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Electrical Properties of Fluorinated Gel Electrolyte and Its Application to Lithium Ion Secondary Battery

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The demand for secondary batteries has grown rapidly with the increase in the market for portable electronic devices such as computers and telephones etc. These secondary batteries require both high power and high energy density. Recently, lithium ion secondary batteries are strongly desired so that they have high voltage, high energy density, light weight and small size [1]. However, the liquid electrolytes using a secondary battery are limited to make the small size battery with high power and energy density. Then, the research of ion-conductive polymer materials which have many excellent features for secondary batteries has started from the 1980s. For example, a secondary battery of solid electrolyte are able to fabricate a thin film configuration with not only high energy efficiency and cycling efficiency but also thin separator to avoid lithium dendrites. Secondary batteries of solid electrolyte have excellent feature, but the ionic conductivity is smaller than the liquid electrolyte. The ionic conductivity of the polymer electrolytes is around 10^{-4} S/cm. It is necessary to obtain an ionic conductivity of more than 10^{-3} S/cm for a working current density of 5 mA/cm^2. Therefore, we focused on gel materials with expected the high ionic conductivity [2-4].

Fluorinated polymeric materials exhibit numerous excellent properties which cannot be achieved by the corresponding non-fluorinated materials. In general, the fluorinated polymeric materials are very poorly soluble in various solvents. It is interesting to search for highly soluble fluorinated polymeric materials with excellent properties imparted by fluorine. Sawada's group have recently reported that a series of fluoroalkylated end-capped silicon co-oligomers containing carboxy groups are highly soluble in various solvents, and are effective in reducing the surface tension of these solvents. These fluoro-silicone co-oligomers were also found to be potent and selective inhibitors against HIV-1 (human immunodeficiency virus type1) replication *in vitro*.

Our group also synthesized the new fluoro-alkylated end-capped oligomers containing both cationic and anionic segments by using fluoro-alkanoyl peroxides. In this development process of fluoroalkylated end-capped oligomeric materials, we discovered that novel fluoroalkylated end-capped 2-acrylamid-2-methylpropanesulfonic acid oligomers could lead to gelation not only in water but also in polar organic solvents under non-crosslinking conditions. Then, we tried to apply the electrolyte of secondary batteries using this fluorinated gelling materials [5,6]. In this paper, we report the gel formation and the electrical properties on gel electrolytes of these fluoroalkylated end-capped oligomers.

Experimental

The reaction of fluoroalkanoyl peroxides with 2-acrylamid-2-methyl-propanesulfonic acid (AMPS) were carried out in heterogeneous solvent systems [AK-225 (mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3- pentafluoropropane and water] by stirring vigorously at 40 °C for 5 h under nitrogen gas. The process of synthesis is outlined in Fig. 1.

AMPS was found to react with fluoralkanoyl peroxides under mild conditions to afford fluoro-alkanoyl end-capped AMPS homoorigomers [R$_F$-(AMPS)$_n$-R$_F$ in 35~58 % isolated yield.

