



Poly(ethylene-co-vinyl alcohol)/sulfonated mesoporous organosilicate composites as proton-conductive membranes

Yuta Chiba, Yoichi Tominaga*

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

ARTICLE INFO

Article history:

Received 12 September 2011

Received in revised form

24 November 2011

Accepted 25 November 2011

Available online 6 December 2011

Keywords:

Mesoporous organosilicate

Poly(ethylene-co-vinyl alcohol)

Proton conductivity

Polymer electrolyte

Fuel cell

Composite

ABSTRACT

Highly ordered mesoporous silica (MPS) and sulfonated mesoporous organosilicate (s-MPOs) were synthesized as novel inorganic additives derived for use in PEM-FCs, and were added to the non-protonic polymer matrix, poly(ethylene-co-vinyl alcohol) (EVOH). The proton conductivities of EVOH composites were measured at 50–100 °C under controlled high humidity values. The EVOH27 (ethylene content: 27 mol%) composite membranes filled with s-MPOs gave a proton conductivity more than 50-times higher than composites filled with simple treated MPS (t-MPS). The s-MPOs having many SO₃H groups was able to form effective proton conductive passages via its periodic structure and so improve conductivity in the polymer. We also investigated the temperature dependence of the conductivity for EVOH composites with ethylene content of 27 and 44 mol%. The EVOH44/s-MPOs composites had better conductivity than EVOH27 at higher temperatures. The greatest value was estimated to be $1.67 \times 10^{-3} \text{ S cm}^{-1}$ without extra acid additives, at 80 °C and more than 96%RH.

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1. Introduction

The polymer electrolyte membrane fuel cell (PEM-FC) is a noteworthy power source, due to its high energy efficiency, simple electrochemical mechanism and easy refueling capability [1]. The Nafion[®] membrane is popular in PEM-FCs, but this system cannot operate above 80 °C because of dehydration of the Nafion[®] membrane at higher temperatures. Nafion[®] has further drawbacks: the proton conductivity depends strongly on the humidity, high cost and corrosion [2]. Many scientists have sought to solve these problems with hydrocarbon-based polymer electrolyte membranes. It is well known that sulfonated poly(ether ether ketone)s, poly(imide)s and poly(sulfone)s act as excellent matrixes in fuel cell applications because of their high chemical and thermal stability [3–8]. These electrolytes require water solvation for effective proton transport, and have poor conductivity at high temperatures (>80 °C) with low humidity (<50%RH). Recently, block copolymers possessing sulfonic acid groups have been shown to overcome these problems by controlling the morphology of hydrophilic and hydrophobic units [9–11]. 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 SiO₂, clay and zeolite can

maintain higher water content, and are suitable for preventing dehydration of Nafion[®] at high temperatures [12–14]. Solid acids, such as sulfonated ZrO₂, increase the concentration of acid sites so as to promote local protonic migration [15,16], and heteropolyacids such as phosphotungstic acid (H₃PW₁₂O₄₀) are widely used in studies aiming to improve the conductivity at relatively high temperatures [17].

We have investigated hexagonally ordered mesoporous silica (MPS) as an inorganic additive for composite polymers [18–21]. Since MPS was discovered by the Kuroda group [22] and the Mobil Co. group [23], there have been many studies of associated synthesis methods [24,25] of hybridization with organic compounds [26] and of the alignment of mesopores in thin-films [27] for the development of MPS in materials science. Recently, MPS containing sulfonic acid groups was synthesized by simple surface treatment or by an in situ method, which is well suited to catalytic applications [28–31]. We first aimed to prepare Nafion[®]/MPS composites. The addition of neat and treated MPS (simple surface treatment on the neat MPS with silane coupling agent) increased proton conductivity in the Nafion[®] matrix, and improved the temperature dependence of the conductivity [32]. In our previous report, we concluded that Nafion[®]/treated MPS composite membranes have higher conductivity than neat Nafion[®] without MPS, because the treated MPS possesses some sulfonic acid groups on the surface, which can enhance the migration of protons in the composites.

