

Research Article

Synthesis, Characterization, and Thermal and Proton Conductivity Evaluation of 2,5-Polybenzimidazole Composite Membranes

Jin-Woo Lee,¹ Kwangin Kim,¹ Sher Bahadar Khan,² Patrick Han,³ Jongchul Seo,⁴ Wonbong Jang,⁵ and Haksoo Han¹

¹ Department of Chemical and Biomolecular Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, Republic of Korea

² Center of Excellence for Advanced Materials Research (CEAMR) and Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

³ Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, USA

⁴ Department of Packaging, Yonsei University, Wonju-si, Gangwon-do 220-710, Republic of Korea

⁵ Department of R&D, LG Display, 1007 Deogeun-ri, Wollong-myeon, Paju-si, Gyeonggi-do 413-811, Republic of Korea

Correspondence should be addressed to Sher Bahadar Khan; drkhanmarwat@gmail.com and Haksoo Han; hshan@yonsei.ac.kr

Received 9 July 2014; Accepted 15 September 2014; Published 29 October 2014

Academic Editor: William W. Yu

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In this contribution, composite membranes (CM-D and CM-S) of 2,5-polybenzimidazole (PBI) were synthesized by adding inorganic heteropoly acids (IHA-D and IHA-S). IHA-D and IHA-S were synthesized by condensation reaction of silicotungstic acid with tetraethyl orthosilicate (TEOS) in the absence and presence of mesoporous silica (SiO₂), respectively. The synthesized composites were structurally and morphologically characterized and further investigated the functional relationships between the materials structure and proton conductivity. The proton conductivity as well as thermal stability was found to be higher for composite membranes which suggest that both properties are highly contingent on mesoporous silica. The composite membrane with mesoporous silica shows high thermal properties and proton conductivity. IHA-D shows proton conductivity of almost $1.48 \times 10^{-1} \text{ Scm}^{-1}$ while IHA-S exhibited $2.06 \times 10^{-1} \text{ Scm}^{-1}$ in nonhumidity imposing condition (150°C) which is higher than pure PBI. Thus introduction of inorganic heteropoly acid to PBI is functionally preferable as it results in increase of ion conductivity of PBI and can be better candidates for high temperature PEMFC.

1. Introduction

Fuel cell has attracted increasing interest because there is extensive requirement of energy but resources of petroleum are limited. Fuel cells are of different types but proton exchange membrane fuel cells (PEMFC) are thought to be the most excellent fuel cells [1, 2]. Various polymers have been used as membrane in fuel cells; however, commercial Nafion was considered as preminent polymer electrolyte membrane because of its elevated proton conductivity since several years. But in reality, Nafion has many drawbacks such as its operational temperatures and its conductivity. Its proton conductivity depends on the occurrence of water and that is

why it cannot operate above 100°C [3]. The contemporary investigation is focused on the optimization of fuel cell device that can operate above 100°C and comparatively low humidity. The advantage of PEMFCs operation over 100°C is well control, greater efficiency, and greater power density [3–5]. Hence, great efforts have been dedicated to the development of substitute proton exchange membrane that could perform at elevated temperature and possess elevated proton conductivity.

During the search of new polymer with high proton conductivity at high temperature, PBI was found to be the most promising candidate for fuel cell because of its low cost and high conductivity at higher temperature under

TABLE I: Doping density of phosphoric acid in PBI and composite membranes.

	Area	Thickness (μm)	Weight before doping (g)	Weight after doping (g)	Amount of doped H_3PO_4 (g)	H_3PO_4 doping density ($\text{g}\mu\text{m}^{-3}$)
2,5-PBI	1 cm \times 1 cm	86	0.0024	0.0173	0.0149	$1.73E - 12$
CM-D	1 cm \times 1 cm	51	0.0036	0.0208	0.0172	$3.37E - 12$
CM-S	1 cm \times 1 cm	82	0.0064	0.0281	0.0217	$2.65E - 12$

anhydrous conditions. PBI also presented excellent oxidative, thermal, and mechanical stability and low methanol crossover [6–11]. However proton conductivity behaviors of PBI are crucially contingent on the phosphoric acid doping level. Higher phosphoric acid doping level escort to elevated proton conductivity [8, 12]. Also escape of unbound or weakly attached acid from PBI membrane affects the proton conductivity of PBI. Many approaches have been developed to prevail over these drawbacks of PBI polymer but the perfection by these approaches is still inadequate.

