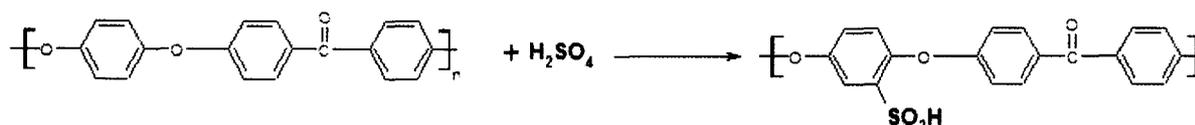


Sulfonated poly(ether-ether ketone) as matrices for proton conductive inorganic-organic composite membranes for fuel cells systems

Song-yul Oh, Hiroyuki Muto, Mototsugu Sakai and Atsunori Matsuda

[INTRODUCTION] In the medium temperature range (100–200 °C), the effective utilization of waste heat from the polymer electrolyte fuel cells (PEFCs) and the depression of the poisoning of Pt catalysts with CO in the fuel gas are expected [1-3]. Perfluorosulfonic ionomers (PFIs) such as Nafion® are currently used as the electrolyte for fuel cells due to their high proton conductivity, whereas they do not sustain prolonged operation at temperatures higher than 100 °C by dehydration. Thus, proton conductive membranes with high thermal stability as well as high conductivity are required as the electrolyte for the medium temperature operation of PEFCs [4]. The chemical structures of the initial and sulfonated form of poly(ether-etherketone) (PEEK) are shown in Scheme 1. PEEK has been well known as a thermostable polymer with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (–O–) and carbonyl (–CO–) linkages. PEEK can be functionalized by sulfonation and the degree of sulfonation (DS) can be controlled by reaction time and temperature. J. Devaux et al. have reported [5] that sulfo group positions in a sulfonated PEEK (SPEEK) are consistent with the appearance as a third substituent on phenyl rings of sulfonic acid or sulfonate salt groups because of the other phenyl rings being deactivated by the neighboring ketone.



Scheme 1. Chemical structures of PEEK and its sulfonated polymers.

Previously, we have prepared thermally stable proton-conducting composite sheets from phosphosilicate gel (P/Si = 1 molar ratio) powders and polyimide precursor. The fuel cells using the composite sheets as an electrolyte operated up to 150 °C under a relatively low water vapor pressure. To achieve a higher performance of the fuel cells, not only a homogeneous mixing of the gel powder and the organic polymer but also a good contact between the composite sheet and Pt-loaded carbon paper in the membrane electrode assembly (MEA) is very important [6-8]. On the other hand, we have recently reported [9-10] that mechanochemically treated cesium salt-phosphotungstic acid composites, which have hydrogen-network based on HSO₄⁻ units, show high proton conductivity in the medium temperature range even under dry conditions. In this work, we attempt to measure the proton conductivity and single cell performance of SPEEK membranes with different DS aiming at their application as matrices for proton conductive inorganic-organic composite membranes for fuel cells

Sulfonated poly(ether-ether ketone) as matrices for proton conductive inorganic-organic composite membranes for fuel cells systems, Song-yul Oh, Hiroyuki Muto, Mototsugu Sakai and Atsunori Matsuda (Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580) Tel : +81-532-44-6800, E-mail : matsuda@tut.ac.jp

systems. The electrochemical properties of SPEEK composite membranes are changed by introduced protonate sites such as sulfo groups (-SO₃H).

[EXPERIMENTAL] The SPEEK was prepared from commercially available PEEK (450 P standard viscosity grade, VICTREX[®]) according to the following procedures. Firstly PEEK was dissolved in concentrated H₂SO₄ with vigorously stirring at room temperature for desired time. Then the polymer solution was poured into large excess ice-cold water under continuous mechanical agitation to obtain the precipitates. The polymer precipitates thus obtained were washed several times with distilled water until the pH of the residue became neutral and then finally dried under vacuum. The obtained SPEEK polymer was dissolved in N,N-Dimethylacetamide (DMAc). After evaporation of almost all of the DMAc, the precursor was cast onto a glass plate and developed to form membranes using a casting knife. The cast membranes were dried at 60 °C for 10 h, then at 100-120 °C for 10 h and finally at 100 °C under vacuum for overnight.

Thermal analyses were performed to measure T_g of the PEEK and SPEEK. Fourier transform infra-red (FT-IR) spectra of the PEEK and SPEEK were recorded between 4600 cm⁻¹ and 400 cm⁻¹. The spectra of PEEK powder were measured by KBr method, and those of SPEEK polymers were obtained for the film formed on a silicon substrate by casting the polymer solution.

The proton conductivity of the polymer membrane samples was measured by the AC impedance spectroscopy technique over a frequency range of 10⁷ - 1 Hz using a system based on a SI 1260 gain phase analyzer (Solartron). The conductivity, σ , of the samples in the transverse direction was calculated from the impedance data, using the relation $\sigma = d/RS$ where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the real, Re(Z), axis.