Here, we aim to demonstrate proton conduction in hydrocarbon-based common polymers using MPS. For practical use and for its cost, we chose poly(ethylene-co-vinyl alcohol)

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

(EVOH) as the candidate polymer matrix. EVOH is composed of a hydrophobic ethylene unit and a hydrophilic vinyl alcohol unit and is commonly used as a packaging material. This polymer has very low gas permeability and is useful for packaging foods which are sensitive to certain levels of oxygen or water. This excellent gas barrier performance is a good way to prevent methanol crossover in DMFC systems. PVA-based proton-conductive membranes have been noted for these extraordinary properties [33,34]. In the present study, we report EVOH composites including two types of sulfonated mesoporous materials, one is treated MPS (t-MPS) and the other is sulfonated mesoporous organosilicate (s-MPOs). We expect the periodic porous structure to be suitable for the migration of protons in the polymer matrix. We prepared EVOH/t-MPS and EVOH/s-MPOs composites, and measured their proton conductivities to determine their suitability as a novel polymer membrane for PEM-FC.

2. Experimental

2.1. Synthesis of neat and sulfonated mesoporous materials

Original mesoporous silica (neat MPS) was synthesized by the sol-gel method using a nonionic surfactant, EO₂₀PO₇₀EO₂₀ (have EO and PO denote ethylene oxide and propylene oxide units, average $M_w = 5800$, Aldrich Co.). The procedure was described in detail in our previous report [32]. Treated MPS (t-MPS) was prepared by simple surface treatment of neat MPS using a silane coupling agent, 3-mercaptopropyl trimethoxysilane (MTS, Aldrich Co.). The MTS (approximately 70 wt% to neat MPS) was dropped into a chloroform solution of the neat MPS, and the mixture was stirred at room temperature for 24 h. The thiol groups were oxidized using H₂O₂ solution (30–36%) for 2 h and H₂SO₄ solution (1.0 M) for 5 h. The precipitate was rinsed several times with water and ethanol, and dried in a vacuum at 60 °C. Sulfonated mesoporous organosilicate (s-MPOs) was synthesized by the same sol-gel method, using EO₂₀PO₇₀EO₂₀. The structure of synthesized s-MPOs is shown in Fig. 1. The surfactant solution including TEOS was stirred at 40 °C for 1 h, and MTS (10 mol% to TEOS) was then dropped into the mixture [29]. The solution was then stirred for 23 h 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 oxidization process was the same as that of the t-MPS. The resulting filler, possessing propyl-SO₃H groups on the surface, was rinsed several times with water and ethanol, and was finally dried in a vacuum at 60 °C.

2.2. Preparation of EVOH composites

Poly(ethylene-co-vinyl alcohol) (EVOH) as a polymer matrix was purchased from Aldrich Co. and was used as received. We used two types of EVOH, with ethylene content of 27 mol% (EVOH27) and 44 mol% (EVOH44), for the sample preparation. The EVOH/filler composite membranes were prepared by the solvent casting method. Neat EVOH was dissolved in mixed solvent (ethanol:water=4:1 wt%) at approximately 60 °C. The filler (neat MPS, t-MPS or s-MPOs) was added to the solution and the mixture was stirred vigorously for at least 12 h. The resulting slurry was cast onto a glass dish and placed in an oven at 60 °C for at least 6 h. The resulting composite samples were all self-standing membranes, and were immersed into purified water before measurement. The water uptakes of an original EVOH27, EVOH27/t-MPS and EVOH27/s-MPOs composite membranes were 15.2, 18.4 and 20.6%, and the dimensional changes were scarcely observed.

2.3. Measurements

Small-angle X-ray scattering (SAXS) measurements were made using a NANO-Viewer system (Rigaku Co.) with Cu K α radiating conditions of 40 kV and 20 mA. The surface area of all mesoporous fillers was determined using a Belsorp 18-plus system (Bell Japan Inc.). The ion-exchange capacity of all fillers 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 adding 0.01 M NaOH, and the potentiometric ratio was measured using a pH meter [29]. The structures of mesoporous fillers were observed by transmission electron microscopy (TEM), using a JEM-2100 system (JEOL Co.). The morphology of the EVOH composite membranes was observed by scanning electron microscope (SEM), using a JSM-6510 system (JEOL Co.). The cross-section of the membranes was coated by Au using sputtering (Eiko IB-2) at 5 mA for 10 min, after the etching. The proton conductivity was measured by a complex AC impedance method, using a chemical impedance meter (Hioki 3532-80) in the frequency range 10 Hz to 1 MHz. A four-probe cell was used, consisting of Teflon® blocks with blackened Pt electrodes (two plates for current application and two wires for voltage measurement). The sample (5 mm \times 40 mm) was placed between two plates (beneath the sample at each end) and two wires (on the center of sample), and these were sandwiched between two Teflon® blocks [35,36]. The conductivity was measured using a constant voltage mode (10 mV). The entire process was carried out in a desktop chamber (Espec ST-110) in which the temperature was controlled between 50 and 100 °C. The measurement cell was set in a water-saturated glass vessel (more than 96%RH) in the chamber for at least 3 h before the measurement, and was maintained at each temperature measured, for at least 60 min.