The addition of inorganic support material to the polymer matrix is also one of the methods to increase the stability and proton conductivity of polymer by electronic charge increase and adsorption capacity [13–17]. One of the inorganic materials is silicotungstic acid which is highly conductive material in the crystalline form with the structure of $\text{H}_4[\text{W}_{12}\text{SiO}_{40}] \cdot n\text{H}_2\text{O}$ [18–22]. Silicotungstic acids have revealed quick electrokinetics and lower susceptibility to CO poisoning at both electrode and electrolyte. Inorganic heteropoly acid reduces electroosmotic drag effectively and retains proton conductivity as much as possible by creating pathway for water molecules [15]. These inorganic materials improve the acid doping level of polymer and thus result in higher proton conductivity [23–26].

In this contribution, 2,5-polybenzimidazole has been prepared and doped with different weight percentage of inorganic heteropoly acid. The pure and composite membranes were structurally elucidated by different sophisticated techniques. The composites membrane exhibited elevated thermal properties and proton conductivity. Furthermore, compared to 2,5-polybenzimidazole, composites membrane displayed better properties in terms of thermal stability and proton conductivity.

2. Experimental

2.1. Materials. Silicotungstic acid hydrate $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$, tetraethyl orthosilicate, and silica (surface area $390 \pm 40 \text{ m}^2/\text{g}$) were purchased from Sigma Aldrich.

2.1.1. Synthesis of 2,5-Polybenzimidazole. 2,5-Polybenzimidazole was prepared by polymerization reaction as reported [27, 28]. 3,3-Diaminobenzidine and pyridine-2,5-dicarboxylic acid were subjected for reaction in a flask and then polyphosphoric acid in the presence of nitrogen atmosphere was added and heated up to 220°C for 30 hours. The product was discharged into deionized water followed by neutralization by using KOH (1 mol/L). The product was then washed with boiling water and dried.

2.2. Preparation of IHA-D and IHA-S. Heteropoly acid matrices (IHA-D and IHA-S) made of silicotungstic acid and TEOS 65:35 (IHA-D) and calcined silicotungstic acid and silica/TEOS 65:35 (IHA-S) were made by silicotungstic acid and TEOS/silica [27, 28]. Usually, for IHA-D, the essential quantity of silicotungstic acid and TEOS were stirred in ethanol and followed by the addition of 8 wt% of HNO_3 and then silicotungstic acid was added. The 1N NaOH solution was then added to the ensuing mixture and stirred for three hours. The powder was obtained by grinding the product in a mortar. For synthesis of IHA-S, we followed the same procedure but we used silicotungstic acid and TEOS/silica and the product was calcined at 540°C for 5 hrs.

2.3. Synthesis of Composite Membranes. Composites membranes were synthesized by using PBI as a polymer while IHA-D and IHA-S were utilized as inorganic materials. PBI was dissolved in acid and IHA-D and IHA-S were added (50 wt%). The ensuing solution was kept on stirring and after 24 hours the solution was cast on a flat glass by spin coating. Membranes of 50–80 μm thickness were acquired then drenched in 95 wt% phosphoric acid for 72 hours. Composite membranes containing IHA-D and IHA-S inorganic heteropoly acid are noted as CM-D and CM-S, respectively.

2.4. Doping Level. Before proton conductivity, membranes were immersed in 95 wt% phosphoric acid at room temperature for 72 hrs and we measured the doping level by measuring weight discrepancy prior to dipping and after removal from phosphoric acid (Table I). 2,5-Polybenzimidazole showed lower doping level while CM-S exhibited high degree of acid sorption (doping level). Mesoporous silica might be the cause of lofty doping level of composites which absorb high amount of phosphoric acid as compared to PBI and CM-D.