NMR spectra were measured using a Varian Unity-plus 500 (500 MHz) spectrometer. IR spectra and absorption spectra were recorded on a HORIBA FT-300 FT-IR spectrophotometer and a Shimazu UV-240 s pectrophotometer, respectively. Viscosity of solution was measured by using a falling-sphere Haake Viscometer D1-G.
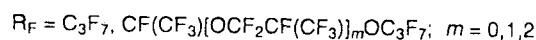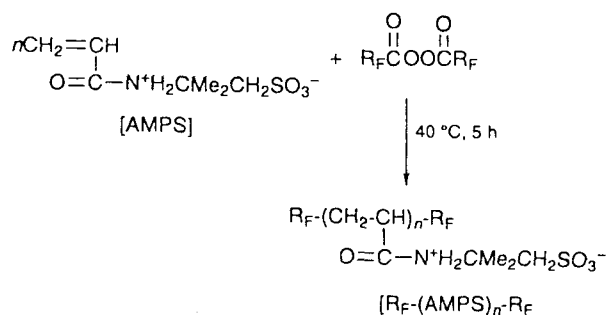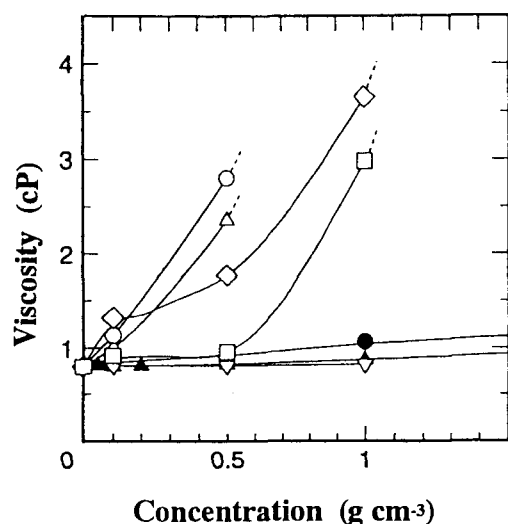

Fig.1 Outline of the synthesis process of the AMPS.

LiPF$_4$, LiBF$_6$, LiCF$_3$SO$_3$ and LiN(CF$_3$SO$_2$)$_2$ were used for lithium salts. Ionic conductivity of the fluorinated gel materials were evaluated by an alternating current measurement method (complex impedance analysis) using Cole-Cole plots under argon gas. The lithium ion secondary batteries have a structure such as a carbon material (negative electrode) / fluorinated gel electrolyte with lithium salt / LiCoO$_2$ (positive electrode). The charge and discharge characteristics of a secondary battery were measured by a standard technique.

Results and Discussion

Viscosities of -(AMPS)$_n$-, C$_3$F$_7$-(AETM)$_n$-C$_3$F$_7$ and perfluoropropylated oligomer containing sulfo segments [C$_3$F$_7$-(MES)$_n$-C$_3$F$_7$] increased little with increasing concentrations as shown in Fig.2, and the gel did not form, although these fluoroalkylated oligomers were shown to form molecular aggregates like micelles in aqueous solution. On the other hand, the viscosity of fluoroalkylated end-capped AMPS oligomers increased greatly with increasing concentration, and it became impossible to measure their viscosity owing to the gelation at concentrations above 0.5 or 1.0 g dm^{-3}.

The striking characteristic of AMPS oligomers is their gelation both in water and in organic polar

Fig.3 Schematic illustration for gelation of R$_F$-(AMPS)$_n$-R$_F$.

R$_F$-(AMPS)$_n$-R$_F$
O : R$_F$ = C$_3$F$_7$
△ : R$_F$ = CF(CF$_3$)OC$_3$F$_7$
□ : R$_F$ = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$
◇ : R$_F$ = CF(CF$_3$)OCF$_2$CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$
▽ : -(AMPS)$_n$- :

● : C$_3$F$_7$ -(CH$_2$CH)$_n$ -C$_3$F$_7$
　　　O=COCH$_2$CH$_2$NMe$_3$Cl$^-$
▲ : C$_3$F$_7$ -(CH$_2$CMe)$_n$ -C$_3$F$_7$
　　　O=COCH$_2$CH$_2$SO$_3$H

