10.88	0.021	12.0
14.51	0.023	12.3

3.3. Hydrodynamic Radius Distributions of PBI in 2.0 mg/ml PBI/DMAc/LiCl Solutions

Fig. (3) shows the hydrodynamic radius R_h distributions for 2 mg/ml PBI in DMAc/LiCl solutions with various $[\text{LiCl}]/[\text{BI}]$ molar ratios. The R_h data were obtained from DLS measurements at a scattering angle $\theta=60^\circ$. These data show the PBI has average $\langle R_h \rangle$ value around 30 ~ 70 nm in the solutions. Fig. (3) shows that $\langle R_h \rangle$ decreased from ~70 nm to ~30 nm as $[\text{LiCl}]/[\text{BI}]$ molar ratio was increased from 3.63 to 8.00, then $\langle R_h \rangle$ increased from ~30 nm to ~73 nm when the $[\text{LiCl}]/[\text{BI}]$ molar ratio was increased from 8.00 to 14.51. There is a lowest $\langle R_h \rangle$ as the $[\text{LiCl}]/[\text{BI}]$ molar ratio is around ~ 8.00. This behavior is similar to the $[\text{LiCl}]/[\text{BI}]$ molar ratio dependencies of shear viscosity $\eta(\omega=1.0 \text{ rad/sec})$ data (Table 2) and mobility and zeta potential data (Table 1).

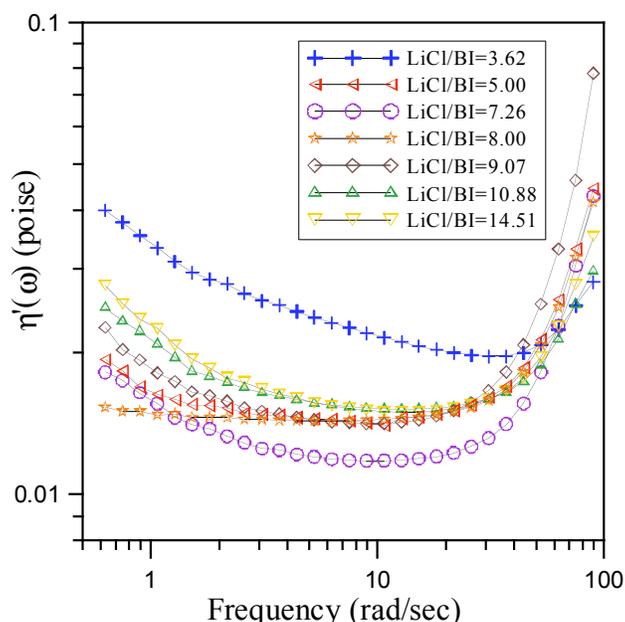


Fig. (2). $\eta(\omega)$ vs frequency ω for PBI/DMAc/LiCl solutions with various $[\text{LiCl}]/[\text{BI}]$ molar ratios, where [BI] is a repeat unit of PBI. The PBI concentration is 2 mg/ml. $[\text{LiCl}]/[\text{BI}]$ molar ratio: (+) 3.62; (\blacktriangle) 5.00; (\circ) 7.26; (\star) 8.00; (\diamond) 9.07; (\triangle) 10.88; (∇) 14.51.