2.5. Characterization of Silica Composite Materials and Membranes

2.5.1. FT-IR Analysis. FT-IR analysis was performed for both the samples of inorganic heteropoly acid and composite membranes. Tested samples were located on the test table with KBr dispersion IR radiation reflection with Varian Resolution Pro in the wave number range of 500 to 4000 cm^{-1} .

2.5.2. Thermal Gravimetric Analysis (TGA). Thermal gravimetric analysis was performed in the temperature range of 30 to 700°C using Q50 (TA instrument) in nitrogen atmosphere with the scanning rate of $20^\circ\text{C}/\text{min}$.

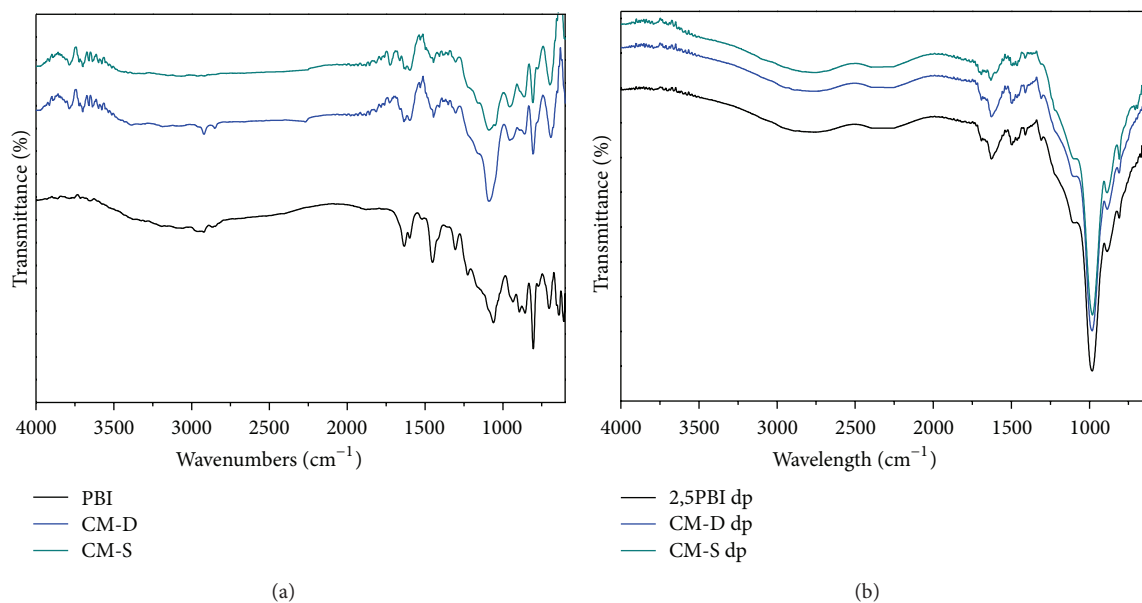


FIGURE 1: FT-IR spectra of PBI and composites before (a) and after (b) acid doping.

2.5.3. X-Ray Diffraction Analysis (XRD). X-ray diffraction analysis was performed with a Philips X-Pert diffractometer using a Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) and operating at 40 kV and 30 mA with 2θ range of $5\text{--}90^\circ$. X-ray diffraction patterns were collected with a scan rate of $5^\circ/\text{min}$.

2.5.4. Scanning Electron Microscopic Analysis (SEM). SEM surface investigation was performed with JEOL (JSM840A) with 10 K magnification for each sample with differentiated contents of TSA in 2,5-polybenzimidazole membrane after coating each sample surface with Au.

2.5.5. Impedance Analysis Measurement. The resistance of the membranes was deliberated by using Auto Lab Impedance Analyzer. The proton conductivities of membranes were recorded up to 150°C . And the proton conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{d}{L_S W_S R}, \quad (1)$$

where d , L_S , W_S , and R are the distance of the electrodes, film thickness, film width, and the resistance of the membrane, respectively [29, 30].