The single fuel cell tests were carried out for the membranes electrode assemblies (MEAs) which consisted of commercially available Pt-loaded carbon paper sheet (Pt : 2.0 mg cm⁻²) as electrodes. The MEAs were obtained by hot pressing the SPEEK membranes between the Pt-loaded carbon paper sheets at 100 °C under about 2 MPa for 1 min. Current-voltage profiles in the fuel cells were obtained by using SI 1252A with SI 1287 electro-chemical measurement system (Solartron). When current-voltage profiles of the fuel cells were measured, humidified H₂ and air by passing through the bubbler were provided to the cells, and the temperature of the cell was fixed at 80 °C. The fuel cell performance greatly depends on the makeup of the cell as well as on the operation conditions of temperature and humidity, so that the assembly processes of the cells and the conditions were optimized for each SPEEK membrane by trial and error.

[RESULTS & DISCUSSION] The T_g for the SPEEK was shown in Fig. 1. The introduction of -SO₃H groups into the PEEK polymer increased the T_g by as much as 70 °C after sulfonation for 144 h relative to T_g of 70 °C for non-sulfonated PEEK. The increase in T_g with the degree of sulfonation results from the increased intermolecular interaction by hydrogen bonding of SO₃H groups (ionomer effect). It is likely that these intermolecular forces hinder the internal rotations compared to non-sulfonated PEEK. From this result, the improvement of the thermal property is expected for PEEK after sulfonation. Judging from these changes of the T_g in the appearance of the PEEK after sulfonation, the thermal stabilities are estimated to be 150 °C.

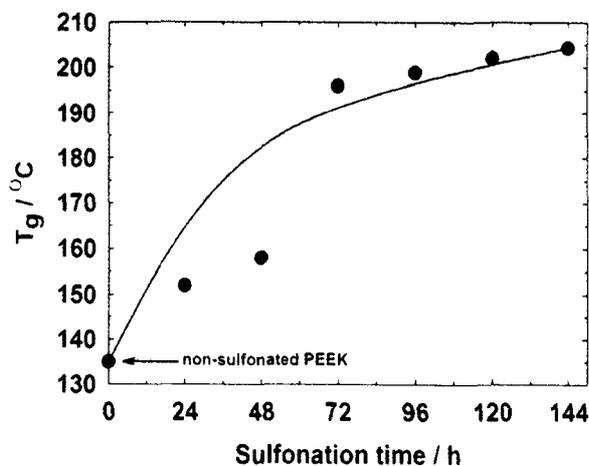


Fig. 1. Glass transition temperatures (T_g) of PEEK as a function of sulfonation time.

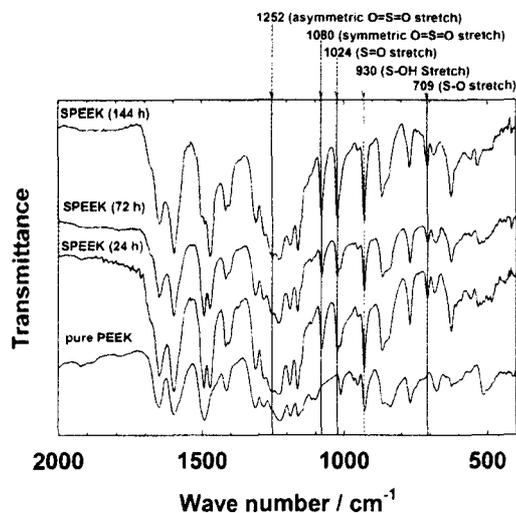


Fig. 2. IR spectra of initial and sulfonated form of PEEK .

Fig. 2 presents the IR spectra of PEEK and SPEEK polymers with various sulfonation times. The assignments of significant peak were explained in Fig. 2. Upon sulfonation, new peaks appear near at 1700, 1252, 1080, 1024, 930 and 709 cm^{-1} . These FT-IR spectral data indicate that the sulfonation of PEEK in sulfuric acid takes place at the para position of the third substituent on phenyl rings.

Fig. 3 and Fig. 4 present the conductivity and the polarization curves of SPEEK membranes as a function of sulfonation time at 80 °C with 80 RH%, respectively. In Fig. 3, the conductivity of SPEEK membranes were increased with increasing sulfonation time. Fig. 4 shows that the power densities of SPEEK membranes were increased with sulfonation, and the maximum power density became as much as 30 mW cm^{-2} for the sample having a sulfonation time of 120 h relative to SPEEK membrane with sulfonation time of 24 h. The sulfonation raises the conductivity and the power densities of the SPEEK membranes not only by increasing the number of protonated sites (SO_3H), but also through formation of water mediated pathways for protons [11]. Conductivity and power density values of sulfonated PEEK samples have been reported in different works [12-13]. Kaliaguine et al. have reported [12] that the SPEEK with various DS have shown conductivity values from $\sigma_{25^\circ\text{C}} = 6.8 \times 10^{-4}$ to $1.1 \times 10^{-1} \text{ S cm}^{-1}$. A. Carbone et al. also have reported [13] that the SPEEK with different casting solvents for sulfonation time of 24 h have shown a maximum power density of about 400 mW cm^{-2} at 0.5 V. In contrast to these results, SPEEK membranes in this work have shown conductivity values from 1.8×10^{-4} to $4.2 \times 10^{-4} \text{ S cm}^{-1}$ and power density values from 36 to 71 mW cm^{-2} , which is still lower than in Refs. These different results are probably due to the nature of initial material and the other experimental features of a measurements technique.