Fig.2 Effect of concentration on viscosity of fluoroalkylated end-copped oligomers measured at 30 °C by using a falling-sphere viscometer.
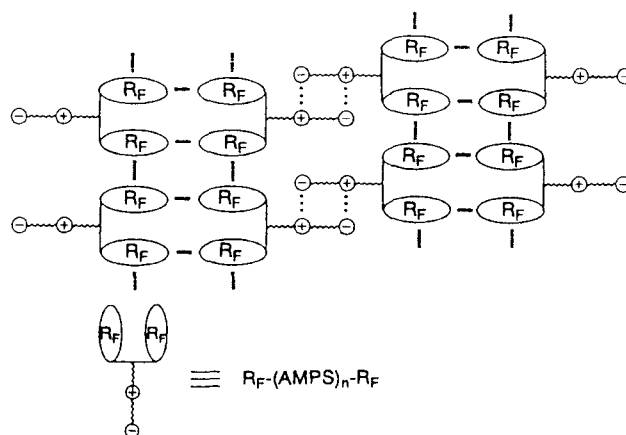
solvents under non-crosslinking conditions. This is because fluoroalkyl segments are solvophobic and aggregate in aqueous and organic media. Therefore, AMPS oligomers can form gels in both water and organic media due to the synergistics interaction between the aggregations of fluoroalkyl units, and the ionic interaction of the amide cations and the sulfonate anions as shown in Fig.3.

Gelation abilities of some fluoroalkylated end-capped AMPS oligomers were also determined by measuring the minimum concentrations of these oligomers necessary for gelation according to the method reported of Hanabusa et al [7]. The mini-mum concentrations for gelation (C$_{min.}$) in water and dimethyl sulfoxide (DMSO) at 30 °C are listed in Table 1.

Figure 4 shows the dependence of ionic conductivities on the difference of a molecule chains (R$_F$) of fluoroalkylated lithium ion gel electrolytes by using AC measurement under argon gas. The highest conductivity was the lithium ion gel having molecule chain of C$_3$F$_7$ among four kinds of R$_F$ molecules which are listed in Table 1. It was cleared that lithium ions can smoothly move in the short molecule chain such as C$_3$F$_7$ rather than the long molecule chain of R$_F$. This is considered that the carrier density in electrolytes decreased by a trap effect with increasing the molecule chain of R$_F$. But the detail mechanism on the ionic transport is not clear.

Table 1 Minimum concentration for gelation ($C_{min.}$) of fluoroalkylated AMPS oligomers in DMSO solvent (g dm^{-3}) at 30 °C.

fluoroalkylated AMPS oligomers [R_F-(AMPS)$_n$-R_F]	$C_{min.}$/g dm^{-3} (gelator / DMSO)
R_F = C_3F_7	182
R_F = C_3F_7 OC(CF_3)F	158
R_F = C_3F_7 OC(CF_3)FCF_2OC (CF_3)F	128
R_F = C_3F_7 OC(CF_3)FCF_2OC (CF_3)F CF_2OC (CF_3)F	321

Since the most high ionic conductivity was obtained in the case of gel electrolyte with the molecule chain of C_3F_7, we measured a conductive dependence due to the difference of a lithium salt under the same condition utilizing fluoroalkylated gel of C_3F_7. The maximum value of an ionic conductivity was obtained by using the lithium salt of $LiN(CF_3SO_2)_2$ as shown in Fig.5. However, the conductivity varied between 8.5 x 10^{-4} and 3 x 10^{-3} S/cm, there was not large difference of conductivity among these lithium salts.
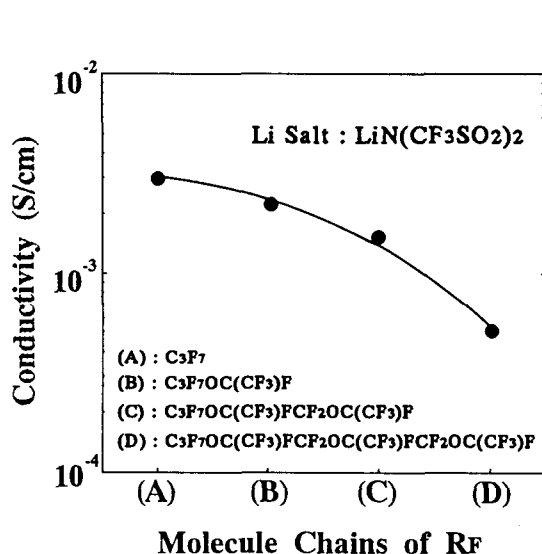