3. Result and Discussion

3.1. Structural Characterization. CM-D and CM-S were structurally characterized by FTIR as shown in Figure 1(a). FTIR spectrum of 2,5-polybenzimidazole exhibited a peak at 3410 cm^{-1} which indicated N-H stretching. The peak exhibited at 1643 cm^{-1} is responsible for C=C bond stretching. Similarly, it exhibited stretching band for C-C bond (1070 cm^{-1}) and C-N (1306 cm^{-1}) and C=N band (1606 cm^{-1}). All the composite membrane showed similar peaks along with

absorption bands at 692, 816, and 1089 cm^{-1} owing to W-O, W-O-W, Si-O, and Si-O-Si stretching, respectively, which indicates that composites have been synthesized [25, 27, 28]. Figure 1(b) shows FTIR spectra of doped PBI and composites. The intensity of peaks at 987 cm^{-1} increased which comes from acid doping.

3.2. Morphological Characterization. XRD pattern of IHA-S shows crystalline while IHA-D exhibited semicrystalline peaks. Lack of crystalline or semicrystalline peaks demonstrates that the synthesized composite membranes are amorphous in nature [31]. XRD spectrum of 2,5-polybenzimidazole membrane exhibits amorphous nature and after composition with IHA-D and IHA-S, the XRD spectrum did not exhibit crystalline peaks which clearly shows that the IHA-D and IHA-S were homogeneously dispersed in the 2,5-polybenzimidazole membrane devoid of any agglomeration or aggregation. The morphological structures of acid-doped composite membrane were also analyzed and shown in Figure 2(b). The XRD patterns of composite membrane show broad halo along with crystalline peaks [27, 28].

Figure 3 shows SEM images of 2,5-polybenzimidazole and composite membranes (CM-D and CM-S). SEM images of composite membrane show aggregation of particles which indicate that IHA-D and IHA-S are grown with high density in PBI matrix. CM-D displayed more aggregation of particles as compared to CM-S while CM-S shows denser structure in contrast to CM-D. The SEM images of the composites show different degree of density with agglomeration of particles.

3.3. Thermal Properties. The influence of IHA-D and IHA-S on the thermal properties of PBI membrane was examined under nitrogen atmosphere before and after acid doping and the TGA graphs are depicted in Figure 4. The initial weight