3. Results and discussion

The physicochemical properties of all mesoporous fillers are summarized in Table 1. The surface area was estimated from N₂ adsorption-desorption isothermal measurements; all samples showed type-IV isotherms, with clear hysteresis loops. This hysteresis is probably due to capillary condensation in the mesopores. Consequently, these synthesized fillers have a periodic mesoporous structure. The surface area of t-MPS and s-MPOs were both slightly lower than that of neat MPS, because of the presence of organic SO₃H groups on the surface. These values are much larger than

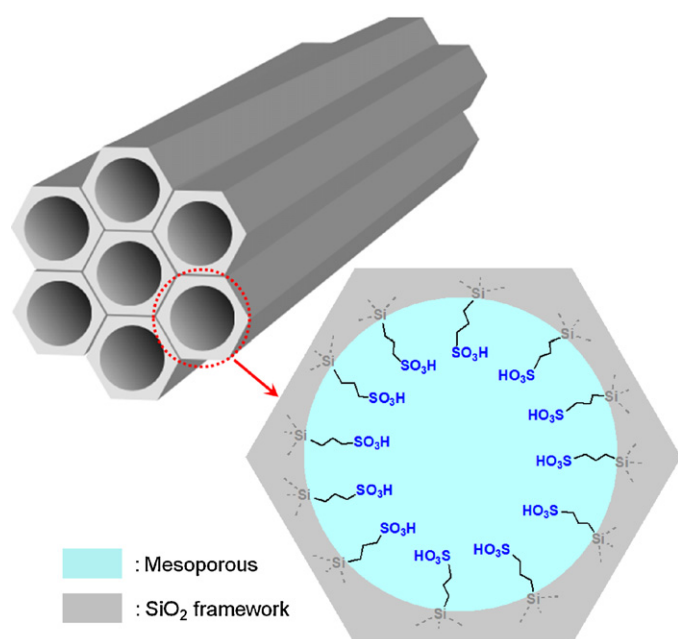


Fig. 1. Structure of sulfonated mesoporous organosilicate (s-MPOs).

Table 1
Physicochemical properties of mesoporous fillers.

Fillers	Surface area ^a (m ² g ⁻¹)	Acidity ^b , H ⁺ (mmol g ⁻¹)	Long period ^c , <i>L</i> (nm)	Pore diameter ^c , <i>d</i> (nm)
Neat MPS	784	0.04	9.4	7.2
t-MPS	663	0.20	9.5	7.1
s-MPOs	693	0.61	8.1	5.2

^a The surface area was determined from the Barrett–Joyner–Halenda (BJH) equation.

^b The ion-exchange capacity was estimated by titration in 2 M NaCl_{aq}.

^c These were estimated from the one-dimensional correlation function (γ) of each SAXS diffraction pattern.

for inorganic fillers (e.g. particle SiO₂), implying that the periodic structure is maintained by the incorporation of coupling agents and oxidation. Neat MPS had very low IEC value, because this filler has no SO₃H groups on its surface. The t-MPS and s-MPOs had oppositely higher IEC than for the neat MPS because of the surface modification. In particular, the IEC of s-MPOs was found to be 3-times higher than that of t-MPS. In a previous study, we synthesized the same t-MPS and estimated the IEC as 0.46 mmol g⁻¹ [32]. We expect the former MPS to have more SO₃H groups and higher