Fig.4 Dependence of ionic conductivities on the difference molecule chains (R_F) of fluoro-alkylated gel electrolytes.
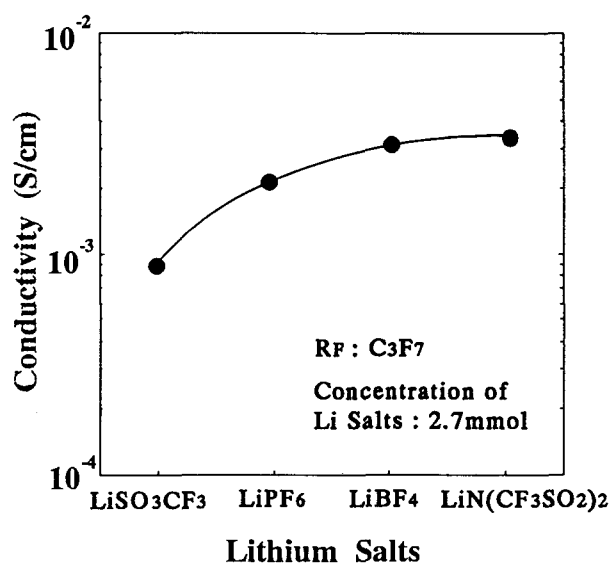
Fig.5 Dependence of ionic conductivities on the difference lithium salts of fluoroalkylated gel electrolytes.

For the next step, to get a more high ionic conductivity, we also measured the dependence of conductivities on the concentration of lithium salts with $LiN(CF_3SO_2)_2$ utilizing fluoroalkylated gel of C_3F_7. Figure 6 shows the dependence of ionic conductivities on the concentration of lithium salt with $LiN(CF_3SO_2)_2$. The conductivity increased with increasing the concentration of $LiN(CF_3-SO_2)_2$, and had a tendency to saturate at a concentration greater than 2.7 mmol/g. As this fluoroalkylated gel materials are difficult to dissolve the lithium salts more than 15 mmol/g, it is considered that a large conductivity could not be obtained by changing concentration of a lithium salt. The maximum conductivity was 4.5 x 10^{-3} S/cm in this study.

We tried to fabricate the secondary batteries by using this fluoroalkylated lithium ion gel electro-lytes. The structure of batteries is a negative electrode of carbon material, gel electrolyte with $LiN(CF_3SO_2)_2$ and a positive electrode of $LiCoO_2$. Figure 7 shows the discharge characteristics of a fabricated battery. The open voltage of this battery was only 1.8 V. It is small not only open voltage but also energy density compare with a Li ion secondary battery utilizing liquid electrolytes. These results should be originated from the low ionic conductivity and the poor concentration of lithium salts in the fluoroalkylated gel electrolytes.

Furthermore, we are improving for both the fluoroalkylated lithium gel electrolytes and the electrode materials to obtain the desired Li ion secondary battery.
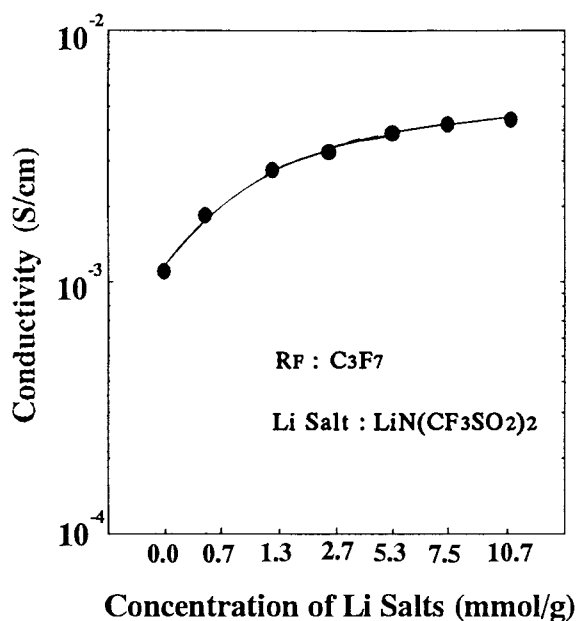