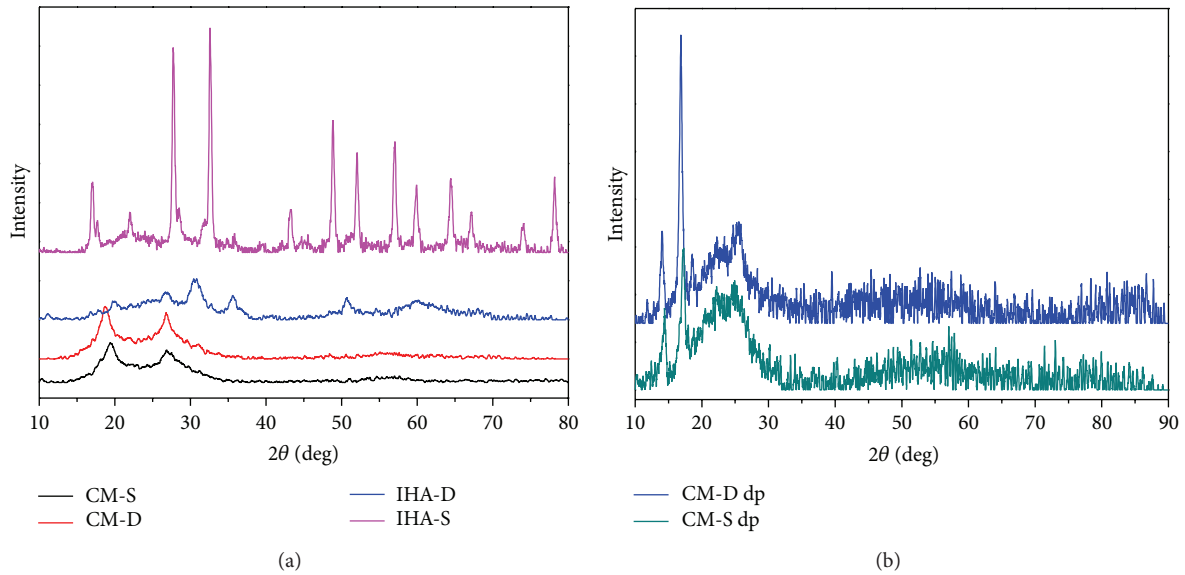


FIGURE 2: WAXD pattern of IHA-D, IHA-S, CM-D, and CM-S (a) and CM-D and CM-S after acid doping (b).

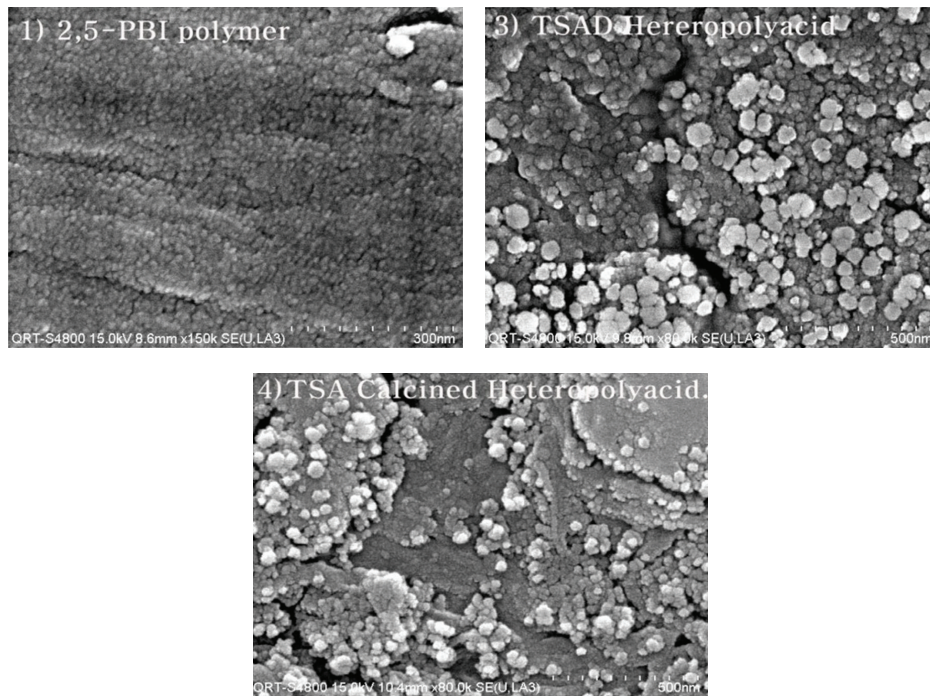


FIGURE 3: SEM images of 2,5-PBI, CM-D, and CM-S.

loss in the TGA data of PBI around 100°C is due to removal of water, other solvents, or any monomer residue [3, 27]. The second decomposition around 400°C is the main decay of the polymer backbone. The composite membranes also show initial weight loss which has higher percentage of loss than PBI. However the second weight loss percentage is lower than PBI but occurred at higher temperature as compared to PBI. Comparing the TGA curves of the composites with PBI, composite membranes showed less thermal degradation which reflect the importance of IHA-D and IHA-S addition

on the thermal stability of the PBI matrix. Further comparing CM-D with CM-S, CM-S showed high thermal stability due to addition of mesoporous silica in silica-combined tungsten oxide heteropoly acid.

