

## Research Article

# Polybenzimidazole and Phosphonic Acid Groups-Functionalized Polyhedral Oligomeric Silsesquioxane Composite Electrolyte for High Temperature Proton Exchange Membrane

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Here, we report composite membrane consisting of poly[2,2'-(*m*-phenylene)-5,5'-(bibenzimidazole)] (PBI) and polyhedral oligomeric silsesquioxane functionalized with phosphonic acid groups (PO(OH)<sub>2</sub>-POSS) for high temperature proton exchange membrane. ~7 phosphonic acid groups are incorporated into the phenyl rings of POSS via bromination in a high yield (~93%), followed by substitution of the bromine elements by phosphonate ester groups *via* a Pd(0) catalyzed P-C coupling reaction. Phosphonic acid groups are formed by the hydrolysis of the phosphonate ester groups in hydrobromic acid solution. At a 50 wt% of PA content in the membranes, PBI/PO(OH)<sub>2</sub>-POSS composite membrane shows larger proton conductivity of  $3.2 \times 10^{-3} \text{ S cm}^{-1}$  than  $2.8 \times 10^{-3} \text{ S cm}^{-1}$  of PBI membrane at 150°C and anhydrous conditions, owing to the multiple phosphonic acid groups of PO(OH)<sub>2</sub>-POSS that can function as proton transport medium at high temperature and low humidity conditions.

## 1. Introduction

Phosphoric acid (PA)-doped polybenzimidazoles (PBIs) have gained great interests for proton exchange membrane (PEMs) due to their intrinsic attributes such as high proton conductivity (up to 200°C), low gas permeability, excellent oxidative and thermal stabilities, and almost zero water drag coefficient [1–5]. In particular, many attempts on PBI-based organic/inorganic composites have been made to improve the proton conductivity of PEMs that can operate at elevated temperature (generally 100–200°C) and low humidity conditions. Examples of inorganic components include silica (SiO<sub>2</sub>) [6, 7], lithium hydrazinium sulfate (LiN<sub>2</sub>H<sub>5</sub>SO<sub>4</sub>) [8], zirconium phosphates (Zr(HPO<sub>4</sub>)<sub>2</sub>·*n*H<sub>2</sub>O) [9], zirconium pyrophosphate (ZrP<sub>2</sub>O<sub>7</sub>) [10], phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·*n*H<sub>2</sub>O) [9], silicotungstic acid (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·*n*H<sub>2</sub>O) [9], and boron phosphate (BPO<sub>4</sub>) [11], all of which have led to the improvement of electrochemical and physical properties of PBI electrolytes.

Polyhedral oligomeric silsesquioxane (POSS) has been intensively studied because of its well-defined, three-dimensional nanoscale organic/inorganic hybrid structure that

provides interesting opportunities for improving the physical and mechanical properties of polymers due to filler effect [12, 13]. The development of this compound as a nanobuilding block is important to a variety of applications including electronics, energy, and biomedical engineering [13, 14]. In particular, the properties of POSS can be tuned by incorporating various functionalities such as acrylates, methacrylates, alcohols, amines, carboxylic acids, epoxides, fluoroalkyls, halides, and imides [13, 15–18].

Phosphonic acid groups are attracting much attention because of their high thermal, hydrolytic, and oxidative stabilities [19–22]. They also undergo autodissociation due to intrinsically amphoteric character, leading to the formation of hydrogen bond network [23, 24], and thus can participate in the transport of protons from site to site without carrier molecules *via* Grotthuss-type mechanism [22, 23, 25]. These distinctive properties are of specific interest to proton conducting electrolytes that operate at high temperature and low humidity conditions. However, it remains a significant challenge to functionalize multiple phosphonic acid groups to molecules (or macromolecular species) due to side reactions such as condensation and aggregation of phosphonic

acid groups [26, 27]. In this study, the phenyl rings of POSS were functionalized with ~7 phosphonic acid groups *via* bromination, followed by phosphonation. The functionalized POSS was incorporated with PBI for use in high temperature PEMs.

