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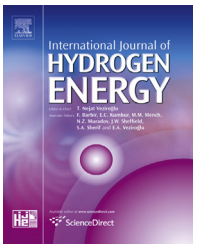

Proton-conducting composite membranes based on polybenzimidazole and sulfonated mesoporous organosilicate

Yoichi Tominaga [a,*], *Tei Maki* [b]

[a] *Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

[b] *EM Application Group, EM Business Unit, JEOL Ltd., Akishima, Tokyo 196-8558, Japan*

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ABSTRACT

Sulfonated mesoporous organosilicate (s-MPOs) was synthesized by the one-step sol–gel method as a novel inorganic additive derived for use in the fuel cell. TEM observations revealed that the s-MPOs has well-ordered structure and many SO_3H groups on the inner surface of the mesopores. The s-MPOs was added to the proton-conductive polymer matrix, polybenzimidazole (PBI) in the presence of H_3PO_4, and the proton conductivities were measured at 60–100 °C under controlled humidity. The PBI composites filled with only 1 wt % of s-MPOs gave proton conductivity more than 10-times higher than the original PBI/H_3PO_4 membrane. The s-MPOs possessing many SO_3H groups were able to form effective proton conductive pathways via its periodic structure and to improve the conductivity. The greatest conductivity was estimated to be 0.21 S cm^{-1} at 80 °C and 98 %RH in case of a PBI/s-MPOs20 (incl. approx. 20 mol% of the SO_3H units in MPS) composite.

1. Introduction

In recent years, polymer electrolyte membrane fuel cell (PEM-FC) have been developed as promising power sources for vehicular transportation and for other applications requiring clean, quiet, and portable power [1,2]. The Nafion® membrane is very popular in PEM-FCs, but this has some drawbacks; the proton conductivity depends strongly on the humidity and high cost. In particular, the Nafion® cannot operate above 80 °C because of dehydration from the membrane at higher temperatures and ambient pressure. Many scientists have sought to solve these problems by using hydrocarbon-based polymer electrolyte membranes [3,4], however, their permeability to oxygen, control of molecular weight and morphology are all crucial in practical use. Addition of inorganic materials to the polymer matrix is another way to improve the conductivity at high temperatures. For instance, hydrophilic inorganic materials such as silica or silica-based particles [5–7], zeolites [8] and solid acids [9–11] can maintain higher water content, and are suitable for preventing the dehydration at high temperatures.

On the other hand, we are investigating hexagonally ordered mesoporous silica (MPS) as a novel inorganic additive for composite polymer electrolytes [12–17]. Since MPS was discovered by the Kuroda group [18] and the Mobil Co. group [19], there have been many studies of mainly synthesis, characterization and functionalization for the materials science. Recently, the MPS possessing sulfonic acid groups was

* *Corresponding author*. Tel.: +81 42 388 7058.
E-mail address: ytominag@cc.tuat.ac.jp (Y. Tominaga).

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synthesized by simple surface treatment or by *in-situ* method [20,21], which is well suited to catalytic applications [22]. To utilize high acidity and well-ordered structure of the sulfonated MPS, we have aimed to prepare novel polymer composites which are based on proton-conductive Nafion® [16] and commercial poly (ethylene-*co*-vinyl alcohol) (EVOH) [17]. The addition of sulfonated MPS increases proton conductivity in the Nafion® matrix, and can improve the temperature dependence of the conductivity. In the EVOH composites, the conductivity of the order of 10^{-3} S cm^{-1} can be achieved.

Here, we aim to demonstrate proton conduction in aromatic hydrocarbon-based polymer composites filled with sulfonated MPS. For practical use under high temperature and for its cost, we chose polybenzimidazole (PBI) as a polymer matrix. PBI is well known as one of engineering plastics because of its very high degradation temperature (over 600 °C) and glass transition temperature (approximately 430 °C). To utilize high heat-resistant and mechanical strength, PBI is widely used for applications such as parts of vehicles and fibers for garments of firefighters [23]. Recently, the PBI/H_3PO_4-based electrolytes for the fuel cell membranes have been studying by many researchers [24–31], since proton conduction was first reported by Wainright and co-workers in the 1990's [23,32]. In this study, we report proton-conductive properties of PBI composites filled with sulfonated mesoporous organosilicate (s-MPOs). In addition, we report detailed characterization of nano-ordered structure of s-MPOs using high-resolution TEM system for the first time.