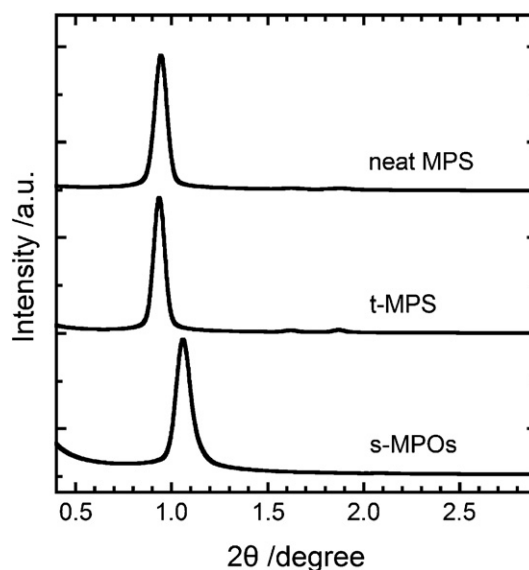
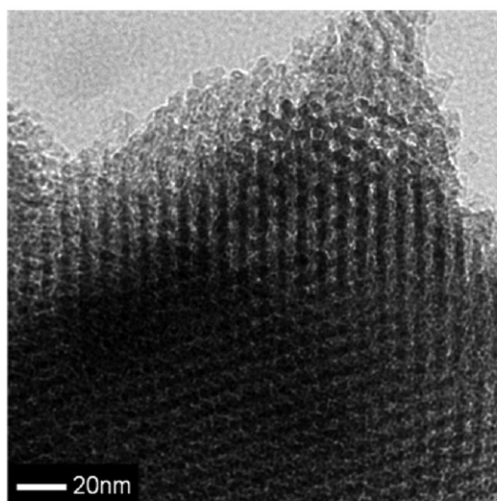
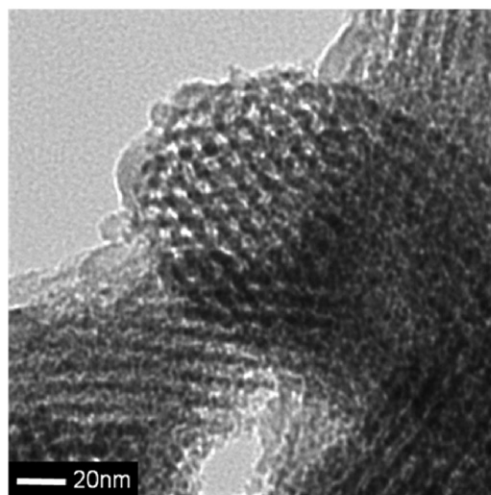
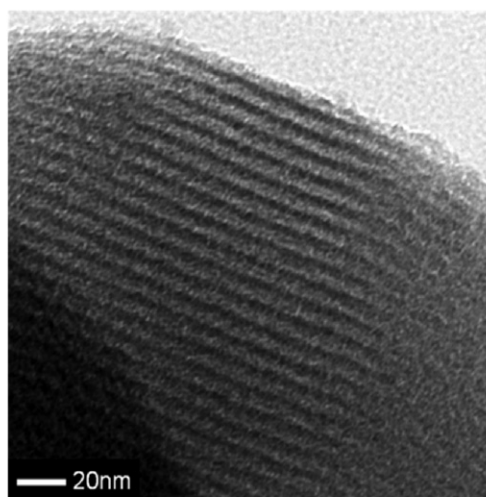


Fig. 2. SAXS diffraction patterns of neat MPS, t-MPS and s-MPOs.



neat MPS



S-MPOs

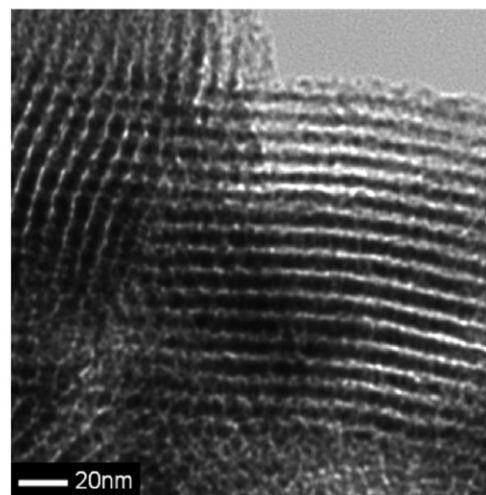


Fig. 3. TEM images of neat MPS and s-MPOs.