## 2. Experimental

**2.1. Materials.** Bromine (Br<sub>2</sub>, >99.5%, Aldrich), tetrakis(triphenylphosphine) palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>, 99.0%, Aldrich), diethyl phosphate ((EtO)<sub>2</sub>POH, 98.0%, Aldrich), triethylamine (TEA, ≥99.0%, TCI), iso-octylphenyl polyhedral oligomeric silsesquioxane (termed as POSS here, Hybrid plastics), hydrobromic acid solution (HBr, 47.0~49.0%, Daejung), sodium bisulfite (NaHSO<sub>3</sub>, 58.5%, Daejung), iron (Fe, >99%, Aldrich), 3,3'-diaminobenzidine (97%, Tokyo Kasei, TCI), poly(phosphoric acid) (PPA, 116% H<sub>3</sub>PO<sub>4</sub>, Junsei), phosphorus pentoxide (97%, Aldrich), and phosphoric acid (PA, 85 wt% aqueous solution, Aldrich) were used as received. Isophthalic acid (99%, Aldrich) was purified by recrystallization in ethanol to obtain white needlelike crystals. Solvents were distilled before use.

**2.2. Bromination of POSS (Br-POSS).** Bromine-substituted POSS (Br-POSS) was synthesized as reported [28]. Briefly, to a 500 mL round-bottom flask equipped with magnetic stirring bar was added POSS (10.0 g, 9.35 mmol), Fe (1.10 g, 19.7 mmol), and 100 mL of CH<sub>2</sub>Cl<sub>2</sub>. Br<sub>2</sub> (3.61 mL, 70.1 mmol) was then added portion-wise, and the solution was stirred for 3 h at room temperature. Subsequently, 100 mL of 10 wt% NaHSO<sub>3</sub> aqueous solution was added to the solution to remove residual Br<sub>2</sub>. The solution was then transferred to a separatory funnel to extract the organic layer and then washed three times with distilled water. The solvent was removed by using the rotary evaporator to produce a powder. The resulting powder was dissolved in ethyl acetate and precipitated into 1000 mL of methanol. The precipitate was obtained through filtering and then dried under vacuum to give a 10.8 g of final white powder (93%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 7.95–6.45 (br, C<sub>6</sub>H<sub>5</sub>), 1.89–0.60 (m, C<sub>8</sub>H<sub>17</sub>). MALDI-TOF: *m/z* = 1375.8, 1453.7, 1534.6, 1610.6, 1688.5, 1767.4, 1846.3.

**2.3. Synthesis of PO(OEt)<sub>2</sub>-POSS.** A 100 mL two-neck reactor equipped with nitrogen and condenser was charged with 18 mL of anhydrous dimethyl sulfoxide (DMSO). Br-POSS (3.00 g, 1.79 mmol), diethyl phosphite (4.59 mL, 35.9 mmol), and TEA (5.00 mL, 35.9 mmol) were added to the reactor, and the mixture was stirred for 10 min; Pd(PPh<sub>3</sub>)<sub>4</sub> (2.07 g, 1.79 mmol) was then injected into the reaction flask with high stream of nitrogen and the solution was heated for 72 h at 100°C. After cooling to room temperature, the solution was precipitated in distilled water (1000 mL). The precipitate was then filtered and dried overnight in a vacuum oven to give brownish powder (86%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 8.36–6.93 (br, C<sub>6</sub>H<sub>5</sub>), 3.96–3.31 (br, CH<sub>2</sub>-O), 1.29–0.19 (br, CH<sub>3</sub> and C<sub>8</sub>H<sub>17</sub>). <sup>31</sup>P NMR (202 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 26.0.

**2.4. Synthesis of Poly[2,2'-(*m*-phenylene)-5,5'-(bibenzimidazole)] (PBI).** PPA (90.2 g) was charged into a 250 mL three-neck reactor equipped with a mechanical stirrer, nitrogen inlet, and calcium chloride drying tube and heated for 30 min at 150°C. DABI (2.78 g, 13.0 mmol) and IPA (2.16 g, 13.0 mmol) were then added gradually, and the solution was stirred for 1 h at 150°C under a slow nitrogen stream and mechanical stirring until it became a homogeneous solution. The reaction temperature was raised to 200°C. After 30 min, phosphorus pentoxide (4.84 g, 17.0 mmol) was added and the reaction continued for 12 h at 200°C with constant stirring using a mechanical stirrer to obtain a very viscous dark brown solution. The reaction mixture was isolated into the polymer in distilled water (1000 mL) and the precipitate was then neutralized with an aqueous solution of NaHCO<sub>3</sub> and rinsed several times with distilled water to remove phosphate salts. It was dried overnight under vacuum. The resulting polymer was ground using a pulverizer (A11 basic, IKA) and washed again to remove any residual phosphoric acid. Finally, the powder was dried at 70°C in a vacuum oven for at least 3 days (>95%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 9.14 (s, 1H), 8.32 (d, 2H), 8.00 (s, 2H), 7.81 (d, 2H), 7.62 (br, 3H).

