Proton-Conduction of Perfluorooctanesulfonic Acid / Poly(propylene carbonate) Composites

Jun-Sang Cho, Yuki Hayashino, Kenji Miyatake,[#] Shinji Takeoka, and Eishun Tsuchida*
Advanced Research Institute for Science and Engineering, Department of Polymer Chemistry, Waseda University,
Tokyo 169-8555

(Received September 22, 1999; CL-990815)

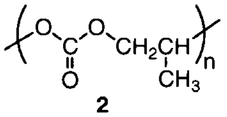
To obtain proton-conducting organic materials with high conductivity under nonaqueous conditions, high thermal stability, and high resistance to acid, we prepared perfluorooctanesulfonic acid (FOSA)/ poly(propylene carbonate) (PPC) composites with different weight ratios. The composite with the weight ratios of 3 shows a high proton-conductivity of 1.9 x 10^{-5} S·cm^{-1} at 30 °C under nonaqueous conditions.

Proton-conducting polymers have been extensively investigated for application as the electrolytes of fuel cells, secondary batteries, electrochemical sensors, electrochromic devices, and so on.[1-5] Most of the previous studies have been devoted to aliphatic ionomers such as sulfonated polystyrene and poly(perfluorosulfonic acid) (Nafion)[6] due to their high proton conductivity (10^2 S·cm^{-1}) under aqueous conditions. The high mechanical stability as a flexible thin film and the easily manufacturing processes of cells using such films is also advantageous. The proton conduction of Nafion is based on the migration of hydronium ions through the aqueous columns of sulfonate aggregates. The conductivity decreases at temperatures above 100 °C due to the evaporation of water and the subsequent destruction of the columns. Some polar polymers such as poly(oxyethylene),[7] poly(vinylalcohol),[8] and poly(ethyleneimine)[9] have been used as a matrix of acids that can replace the role of water. The resulting (polymer/acid) composites show proton-conduction under nonaqueous conditions. However, the proton-conductivity and the stability of the composites are still challenging. The small counter anions as well as protons often migrate in the opposite direction against proton migration, thus leading to an unfavorable polarization.

Perfluorooctanesulfonic acids (FOSA) (**1**) play the role as a proton source with a high acid dissociation constant and has a higher density of the sulfonate group compared to Nafion. Poly (propylene carbonate) (PPC) (**2**) is a polar polymer having a high degradation temperature (T_d; 10 % weight loss temperature) of 258 °C and provides a flexible and amorphous base matrix (-43 °C of T_g) for proton dissociation and conduction.

$CF_3(CF_2)_7SO_3H$

1



2

Compound **1** was prepared by the hydrolysis of perfluorooctanesulfonate fluoride (Aldrich Co., Ltd.) with sodium hydroxide, followed by the ion exchange procedure. In the FT-IR spectrum of the resulting transparent gel, the existence of sulfonic acid was confirmed from the strong characteristic peak at 1196 cm^{-1} assigned to the S=O stretching band of the sulfonic acid group. Polymer **2** (Aldrich Co., Ltd.) with M_w: 77000 and M_n: 50000 did not show a clear T_m, indicating amorphous structure of the polymer.

The composites of **1/2** with different weight ratios (1/1, 2/1, and 3/1) were prepared in a DMF solution. The solution (33 wt%, 0.1 ml) was soaked into a glass wool filter (thick=0.3 mm, porosity=80 %, pore size=60 μm) under reduced pressure and dried at 80 °C for 8 h. The filters were annealed at 80 °C for another 5 h in a glove box (H_2O < 10 ppm, MO-10/20, Vacuum Atmosphere Co., Ltd.) under a dry argon (99.9999 %) atmosphere before the conductivity measurement. The water content of the composites was determined by a Karl-Fischer method with a moisture titrator (MKC-510, KEM Co., Ltd.). Based on scanning electron microscopy, the gel-like composite homogeneously covered on the glass fiber of the filter. The cell was comprised of the filter sandwiched between gold disk electrodes by means of a clamp, which was tightened until a constant meter reading was obtained to assure the best interfacial constant. The ac proton conductivity was calculated from the complex impedance plot (Cole-Cole plot) using a computer curve-fitting technique.

Figure 1 shows the proton-conductivity of the filters containing the composites with various weight ratios of **1/2**. The proton-conductivity increases with the increasing ratio of **1/2** because the proton density increases with the ratio. The **1/2** composite having the ratio of 3 shows the highest proton-conductivity of 1.9 x 10^{-5} S·cm^{-1} at 30 °C and 1.1 x 10^{-3} S·cm^{-1} at 150 °C under nonaqueous conditions ($H_2O \leqq 0.5$ wt%). However, when the ratio is 4, the proton-conductivity decreases lower than that of only **1** (6.2 x 10^{-7} S•cm^{-1} at 30 °C and 2.5 x 10^{-5} S·cm^{-1} at 150 °C), because of the phase separation in the turbid film. The proton-conductivity of the **1/2** composite with the ratio of 3 slightly decreases to 8.9 x 10^{-4} S·cm^{-1} (150 °C) at the second measurement due to the evaporation of remaining moisture in the composite.