2. Experimental

2.1. Synthesis of s-MPOs

Sulfonated mesoporous organosilicate (s-MPOs) was synthesized by the one-step sol–gel method using a nonionic surfactant, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich). The structural image of synthesized s-MPOs is shown in Fig. 1 below. Tetraethyl orthosilicate (TEOS, Kanto Chemical, 95%) was slowly added to the surfactant aqueous solution in which the pH was adjusted to 1.0 using 36% HCl (Kanto Chemical), and 10 or 20 mol% 3-mercaptopropyl trimethoxysilane (MTS, Aldrich, 95%) to the TEOS and H_2O_2 solution (Kanto Chemical, 30–36%) was then dropped simultaneously into the mixture [21]. The solution was stirred for 23 h at 35 °C and aged at 100 °C for 24 h. The reactant was filtered and the precipitate was refluxed with ethanol in a Soxhlet extractor for 48 h. The resulting fillers possessing propyl-SO_3H groups on the surface, s-MPOs10 and s-MPOs20 (the numbers 10 and 20 mean the molar ratio of MTS to TEOS used in the synthesis procedure), were rinsed several times with water and ethanol, and was finally dried in a vacuum at 60 °C.

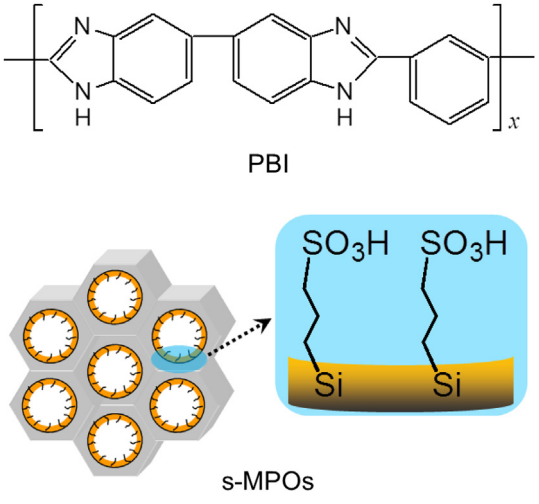

Fig. 1 – Structure of polybenzimidazole (PBI) and sulfonated mesoporous organosilicate (s-MPOs).

2.2. Preparation of PBI/s-MPOs composite membranes

Polybenzimidazole (PBI, average M_w: 4.0×10^4) was donated from company as a 10 wt% solution of N,N-dimethylacetamide (DMAc). PBI/s-MPOs composite membranes were prepared by the solvent casting method. The DMAc solution was used as received and 1 wt% (to PBI) of s-MPOs was added to the solution. The mixed solution was stirred vigorously at room temperature and was carried out ultrasonic treatment for 15 min. The solution was then cast onto glass petri dish and dried in air at 60 °C. Pre-dried sample was finally dried under vacuum at 120 °C for 3 h. All resulting composites were obtained as homogeneous and self-standing membranes. These composites and neat PBI membranes were immersed into 75 wt% of phosphoric acid aqueous solution at room temperature for 24 h before conductivity measurements.

2.3. Characterization of s-MPOs

Small-angle X-ray scattering (SAXS) measurements were made using a SmartLab system (Rigaku Co.) with CuKa radiating conditions of 45 kV and 200 mA. The surface area of s-MPOs was determined using a Belsorp 18-plus system (Bell Japan Inc.). The ion-exchange capacity of s-MPOs was determined by the titration method. The filler (0.05 g) was added to the 2 M NaCl solution and was stirred adequately. The solution was titrated by the addition of 0.01 M NaOH solution, and the potentiometric ratio was measured using a pH meter. The nano-ordered structures of s-MPOs were observed by transmission electron microscopy (TEM) system constructed by JEOL Co. Ltd. We used conventional microtome method for the preparation of ultrathin specimens which were obtained by embedded s-MPOs fillers in heater-cured epoxy resin Epon812 (TAAB Co. Ltd.). Polymerization of the epoxy resin with s-MPOs was conducted in an isothermal bath for 1 day where the temperature was maintained at 45 °C, and the bath was kept at 60 °C for 2 days. After the polymerization, the embedding agent was removed from gelatin capsule. The cured resin was sliced into approximately 70 nm-thick using an Ultramicrotome UC7 (Leica Co. Ltd.), and obtained sections were then mounted on a 100-mesh Cu grid with elastic carbon membrane. The TEM observations were carried out using an energy-filtered TEM (JEM-2200FS). For the analysis of atom species, we used an FTEM (JEM-2800) equipped with an EDS (DrySD 100 GV). The EDS measurement was performed with an electron probe diameter of 1.0 nm at a scanning time of

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