**2.5. Preparation of Composite Membranes.** 4.0 g of PBI powder and 1.0 g of PO(OEt)<sub>2</sub>-POSS were dissolved in a 166 g of *N,N*-dimethylacetamide (DMAc) at 80°C. The mixed solution was then spread onto a clean flat glass plate. The thickness of the solution was controlled using an adjustable doctor blade, and the casted solution was left to dry at 80°C for 12 h until no DMAc evaporation was noted. After cooling to room temperature, the obtained film was soaked in distilled water and peeled off the substrate. The resulting film was dried using gel dryer at 60°C for 1 h, and then the film was further dried under vacuum for 12 h. To convert POSS in phosphonated ester form (PO(OEt)<sub>2</sub>-POSS) into that in phosphonic acid form (PO(OH)<sub>2</sub>-POSS), the composite membranes containing PO(OEt)<sub>2</sub>-POSS were soaked in concentrated HBr solution at reflux for 24 h. The composite films were thoroughly washed with distilled water several times to neutralize and to remove excess acid and then dried using gel dryer at 60°C for 1 h, and then the film was further dried in a vacuum oven for 12 h. The PBI and PO(OH)<sub>2</sub>-POSS composite film obtained was weighed (*W*<sub>1</sub>) and immersed in 1000 mL of the PA solution with 60 wt% concentration at 80°C for 4 h. The PA-doped membrane was taken out of the PA solution and then blotted with filter paper. The membrane was dried at 70°C under vacuum for 2 days and weighed again (*W*<sub>2</sub>). The weight difference, (*W*<sub>2</sub> – *W*<sub>1</sub>), was assumed to be the weight of the absorbed PA. The PA content of the membrane was then calculated as the weight percent (wt%) of PA absorbed in the membrane using

$$\text{PA content (wt\%)} = \frac{(W_2 - W_1)}{W_2} \times 100. \quad (1)$$

**2.6. Characterization.** Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS)

was recorded on a Voyager-DE™ STR Biospectrometry Workstation (Applied Biosystems Inc.) set in the positive reflection mode using dithranol as the matrix. The MALDI-TOF/MS instrument was equipped with a nitrogen laser which was emitting at 337 nm with a 3 ns pulse width. The  $^1\text{H}$  and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra were collected on Bruker Avance 500 with a proton frequency of 500 MHz. During the experiments, deuterated dimethyl sulfoxide was used as the solvent and tetramethylsilane (TMS) was used as the internal standard. Fourier transform infrared (FT-IR) spectra of dried membranes and powder samples were recorded in the attenuated total reflectance (ATR) mode in the frequency range of  $4000\sim 650\text{ cm}^{-1}$  on a Nicolet 6700 instrument (Thermo Scientific, USA). The spectrum was recorded as the average of 32 scans with the resolution of  $8\text{ cm}^{-1}$ . Each of the samples was put in equal physical contact with the sampling plate of the spectrometer accessory to avoid differences caused by pressure and penetration depth. The chemical composition and concentration of the material were determined by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss SUPRA 55VP), operated at an accelerating voltage of 15 kV and equipped with energy-dispersive spectroscopy (EDS) capabilities. Proton conductivity was measured using a four-point probe. Impedance was measured using a ZAHNER IM-6ex impedance analyzer in potentiostat mode with a perturbation amplitude of 10 mV over frequencies of 1 Hz to 1 MHz. Impedance at a controlled humidity and temperature was measured from Nyquist plots. Proton conductivity ( $\sigma$ ) was calculated using  $\sigma = d/RS$ , where  $d$  is the distance between the reference and sensing electrodes and  $S$  is the cross-sectional area (thickness  $\times$  width) of the doped membrane.  $1\text{ cm} \times 5\text{ cm}$  membranes were introduced to the conductivity cell and heated to  $160^\circ\text{C}$  and held for 30 min. Measurements were taken as the cell then cooled to  $100^\circ\text{C}$  in  $10^\circ\text{C}$  steps.