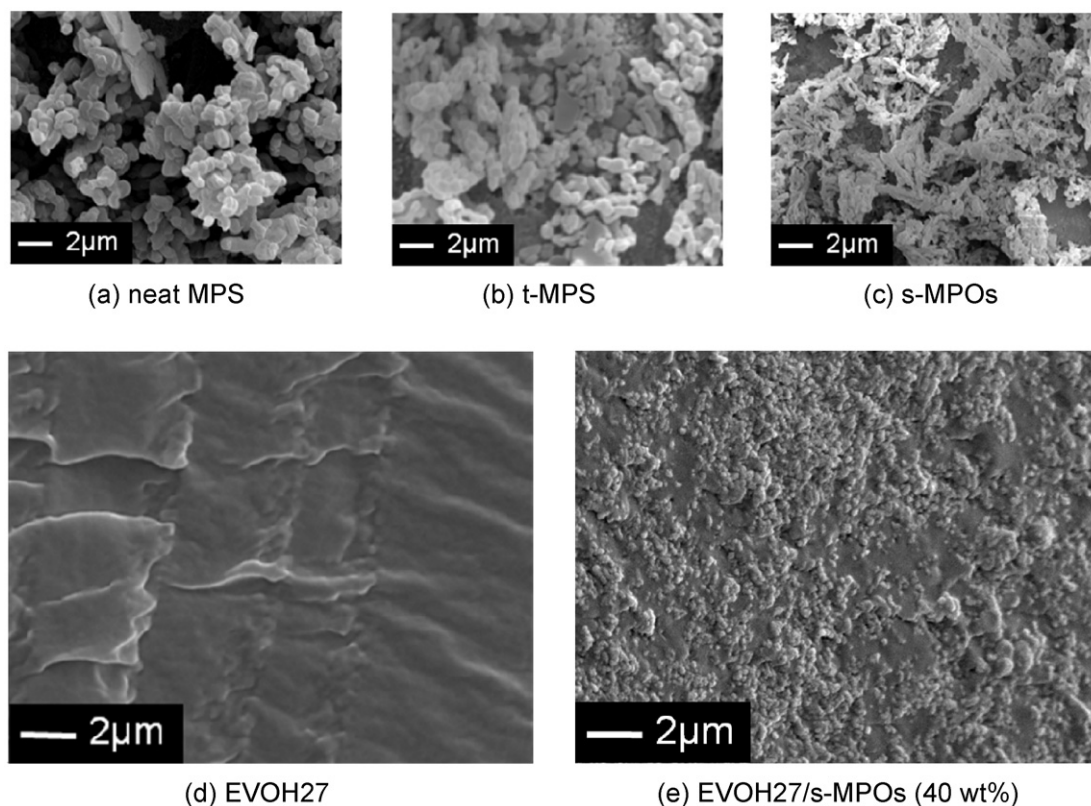


Fig. 4. SEM images of (a) neat MPS, (b) t-MPS, (c) s-MPOs, (d) neat EVOH27, and (e) EVOH27/s-MPOs composite (40 wt%).

IEC. In the present study, the highest value was for s-MPOs, because the method of preparation can introduce many SO_3H groups.

Fig. 2 shows SAXS diffraction patterns of all mesoporous fillers. These spectra show that these fillers possess well-ordered mesoporous structures. From the SAXS diffraction patterns it was confirmed that neat MPS and t-MPS exhibit three peaks, identified as (1 0 0), (1 1 0) and (2 0 0), at approximately 0.9° , 1.6° , 1.8° for the hexagonal structure [23]. The peak-top value at 0.9° of s-MPOs was shifted slightly to higher angles relative to neat MPS and t-MPS. This could be due to the incorporation of SO_3H groups, which can change the apparent long-range structure of the MPS. The periodic structure can be estimated from the one-dimensional correlation function (γ) of the SAXS data. A large unit cell and the pore diameter of the mesoporous fillers can be determined from the SAXS data; these values were summarized in Table 1. For s-MPOs, these two values were clearly lower than for neat MPS and t-MPS. This indicates that the SO_3H groups on the surface are the most commonly introduced of all mesoporous fillers [28]. It is known that the periodic structure is disordered by the increase of organic components. The presence of an elevated concentration of the organic component during co-condensation apparently perturbs the formation and self-assembling aggregation of the nonionic surfactant. The 10 mol% molar ratio of the organic component might be adequate to maintain the periodic structure and to give the high IEC.