In case of acid doped PBI, first degradation took place in the region of 160 to 460°C, followed by second weight loss. CM-S showed first degradation in the region of 200~500°C, followed by a second loss from 550°C. Comparing TGA characteristics of doped composite membrane, the higher content of inorganic heteropoly acid precursors resulted in

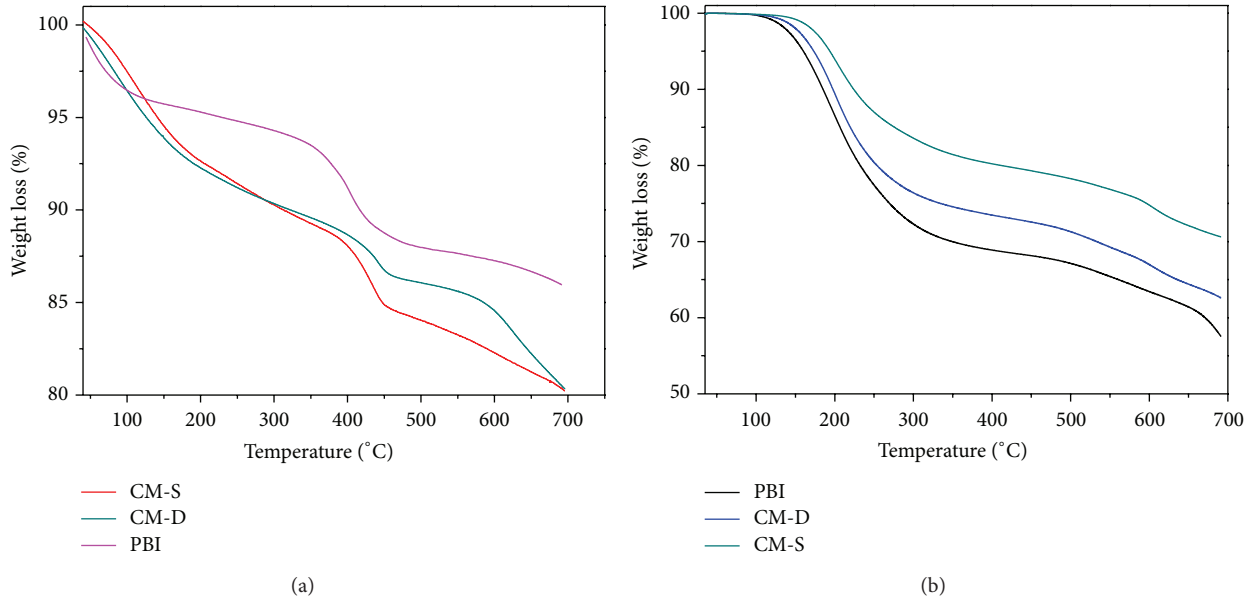


FIGURE 4: TGA curves of 2,5-PBI and composites before (a) and after (b) acid doping.

TABLE 2: TGA results of PBI and composite membranes before and after doping.

	Onset temperature (°C)	
	$T_{d5\%}$	$T_{d10\%}$
2,5-PBI	168.58	318.82
CM-D	141.38	313.13
CM-S	130.48	298.48
2,5-PBI DP	160.50	185.03
CM-D DP	173.20	197.52
CM-S DP	193.68	224.00

higher thermal stabilities of the organic matrix even when doped. Table 2 reviews 5% and 10% weight losses of composite membrane, defined as $T_{d5\%}$ and $T_{d10\%}$, respectively.

3.4. Proton Conductivity. 2,5-Polybenzimidazole, CM-D, and CM-S were studied for fuel cell application which is a significant application of polymer membranes. Also, charge density majorly affects the proton conductivity of fuel cell; however, acid charge density is one of the factors to estimate conductivity because there are many factors to be considered [32]. CM-D showed lowest proton conductivity, most likely because mesoporous silica was ruled out in the step of inorganic heteropoly acid impregnation in testing for its effect on conductivity variations. In case of CM-S, dehydration by calcination of inorganic heteropoly acid on support material increases the interaction anchor power with silicotungstic acid. In spite of dehydration from inorganic heteropoly acid, composite polymer membrane showed the second best proton conductivity, so this is also desired to prepare.