3.4. Discussion of Dilute PBI/DMAc/LiCl Solutions Properties

From the results of Tables 1 and 2, and Figs. (2, 3), we found that there were maxima values of mobility and zeta potential and minima values of solution viscosity and R_h as the $[\text{LiCl}]/[\text{BI}]$ molar ratio of PBI/DMAc/LiCl solutions was around ~8.0. These results suggest that there are inter-polymer associations through hydrogen bonding of $-\text{N}-\text{H}$ with $-\text{N}=\text{C}-$ groups of imidazole functional groups in the PBI/DMAc solutions without mixing with LiCl. The mixing of LiCl into PBI/DMAc solutions results in the bonding of Li^+ ions on the imidazole group which causes dissociation of inter-polymer hydrogen bonds between $-\text{N}-\text{H}$ and $-\text{N}=\text{C}-$ groups as the $[\text{LiCl}]/[\text{BI}]$ molar ratio of PBI/DMAc/LiCl solution was increased from 0.0 to 8.0. The bonding of Li^+ ions on the imidazole groups of PBI results in the increase in the zeta potential. The dissociation of inter-polymer hydrogen bonds between $-\text{N}-\text{H}$ and $-\text{N}=\text{C}-$ groups results in the increase of polymer mobility and the decreases of solution viscosity and polymer particles sizes R_h . When the $[\text{LiCl}]/[\text{BI}]$ molar ratio of PBI/DMAc solutions is higher than 8.0, further mixing of LiCl into PBI/DMAc solution results in hydrophobic associations of PBI molecules in DMAc. Thus zeta potential and polymer mobility decrease as the $[\text{LiCl}]/[\text{BI}]$ molar ratio in the solutions is increased above 8.0 (Table 1). The inter-polymer association also causes increases of solution viscosity (Table 2) and PBI aggregated particles sizes (Fig. 3) as the $[\text{LiCl}]/[\text{BI}]$ molar ratio is higher than 8.0.

3.5. Characterizations of PBI/ H_3PO_4 Membrane and PBI/ H_3PO_4 -PTFE Composite Membrane

The porous PTFE used for PBI/PTFE composite membrane preparation had an average pore size of $0.5 \pm 0.1 \mu\text{m}$ and porosity of $85 \pm 5\%$. The fabrication of PBI/ DMAc/

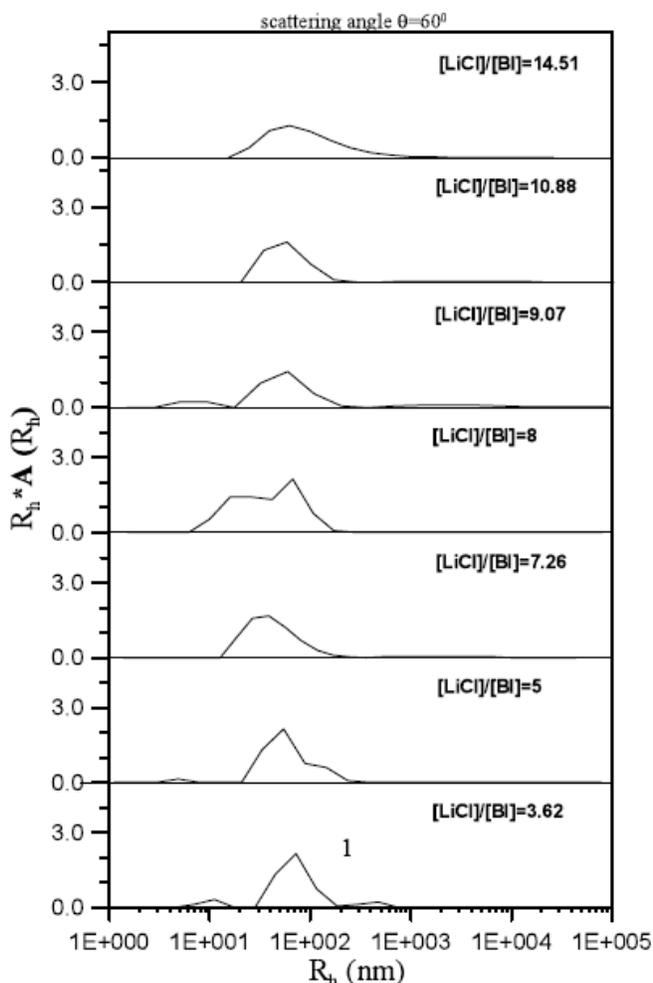


Fig. (3). DLS R_h distributions of PBI/DMAc/LiCl solutions with various $[LiCl]/[BI]$ molar ratios (numeric values indicated in figure), $[PBI]=2$ mg/ml, scattering angle $\theta=60^\circ$. $[LiCl]/[BI]=14.51, 10.88, 9.07, 8.00, 7.26, 5.00, 3.62$ in molar ratio (from top to bottom).