Fig. 3 shows TEM images of the neat MPS and s-MPOs. The TEM images of t-MPS were omitted, because the framework is the same as with the neat MPS, and the SAXS data are also very similar to each other. Introduction of the SO_3H groups on the surface has no effect on the periodic structure of t-MPS. In Fig. 3, the neat MPS and s-MPOs obviously have well-ordered arrays of mesopores. The distance between the mesopores of neat MPS is estimated to be approximately 8–9 nm, in good agreement with the SAXS data. The wall thickness of s-MPOs appears to be larger than that of neat MPS,

and the pore size of s-MPOs is smaller, because of the introduction of SO_3H groups on the internal surface. Fig. 4 shows SEM images of all mesoporous fillers, and the cross sections of neat EVOH27 and the composite membranes. Micro-ordered oval domains are clearly observed in these fillers. The s-MPOs domains are apparently smaller than for the neat and t-MPS. The difference in the domain size between neat or t-MPS and s-MPOs is apparently due to the introduction of SO_3H groups. On the other hand, well-dispersed s-MPOs domains in the EVOH27 were clearly observed in Fig. 4(e). Our previous work also found a better dispersion state of the mesoporous fillers in the Nafion[®] matrix and effects on the conductivity increase [32]. This may be due to the hydrophilic property of the s-MPOs.

The temperature dependence of the proton conductivity for the EVOH/mesoporous filler composites is shown in Fig. 5. The filler content of these samples in Fig. 5 was fixed at 40 wt%. For EVOH27/neat MPS composites we were not able to measure the conductivity, because the MPS has no SO_3H groups on the surface, giving higher IEC. For a EVOH27/t-MPS composite the proton conductivities were more than $10^{-5} \text{ S cm}^{-1}$ at $50\text{--}80^\circ\text{C}$ because of the presence of the SO_3H groups on the MPS surface, but the conductivity fell drastically above 80°C . This may indicate that dehydration from the composite membrane occurs readily and prevents proton conduction in the EVOH. The thermogravimetric analysis shows that the EVOH dehydrates at higher temperatures under humid conditions [37]. According to the IEC value, the t-MPS has fewer SO_3H groups than s-MPOs and it is probably difficult to maintain water inside the mesopores. As a result the migration of protons via the MPS was inhibited, and the proton conductivity of the t-MPS composite was lowered. On the other hand, the conductivity of the s-MPOs composite was much higher than that of the t-MPS at all temperature measured (e.g. appl. 36-times at 80°C), because the IEC of s-MPOs was 3-times greater than that of t-MPS. The

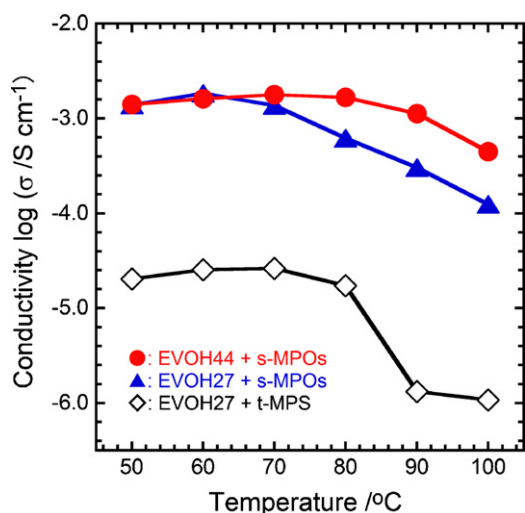


Fig. 5. Temperature dependence of proton conductivity (>96%RH) for EVOH27 and EVOH44 composite membranes (filler content: 40 wt%).

s-MPOs has more SO_3H groups and can maintain higher water content than t-MPS. The presence of many SO_3H groups as a result of the internal the periodic structure of is effective in promoting proton conduction and can improve the conductivity in the polymer composite. However, the conductivity of EVOH27/s-MPOs composite slowly decreases with increasing temperature. A possible cause is the degradation of EVOH by acid groups under humid conditions. Poly(vinyl alcohol) (PVA) is a polymer that can dissolve in hot water and in acid solvents. The vinyl alcohol segments in the EVOH may assist in dissolving and probably in degrading. Degradation is also promoted by the voltage applied during conductivity measurements under acid conditions. These problems may prevent proton conduction via interacting mesoporous networks through membranes and cause the decrease in the conductivity. We therefore proposed EVOH having higher ethylene content (EVOH44) as the polymer matrix, to improve conductive properties at higher temperatures. The crystallinity of EVOH derives from the ethylene segments and the gas permeability from the vinyl alcohol segments [38]. The EVOH44/s-MPOs composite showed displayed higher conductivity than with EVOH27 and was more stable above 80 °C. We believe that the increase in ethylene content prevented EVOH degradation of EVOH under humid conditions and improved the proton conductivity at high temperatures.