The proton conductivity of the phosphoric acid-doped 2,5-polybenzimidazole and phosphoric acid-doped composite membranes (CM) was measured at 150°C as shown

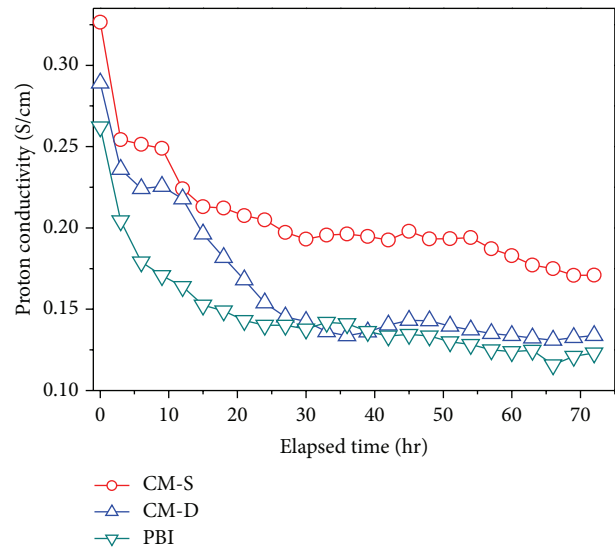


FIGURE 5: Proton conductivities of composite membranes.

in Figure 5. 2,5-Polybenzimidazole and composite membranes give initial proton conductivity of $2.65 \times 10^{-1} \sim 3.3 \times 10^{-1} \text{ Scm}^{-1}$ at 150°C. CM-S exhibited highest proton conductivity ($2.06 \times 10^{-1} \text{ Scm}^{-1}$) compared to all other membranes and was even higher than that reported by Lee et al. [27]. This clearly indicates that mesoporous silica with tungstic acid Keggin network structure improves the conductivity behavior of the membranes due to high absorption level of phosphoric acid, thus creating a pathway for proton transfer. 2,5-Polybenzimidazole and composite membranes showed proton conductivity in the following order $\text{CM-S} > \text{CM-D} > 2,5\text{-polybenzimidazole}$ with proton conductivity values $2.06 \times 10^{-1} > 1.48 \times 10^{-1} > 1.12 \times 10^{-1} \text{ Scm}^{-1}$.

The proton conductivities of all composites are much higher than Nafion 117 which exhibits a proton conductivity of 0.187 Scm^{-1} at 90°C and 100% humidity [33]. The proton conductivity of Nafion 117 depends on the trapped water inside its structure for the most part, which limits its performance at the temperature above 100°C . Proton conductivities of the composites increased with increasing temperature when operating temperature was increased gradually from 40°C to 150°C ; proton conductivity was also increased, although at a low rate, compared to Nafion 117 operating at the limited operating condition temperature below 100°C [3].

The proton transport driving force comes from the phosphoric acid connected to inorganic heteropoly acid in composite membranes and proton conductivities depend on the quantity of hydrogen bonding and free acids called hydronium ions in which they are not bonded to the membranes [33]. Compared to 2,5-polybenzimidazole, the composites exhibited higher proton conductivities at the same temperatures, owing to density of the inorganic heteropoly acid in the composite which gives 2,5-polybenzimidazole a higher phosphoric acid doping level. Hydrogen from both bonded and free acids in phosphoric acid that result from ionic bonding with Keggin-type tungstic acid is captured in porous inorganic material, filling the composites with hydrogen, thus rendering high proton conductivity [34]. It is well known that proton conductivity of the membrane is mainly dependent on the doping level of phosphoric acid. Thus CM-S membrane could have better proton conductivity than 2,5-polybenzimidazole membranes after being doped with phosphoric acid.

4. Conclusion

2,5-Polybenzimidazole and its composites membranes were prepared and tested for high temperature PEMFCs application. It was concluded that addition of inorganic heteropoly acid to the PBI produced an ironically bonded structure, which resulted in rise of thermal stability and thus, according to TGA, 2,5-polybenzimidazole and composites membrane are able to operate up to 200°C . CM-S demonstrated highest proton conductivity at $2.06 \times 10^{-1} \text{ Scm}^{-1}$ at 150°C owing to the high contents of inorganic heteropoly acid in 2,5-polybenzimidazole.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea grant funded by the Korean Government (MEST), Contract Grant no. NRF-2009-C1AAA001-0092926, and Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (no. 2013078867).

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