LiCl solutions on porous PTFE thin films and the properties of PBI/PTFE composite membranes strongly depend on the solutions properties of PBI/DMAc. As shown in Fig. (2), the PBI particles sizes distribute from 20 nm to 800 nm in DMAc/ LiCl solutions. It is obvious the solution with lower polymer aggregations should be more suitable for the impregnation PBI molecules into the porous PTFE film. Because of lowest solution viscosity, lowest PBI particles sizes, and highest polymer mobility, the PBI/DMAc/LiCl solution with a $[LiCl]/[BI]$ molar ratio of 8.0 was used for preparing PBI/PTFE composite membranes in the present work. Fig. (4a, b) show the SEM micrographs of the surfaces of porous PTFE thin film and PBI/PTFE composite membrane without doping phosphoric acid. The SEM micrograph of Fig. (4a) shows that there are fibers with

knots visible in the membrane and among the fibers and knots there are micro pores in the PTFE film. Fig. (4b) shows the micro pores of the PTFE film had been filled and completely covered with PBI. The membrane thickness (l), phosphoric acid doping level ($[H_3PO_4]/[BI]$ in molar ratio), proton conductivity (σ), and resistance per unit area (l/σ) of pure PBI membrane and the PBI/PTFE membrane after doping with phosphoric acid are shown in Table 3. Table 3 shows that though the σ of PBI/H₃PO₄-PTFE is lower than that of PBI/H₃PO₄, the PBI/H₃PO₄-PTFE has a lower l/σ than PBI/H₃PO₄, due to the lower l of PBI/H₃PO₄-PTFE than PBI/H₃PO₄.

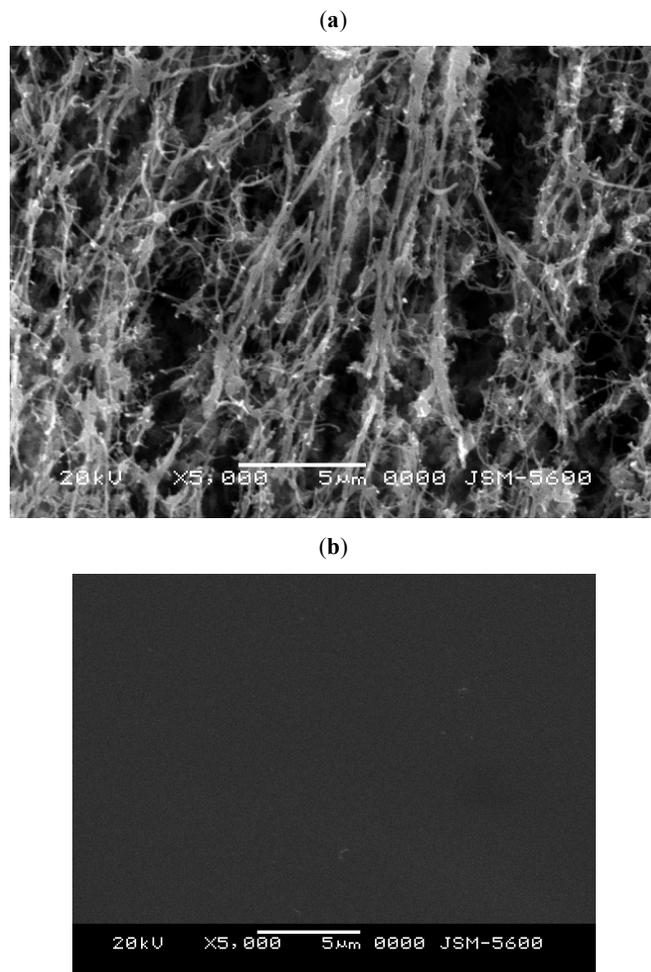


Fig. (4). SEM micrographs (x5000). (a) porous PTFE film; (b) PBI/PTFE composite membrane.

3.6. High Temperature PEMFC Unit Cell Performance Test

For the purpose of a reference, we also prepared a pure PBI membrane by solution casting from a PBI/DMAc/LiCl solution with a $[LiCl]/[BI]$ molar ratio of 8.0. The

Table 3. Properties of PBI/H₃PO₄ and PBI/H₃PO₄-PTFE Membrane

Membrane	Thickness l (μm)	$[H_3PO_4]/[BI]$ (mol Ratio)	*Conductivity σ (10^{-3} S/cm)	l/σ (cm^2/S)
PBI/H ₃ PO ₄	98	4.11	17.4	0.56
PBI/H ₃ PO ₄ -PTFE	22	3.73	4.76	0.46

* Measurements were performed at 150°C with RH= 18±2%.