The relation between the proton conductivity of EVOH composites and the filler content is shown in Fig. 6. The conductivity of EVOH27 and EVOH44 composites both increased with increasing s-MPOs content. It is obvious that the EVOH44 composites have greater conductivity than for EVOH27 at every filler content. In particular, the conductivity of EVOH44/s-MPOs composite (40 wt%) was highest, with a value estimated to be $1.67 \times 10^{-3} \text{ S cm}^{-1}$ at 80 °C. The conductivities of EVOH27 composites are apparently limited with increasing filler content, because excess filler may form aggregates and inhibit proton conduction. We conclude that a filler content of 40 wt% is best for the EVOH composites. The conductivity is similar to values for hydrocarbon-based electrolyte membranes such as PEEK and PBI [39–45]. We also investigated Nafion®/MPS composites and confirmed the effects of s-MPOs on proton conduction, especially at higher temperatures. In the present study, the s-MPOs composites gave a conductivity of $10^{-3} \text{ S cm}^{-1}$ without extra acid additives, whereas non proton-conductive EVOH is used as the polymer matrix. We expect that s-MPOs will be a good inorganic additive for perfluorosulfonic polymers or proton-conductive hydrocarbon-based polymers.

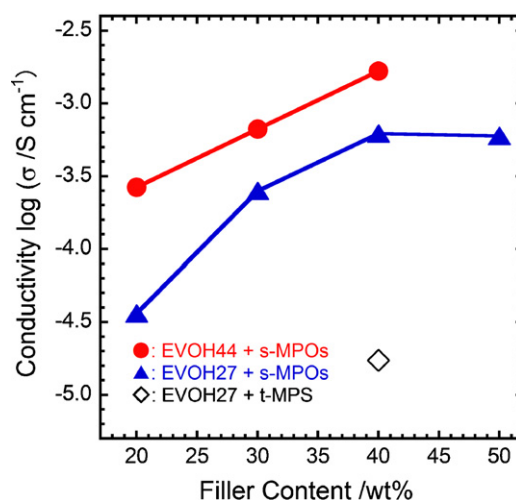


Fig. 6. Relation between proton conductivity at 80 °C (>96%RH) and s-MPOs content for EVOH27 and EVOH44 composite membranes.

4. Conclusions

We synthesized sulfonated mesoporous organosilicate (s-MPOs) and prepared composites based on poly(ethylene-co-vinyl alcohol) (EVOH) as a novel proton-conductive membrane. The IEC of s-MPOs was found to be 3-times higher than that of t-MPS, and was estimated to be 0.61 mmol g^{-1} . Our SAXS and TEM measurements showed that all mesoporous fillers used in this study have well-ordered arrays of mesopores. The wall thickness of s-MPOs was larger, and the pore size of s-MPOs was smaller, than for neat MPS, because of the introduction of SO_3H groups on the internal surface. In SEM observations of cross-sections of EVOH27/s-MPOs composite, well-dispersed s-MPOs domains were clearly observed. The s-MPOs composites gave a proton conductivity of more than $10^{-3} \text{ S cm}^{-1}$ without extra acid additives, whereas non proton-conductive EVOH was the polymer matrix. The use of EVOH having higher ethylene content (EVOH44) was effective in improving the conductivity at higher temperatures. The s-MPOs should be a good inorganic additive for perfluorosulfonic polymers or proton-conductive hydrocarbon-based polymers.

Acknowledgements

We acknowledge financial supports for young scientists from Yazaki Memorial Foundation (2007) and Iketani Science and Technology Foundation (2008). We also thank Dr. Shigeo Asai (Tokyo Inst. Tech.) and Dr. Teruyuki Nakato (Kyushu Inst. Tech.) for SAXS and BET surface area measurements of all mesoporous materials.

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