### 3. Results and Discussion

Iso-octylphenyl polyhedral oligomeric silsesquioxane, which we term POSS here, was brominated by a coupling reaction in high yield (ca. 93%) as reported (abbreviated as Br-POSS, Figure 1) [28, 29] and characterized by using MALDI-TOF/MS,  $^1\text{H}$  NMR and ATR FT-IR. MALDI-TOF/MS of Br-POSS shows a series of peaks separated by 79 amu of bromine, centered at  $1610\text{ m/z}$  (Figure 2). It indicates that an average of  $\sim 7$  bromine elements per POSS was incorporated. This observation was further supported by  $^1\text{H}$  NMR spectra (Figure 3). The bromination of POSS results in the broadening of proton peaks associated with the phenyl rings of POSS ( $\delta = 8.1\sim 6.3\text{ ppm}$ ), while the peaks of isooctyl moiety ( $\delta < 2.0\text{ ppm}$ ) remain unchanged, demonstrating that bromine elements are incorporated into the phenyl rings of POSS. The extent of bromine elements incorporated was calculated by the comparison of integrals of proton peaks associated with the phenyl ring and the isooctyl moieties. The average number of the bromine elements per POSS determined by

$^1\text{H}$  NMR spectra was  $\sim 7.6$ , close to MALDI-TOF/MS-determined value. Figure 4 shows ATR FT-IR spectra of Br-POSS. The characteristic absorption band assigned to stretching vibration for aromatic halogen compound appears at  $1009\text{ cm}^{-1}$ . The bands at  $894$ ,  $810$ , and  $784\text{ cm}^{-1}$  are also ascribed to bromine-incorporated phenyl rings of POSS.

The bromine elements of Br-POSS were substituted with phosphonate ester groups *via* a Pd(0) catalyzed P-C coupling reaction, which was carried out with diethyl phosphite ((EtO) $_2$ POH) and tetrakis(triphenylphosphine) palladium(0) (Pd(PPh $_3$ ) $_4$ ) as a catalyst with trimethylamine (TEA) [26, 30, 31]; the resulting compound is named PO(OEt) $_2$ -POSS (Figure 1). We observed the peaks of the CH $_2$  and CH $_3$  protons of phosphonate ester groups at  $\delta = 3.80$  and  $1.15\text{ ppm}$ , respectively, in  $^1\text{H}$  NMR spectra, as a consequence of substitution of phosphonate esters for bromine elements (Figure 3) [31]. Figure 5 presents  $^{31}\text{P}$  NMR spectra of PO(OEt) $_2$ -POSS and diethyl phosphite, a monomer used for the substitution reaction. The phosphorous signal associated with phosphonate ester units of PO(OEt) $_2$ -POSS is shifted downfield by  $\sim 17\text{ ppm}$  as compared to that of diethyl phosphite because of the substitution reaction. ATR FT-IR spectra also provide the information regarding the substitution reaction (Figure 4). The phosphoryl linkage (P=O) stretching appears at around  $1680\text{ cm}^{-1}$ . The bands at  $1048$  and  $1023\text{ cm}^{-1}$  are assigned to P-O-C absorptions of the ester group, and the band at  $949\text{ cm}^{-1}$  is attributed to P-O-C vibrations [27, 31]. SEM/EDS measurement was conducted to verify substitution from bromine elements to phosphonate ester groups (Figure 6). No notable peaks of bromine elements are observed. A single peak of phosphorus appears at  $\sim 2.1\text{ keV}$  and its intensity is comparable with that of silicon at  $\sim 1.9\text{ keV}$ . Assuming that the substitution occurred completely, the number of phosphorous elements per POSS should be  $\sim 7$ , which is the same with that of silicon of POSS. Accordingly, the atomic weight ratio of phosphorus to silicon for PO(OEt) $_2$ -POSS determined through EDS is unity, supporting the assumption that bromine elements were completely substituted by phosphonate ester groups.