PBI/H₃PO₄ membrane and PBI/H₃PO₄-PTFE composite membrane were used to prepared MEAs. The PEMFC single cells performance tests were carried out at 150°C under H₂ and O₂ flow rates of 300 ml/min. Fig. (5) shows the cell potential *V* versus current density *i* curves of these two MEAs. Fig. (5) shows the voltages of single fuel cells fall as current density increases. One of the reasons for the falling down of the voltage with increasing current density is the so called “ohmic loss” which comes from the resistance to the flow of ions through the polymer electrolyte membrane [2]. It is found that MEA prepared from PBI/H₃PO₄-PTFE composite membrane had a lower negative slope of *V* versus *i* at $i \geq 200$ mA/cm² and thus a lower “ohmic loss” and a better fuel cell performance than PBI/H₃PO₄ membrane. The better fuel cell performance of PBI/H₃PO₄-PTFE than PBI/H₃PO₄ can be attributed to the thinner thickness *l* and a lower resistance (i.e. l/σ) of PBI/H₃PO₄-PTFE than PBI/H₃PO₄.

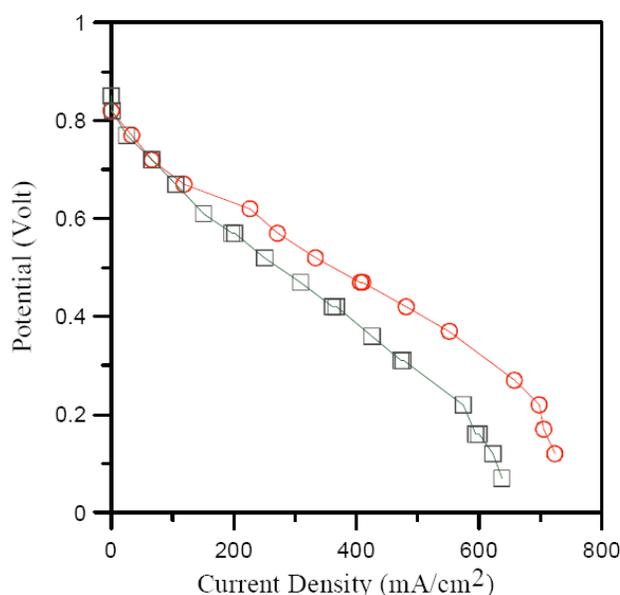


Fig. (5). PEMFC single cell voltage versus current density of MEA prepared from PBI/H₃PO₄ (98 μm) and PBI/H₃PO₄-PTFE (22 μm) and operated at 150°C with unhumidified H₂/O₂ flow rates of 300 ml/min. (□) PBI/H₃PO₄; (○) PBI/H₃PO₄-PTFE.

4. CONCLUSIONS

Because of strong inter-polymer hydrogen bond, PBI is hard to be dissolved in solvents. By mixing LiCl into PBI/DMAc solutions, PBI can be dissolved and dispersed in DMAc solutions. In this study, we show the 2 mg/ml dilute PBI/DMAc/LiCl solutions has a lowest solution viscosity and smallest PBI aggregate particles sizes when the molar ratio of [LiCl]/[BI] molar ratio is around ~ 8.0 in the PBI solution. The PBI/DMAc/LiCl solution with a [LiCl]/[BI] molar ratio of 8.0 was used to prepare PBI membrane and PBI/PTFE composite membrane. Owing to the high mechanical strength of porous PTFE, the thickness of PBI/H₃PO₄-PTFE composite membrane is allowed to be lower than that of pure PBI/H₃PO₄ membrane. The lower membrane thickness of PBI/H₃PO₄-PTFE than PBI/H₃PO₄

results in a lower l/σ of PBI/H₃PO₄-PTFE. Thus the MEA prepared from PBI/H₃PO₄-PTFE has a better fuel cell performance than that prepared from PBI/H₃PO₄.

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