Fig.6 Dependence of ionic conductivities on the concentration of fluoroalkylated gel electrolytes with $LiN(CF_3SO_2)_2$.
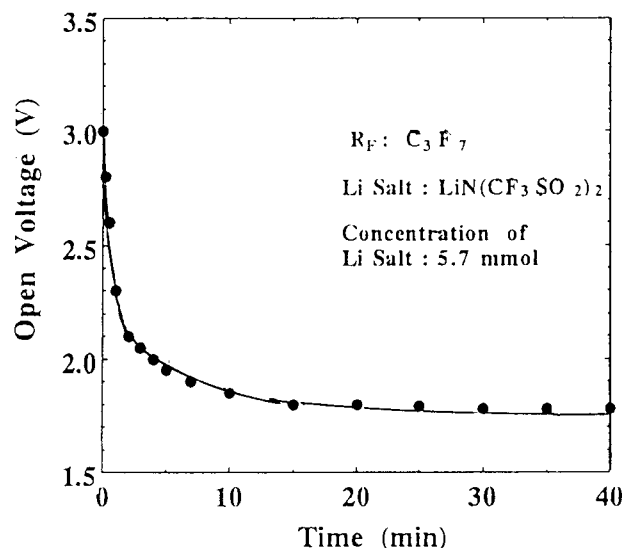
Fig.7 Discharge characteristics of the open voltage on a fabricated battery.

Summary

The results of present experimental study are summarized as follows.

1) Fluoroalkylated end-capped AMPS oligomers confirmed to be gelation both in water and in organic polar solvents under non-crosslinking conditions.

2) These fluoroalkylated gel materials can be easily produced a lithium ion gel electrolytes by using lithium salts.

3) Ionic conductivities depended on the R_F molecular chains of fluoroalkylated gel electrolytes, and the largest conductivity was the lithium ion gel having molecule chain of C_3F_7 among four kinds of R_F chains.

4) The conductivity due to the difference of lithium salts utilizing fluoroalkylated gel of C_3F_7 varied only between 8.5×10^{-4} and 3×10^{-3} S/cm, and there was not large difference.

5) Ionic conductivities also increased with increase-
ing the concentration of $LiN(CF_3SO_2)_2$, and had a tendency to saturate at a concentration greater than 2.7 mmol/g.

6) The highest conductivity was 4.5×10^{-3} S/cm under the R_F chain length of C_3F_7, the lithium salt using $LiN(CF_3SO_2)_2$ and concentration of 10.7 mmol/g, respectively.

7) Open voltage of fabricated battery was 1.8 V, and small value compare with a Li ion secondary battery utilizing liquid electrolytes.

References

1] Y. Nishi: OYOBUTURI, 57, 576 (1998)

2] T. Nagatomo, H. Kakehata, C. Ichikawa and O. Omoto: Jpn. J. Appl. Phys., 24, L397 (1985).

3] T. Kabata, O. Kimura, S. Yoneyama and T. Osawa: Prog. Bat.& Solar Cels., 8, 191 (1989).

4] S. Takeoka, H. Ohno and E. Tsuchida: Polym. Adv. Technol., 4, 53 (1992).

5] H. Sawada, M. Itho, K. Lie, J. Kyokane, T. Kawase and K. Yoshino: J. Jpn. Oil Chem. Soc., 47, 685 (1998).

6] H. Sawada, S. Katayama, Y. Ariyoshi, T.Tomita and M. Baba: J. Mater. Chem., 8, 1517 (1998).

7] K. Hanabusa, Y. Naka, T. Koyama and H.. Shirai: J. Chem. Soc., 104, 5547 (1987)