Synthesis and Evaluation of Fullerene Derivatives for Proton Conducting Materials

Ken Akizuki, Yuko Takeoka, Masahiro Rikukawa
Kohei Sanui
Department of Chemistry, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

Acid-base polymer electrolytes have already been studied as candidates for high temperature polymer electrolyte membrane (PEM) fuel cells.[1] The use of these PEM systems improves the energy efficiency of fuel cells, minimizes CO poisoning of Pt catalyst, and lowering the size of the humidifier.[2] The released acid from these membranes and its corrosion to fuel cells systems still remains as major problems. For this reason, alternative electrolyte materials that show high proton conductivity without additional humidification are required. In this study, we synthesized fullerene derivatives bearing acidic groups to provide novel proton conducting materials. The preparation of complexes from the fullerene derivatives and polymer electrolytes that have phosphoric acid groups (CEP) was also attempted, and their proton conductivity and thermal properties of the fullerene derivatives and the resulting complexes were investigated.

Experimental

Fullerene derivatives which have hydroxyl groups (Fullerenol), sulfonic acid groups (HSF), and butylsulfonated groups (BS-PHF) were synthesized.[3] CEP/Fullerene derivative complexes were fabricated by mixing *N,N'*-dimethylacetamide solutions of CEP and fullerene derivatives. Fullerene derivatives were characterized by FT-IR, TOF-MS, and elemental analysis. Thermal properties were evaluated by thermogravimetric analysis. The proton conductivity of the fullerene derivatives and the resulting complexes under anhydrous condition was measured by the complex impedance method.

Results and discussion

FT-IR spectra of Fullerenol, HSF, and BS-PHF are shown in Figure 1. Two new absorption bands assigned to O-SO_3H stretching were observed in the spectrum of HSF. The absorption bands attributed to C-H streching of methylene units and S=O streching also apperared in the BS-PHF spectrum. From these results, the sulfonation and the butylsulfonation of Fullerenol were identified. The results of TOF-MS and elemental analysis suggested that the number of the substituents of fullerene derivatives is almost 12.

Thermal stability of the fullerene derivatives was investigated by TG-DTA. The thermal decomposition temperature of each fullerene derivative was about 150 ºC. This decomposition is due to the detachment of the substituents from fullerene backbones, as determined by FT-IR measurement.

The water uptake of the fullerene derivatives was estimated by measuring the change in the mass before and after hydration. The equilibrium water uptake of the fullerene derivatives increased with increasing the relative humidity. The water uptakes of Fullerenol, HSF, and BS-PHF hydrated under 100 % R.H. were 44 wt.%, 480 wt.%, and 600 wt.%., respectively. In addition, the water uptake of a CEP/HSF membrane was higher than that of a CEP membrane. The results of water uptake suggest that fullerene derivatives with acidic groups, especially sulfonic acid groups, absorb water and strongly maintain water molecules in the membranes.

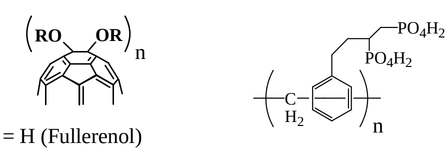
Arrhenius plots of conductivity for CEP and CEP/Fullerenol (0.5~5 wt.%) membranes under anhydrous condition are shown in Figure 2. The proton conductivity of a CEP/Fullerenol (5 wt.%) membrane achieved 5.3 × 10^{-5} S cm^{-1} at 120 ºC, which is 10 times higher than that of a CEP membrane. The proton conductivity of a CEP/HSF (0.5 wt.%) membrane was also higher than that of a CEP membrane. These results indicate that the proton conductivity of the resulting complexes depend on the contents of fullerene derivatives and the acidity of substituents bonded to fullerene backbones. This method with fullerene derivatives can improve the proton conductivity and the maintenance of water molecules for acid-base polymer complex electrolytes.

Acknowledgement

The authors wish to thank Uni-chemical Co. for supplying CEP.

Reference

[1] Y. L. Ma, J. S. Wainright, M. H. Litt, and R. F. Savinell, J. *Electrochem. Soc.*, 151, A8 (2004)
[2] M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, 25, 3 (2000)
[3] L. Y. Chiang, L. Y. Wang, J. W. Swirczewski, S. Soled, and S. Cameron, *J. Org. Chem.*, 59, 3960 (1994)



R = H (Fullerenol)
SO_3H (HSF)
$C_4H_8SO_3H$ (BS-PHF)

Fullerene derivatives **CEP**

Scheme Chemical structure of Fullerene derivatives and CEP.

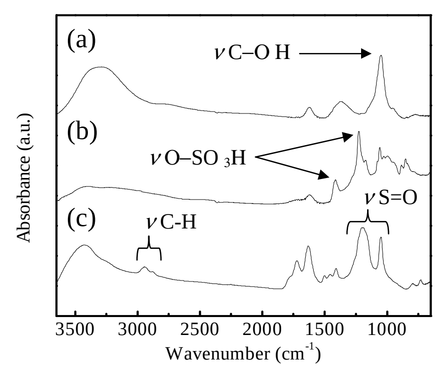


Figure 1 FT-IR spectra of (a) Fullerenol, (b) HSF, and (c) BS-PHF.

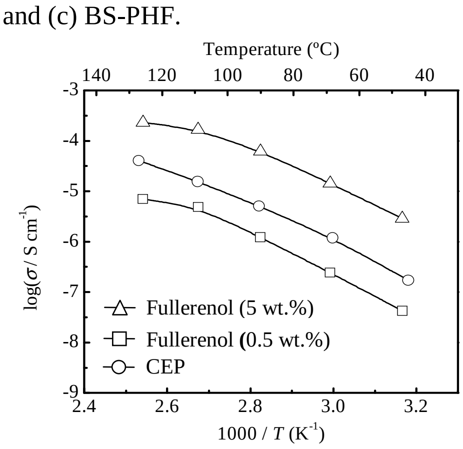


Figure 2 Arrhenius plots of conductivity for CEP/Fullerenol (0.5 ~ 5 wt.%) membranes under anhydrous condition.