Following the protocol we and others have explored, poly[2,2'-(*m*-phenylene)-5,5'-(bibenzimidazole)] (PBI) was synthesized by a condensation polymerization and fabricated into a freestanding membrane through a solution casting method commonly used, which was also applied to the fabrication of PBI/PO(OEt) $_2$ -POSS composite membrane. The phosphonate ester units of PO(OEt) $_2$ -POSS were readily converted into the phosphonic acid ones, denoted as PO(OH) $_2$ -POSS, by hydrolysis in hydrobromic acid (HBr) solution as demonstrated in Figure 1. In addition, in ATR FT-IR spectra, the characteristic bands associated with phosphonate ester groups of PO(OEt) $_2$ -POSS disappear, implying the substitution of phosphonic acids for phosphonate esters (Figure 4). More importantly, PO(OEt) $_2$ -POSS is soluble in organic solvents such as DMSO and DMAc while its solubility decreases significantly, once the hydrolysis is performed, which is most likely due to strong hydrogen bond network formed between phosphonic acid groups [31, 32]. Due to such dissolution issue of PO(OH) $_2$ -POSS in organic solvents,

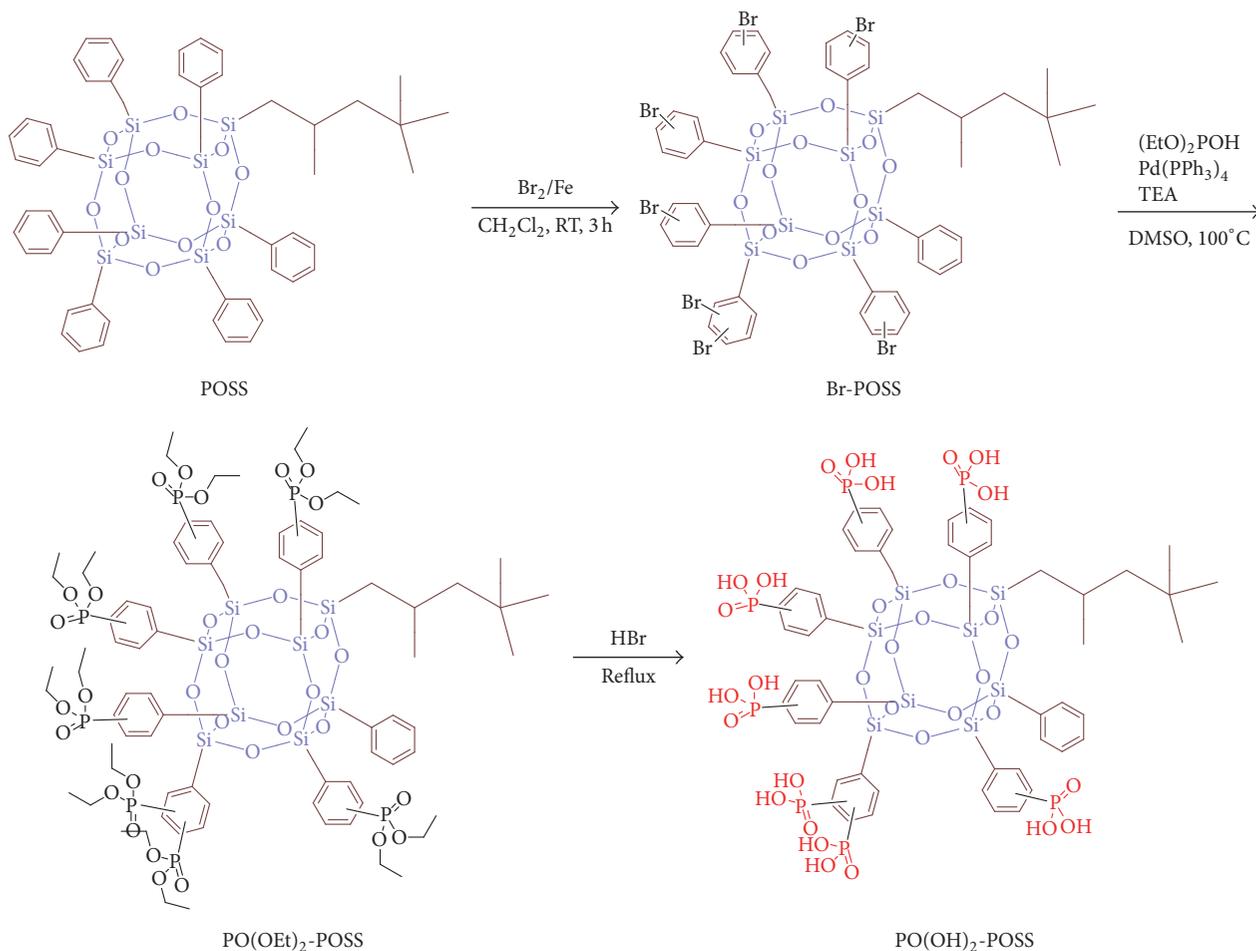


FIGURE 1: Synthesis of phosphonic acids-functionalized POSS.