Figure 2 shows the temperature dependence of the proton-

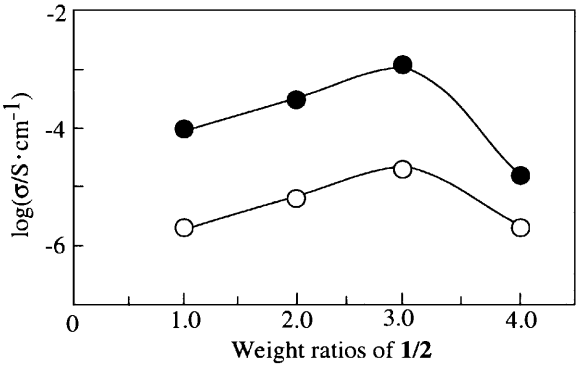


Figure 1. Proton-conductivity of the **1/2** composites (○; 30 °C, ●; 150 °C) with various weight ratios of **1/2**.

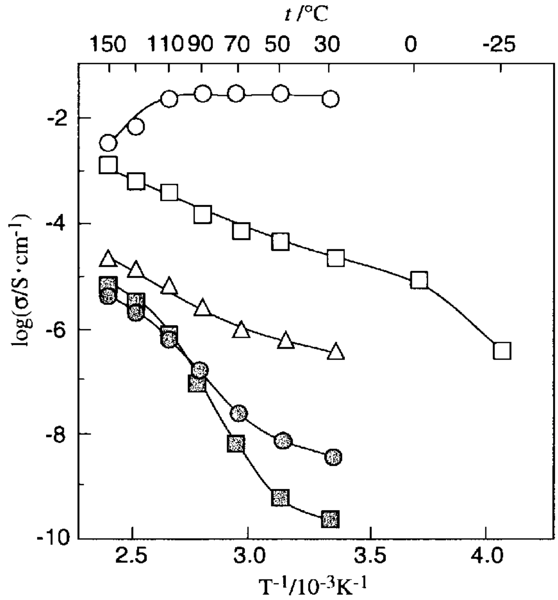


Figure 2. Temperature dependence of the proton-conductivity of the only **1** (△; nonaq.), **1/2** composite (3/1, ○; aq., □; nonaq.), only Nafion (▨; nonaq.), and Nafion/**2** composite (3/1, ◍; nonaq.).

conductivity of the **1/2** composite with the weight ratio of 3, only **1**, the Nafion/**2** composite with the weight ratio of 3, and the Nafion membrane only, under aqueous or nonaqueous conditions. The proton-conductivity of the **1/2** composite containing 0.5 wt% water increases with temperature. The proton-conductivity showed about 2 orders of magnitude higher than that of only **1**, because **2** acts as a good polar polymer matrix for the proton dissociation of **1**, instead of water. Furthermore, the composites show a high proton-conductivity compared with that of the membranes of Nafion or the Nafion/**2** composite under nonaqueous conditions. This is due to the high proton density of **1** compared with Nafion and the homogenous structure of the **1/2** composite. The proton-conductivity of the composite at low temperatures (below 0 °C) drops severely to 3.4 x 10^{-7} S·cm^{-1}, suggesting that the micro Brownian motion would be suppressed below the T$_g$ (10 °C) of the composite.

Under aqueous conditions (H_2O ≧ 10 wt%), the proton-conductivity of the composite increases with the increasing amount of water content due to the increased density of the hydronium ions. The composite shows a high proton-conductivity of over 3.5 x 10^{-2} S·cm^{-1} in the temperature range from 30 °C to 100 °C, however, over 110 °C, it decreases as low as that of the nonaqueous composite due to the vaporization of the water.[10]

In conclusion, we have found that the filter containing the gel-like composite of perfluorooctanesulfonic acid and poly(propylene carbonate) shows a high proton-conductivity of 1.9 x 10^{-5} S·cm^{-1} at 30 °C under nonaqueous conditions. Moreover, the composite has a good thermal stability up to 150 °C. These results suggest that the composite filter is potentially useful as a solid electrolyte with excellent proton-conduction, especially in high temperatures.

E. T. is a CREST Investigator, Japan Science and Technology Corporation (JST). K. M. acknowledges the receipt of JSPS Postdoctoral Fellowships for Research Abroad.

References and Notes

Present address; Department of Polymer Chemistry, McGill University, Montreal, PQ, H3A2K6, Canada

1 J. Jensen and M. Kleitz, "Solid State Protonic Conductors for Fuel Cells and Sensors," Odense University Press, Odense (1982).

2 A. J. Appleby and F. R. Foulkes, "Fuel Cell Handbook," Van Nostrand Reinhold, New York (1989).

3 A. Lasker and S. Chandra, "Superionic Solid Electrolyte,"Academic Press, Boston (1990).

4 K. D. Kreuer, *Chem. Mater.,* **8**, 610 (1996).

5 S. Malhotra and R. Datta, *J. Electrochem. Soc.,* **144**, L23 (1997).

6 B. Gupta, F. N. Buchi, and S. S. Scherer, *Solid State Ionics,* **61**, 213 (1993).

7 A. Eisenberg and H. L. Yeager, "Perfluorinated Ionomer Membranes," ACS Symposium Series 180, American Chemical Society, (1982).

8 P. Donoso, W. Gorecki, and C. Berthier, *Solid State Ionics,* **28-30**, 969 (1988).

9 P. N. Gupta and K. P. Singh, *Solid State Ionics,* **86-88**, 319 (1996).

10 K. Miyatake, K. Fukushima, S. Takeoka, and E. Tsuchida, *Chem. Mater.,* **11**, 1171 (1999).