Despite these high electrochemical properties of SPEEK, high DS leads to a poor durability for hot water. It may be due to the introduced SO_3H group, which is hydrophilic component. Therefore, we attempt to preparation of SPEEK composite membranes with inorganic solid acids, such as heteropoly acids (HPAs) and its mechanochemically synthesized composite materials, in order to improve the hot water durability. The electrochemical properties and chemical durability of SPEEK

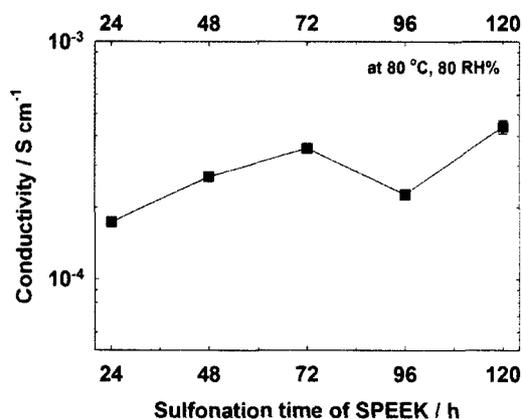


Fig. 3. The ion conductivities of SPEEK membranes as a function of sulfonation time .

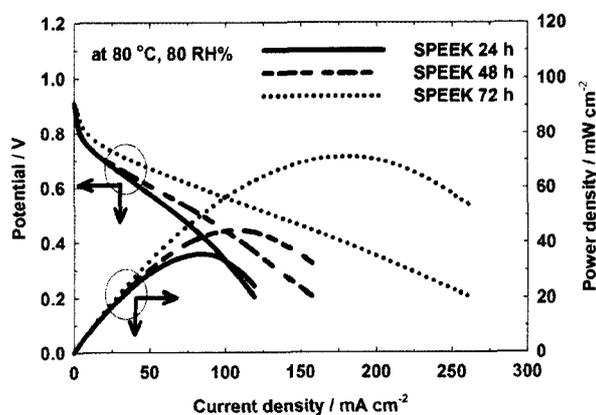


Fig. 4. The polarization curves of SPEEK membranes as a function of sulfonation time .

composite membranes with various inorganic solid acids are now under study. It can be expected that the durability of SPEEK in hot water and the proton conductivity can be improved by introducing the inorganic solid acids.

[CONCLUSIONS] A series of flexible, thermally stable SPEEK proton conductive membranes have been successfully prepared. From thermal analysis results, the thermostability of PEEK was improved by introduced SO_3H groups. The sulfonation raises the conductivity and power density of the SPEEK membranes not only by increasing the number of protonated sites (SO_3H), but also by forming the water mediated pathways for protons. Fuel cells using SPEEK membranes showed maximum power density values from 36 to 71 $\text{mW}\cdot\text{cm}^{-2}$ at 80 °C and at 80 RH%. Composite membranes of SPEEK and mechanically milled heteropoly acid can be prepared. SPEEK is promising as matrices for the proton conductive inorganic-organic composite membranes for fuel cells systems.

[REFERENCES]

- [1] O. Savadogo; J. Power Sources, 127, 135 (2004)
- [2] I. Honma et al.; J. Electrochem. Soc. 149, A1389 (2002)
- [3] A. Matsuda et al.; Electrochim. Acta 47, 939 (2001)
- [4] K.T. Adjemian et al.; J. Electrochem. Soc. 149, A256 (2002)
- [5] J. Devaux et al.; POLYMER 26, 1994 (1985)
- [6] A. Matsuda et al.; Solid State Ionics. 162-163, 247 (2003.)
- [7] N. Nakamoto et al.; J. Power Sources 138, 51 (2004)
- [8] A. Matsuda et al.; Solid State Ionics 177, 2437 (2006)
- [9] A. Matsuda et al.; Solid State Ionics, 176, 2899 (2005)
- [10] A. Matsuda et al.; Solid State Ionics, 177, 2421 (2006)
- [11] S.M.J. Zaidi et al., J. Membr. Sci. 173, 17 (2000)
- [12] S. Kaliaguine et al.; Catal. Today, 82, 213 (2003)
- [13] A. Carbone et al.; J. Power Sources, 163, 18 (2006)