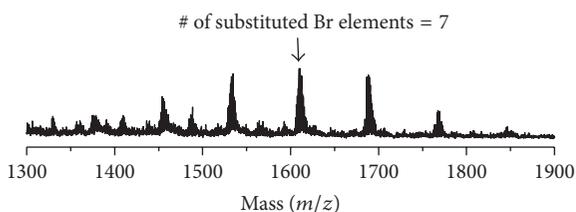
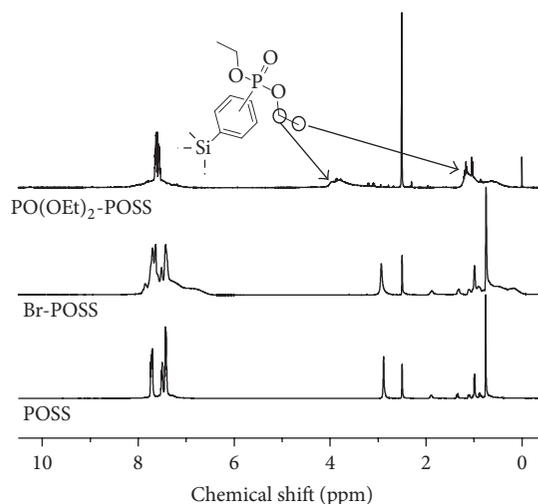


FIGURE 2: MALDI-TOF/MS of Br-POSS.

PO(OEt)<sub>2</sub>-POSS, which is soluble in DMAc, was mixed with PBI for freestanding film formation prior to hydrolysis. The doping of the composite membrane in 60 wt% PA solution imparts proton conducting capability of the membrane. The PA content absorbed in the membranes is ~50 wt%.

Figure 7 shows the proton conductivities of the PA-doped membranes with temperature ranging from 100 to 150°C under anhydrous conditions. Not surprisingly, the proton conductivity increases with increasing temperature, an observation common to all studies on PA-doped PBI derivative membranes [5, 25, 33–36]. In particular, PBI/PO(OH)<sub>2</sub>-POSS composite membrane provides greater proton conductivity,  $3.2 \times 10^{-3} \text{ S cm}^{-1}$ , than PBI membrane ( $2.8 \times 10^{-3} \text{ S cm}^{-1}$ ) at

FIGURE 3: <sup>1</sup>H NMR spectra of POSS, Br-POSS, and PO(OEt)<sub>2</sub>-POSS.

a given temperature. The conductivity against temperature exhibits the Arrhenius behavior ( $\sigma = \sigma_0 \exp(-E_a/RT)$ ), where  $\sigma_0$  is the preexponential factor and  $E_a$  is the activation energy

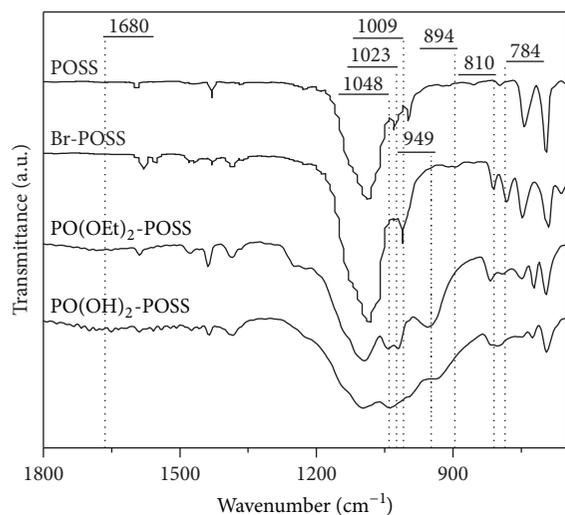


FIGURE 4: ATR FT-IR spectra of POSS, Br-POSS, PO(OEt)<sub>2</sub>-POSS, and PO(OH)<sub>2</sub>-POSS.

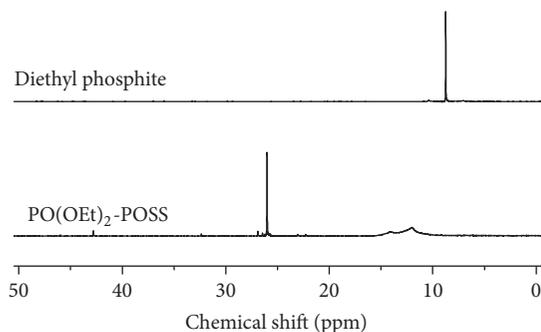


FIGURE 5: <sup>31</sup>P NMR spectra of diethyl phosphite and PO(OEt)<sub>2</sub>-POSS.

for the proton conduction), indicating that proton conduction in the membrane follows a proton-hopping dominant mechanism (Grotthuss-type mechanism) as reported by other reports [33, 34, 37]. We thus speculate that ~7 phosphonic acid groups of PO(OH)<sub>2</sub>-POSS provide a better pathway for proton conduction as they bridge the apparent gap between PAs (and/or PA and PBI) *via* the hopping mechanism.

#### 4. Conclusions

In summary, we succeeded in functionalizing POSS with ~7 phosphonic acid groups. Following bromination, ~7 bromine elements of POSS were substituted with phosphonate ester groups, which were further hydrolyzed into phosphonic acid groups in hydrobromic acid solution. The solubility of the POSS significantly decreased after the hydrolysis, which might be due to hydrogen bond network formed between phosphonic acids. The functionalized PO(OH)<sub>2</sub>-POSS was hybridized with PBI and the composite was fabricated into freestanding membrane, followed by doping in PA solution.

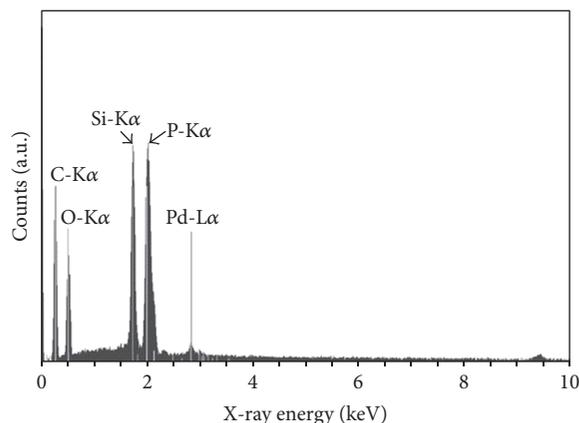


FIGURE 6: SEM/EDS spectroscopy of PO(OEt)<sub>2</sub>-POSS.

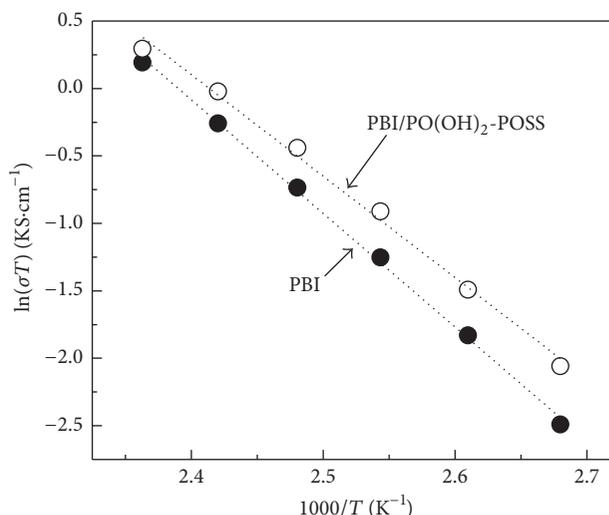


FIGURE 7: Proton conductivities of PA-doped PBI and PBI/PO(OH)<sub>2</sub>-POSS membranes with temperature ranging from 100 to 150°C under anhydrous conditions. PA content of the membranes is ca. 50 wt%.

The PA-doped composite membrane retains proton conductivity greater than that of PBI membrane at high temperature over 100°C and low humidity conditions. We conclude that phosphonic acids-functionalized POSS as a filler provides considerable increase in proton conducting capability of polymer electrolyte operating at high temperature.

#### Competing Interests

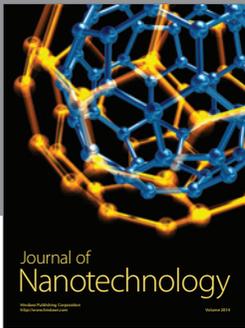
The author declares that there are no competing interests regarding the publication of this paper.

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