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Citation	電気材料技術雑誌. 2001, 10(2), p. 165-167
Version Type	VoR
URL	https://hdl.handle.net/11094/81689
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Electrical Properties of Fluorinated Gel Electrolytes using High Conducting Solution

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Introduction

The secondary batteries have 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 power energy, light and small size [1].

However, the liquid electrolytes using a secondary battery are limited to make a battery of small size with high power energy density. Then, the research of ionic conducting polymer materials having many excellent features for secondary batteries has started from the 1980s. For example, a secondary battery using solid electrolyte are able to fabricate a thin film configuration with not only high energy efficiency and cycling efficiency but also without thin separator to avoid lithium dendrites. Secondary batteries of solid electrolyte have an 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/cm². Therefore, we focused on gel materials with expected the high ionic conductivity [2-4].

Since the novel fluoroalkylated end-capped 2-acrylamid-2-methylpropanesulfonic acid (AMPS) oligomers cleared to take place gelation not only in water but also in polar organic solvents under non-crosslinking conditions, we tried to apply the electrolyte of secondary batteries using these materials [5,6]. The conductivity of gel electrolytes strongly depended on the ionic solution. Then, in order to obtain the large ionic conductivity more than 10^{-2} S/cm, we produced the gel electrolytes using the novel ionic solution such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

In this report it is discussed about the electrical properties of the lithium ionic electrolytes, and also is measured the characteristics of the secondary batteries that were fabricated by a constitution of carbon negative electrode, fluorinated gel electrolytes using the ionic solution and positive electrode of LiCoO₂.

Experimental

Non-crosslinked fluorinated gel materials were prepared by reacting fluoroalkanoyl peroxides with 2-acrylamid-2-methylpropanesulfonic acid (AMPS) oligomer containing fluoroalkylated end-capped units $\{[-Rf-(AMPS)_q]_p\}$, and also were prepared 2-glucosyloxyethyl methacrylate (GEMA) and 3-acrylopropyl phosphoric acid (APPA) under same condition. Several kinds of lithium salts [LiPF₄, LiBF₆, LiCF₃SO₃, and LiN(CF₃SO₂)₂] were utilized for ionic materials of these fluorinated gel electrolytes.

Ionic conductivity of the fluorinated gel materials were evaluated by a 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 / LiCoO₂ (positive electrode). The charge and discharge characteristics of a secondary battery were measured by a standard technique.

Results and Discussion

The molecular structure of AMPS and GEMA oligomers are as shown in Fig.1. These oligomers are their gelation both in water and in organic polar solvents under non-crosslinking conditions. This is because fluoroalkyl segments are solvophobic and aggregate in aqueous and organic media. For example, 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.1.

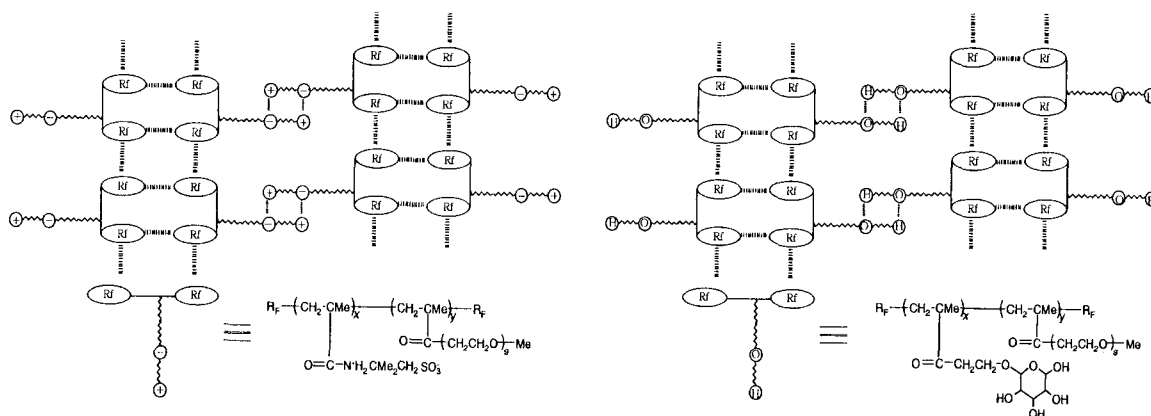


Fig.1 The molecular structures of AMPS and GEMA oligomer, and schematic illustration for gelation of RF-(AMPS)_n-RF and RF-(GEMA)_n-RF.

Figure 2 shows the dependence of ionic conductivity on the difference of lithium salts about AMPS oligomer and GEMA oligomer. The highest conductivity was the gel electrolytes having the LiN(CF₃SO₂)₂ among four kinds of lithium salts. The ionic conductivity of fluoroalkylated gel using GEMA oligomer was large rather than AMPS oligomer. It was cleared that lithium ions can smoothly move in the molecule chain such as GEMA oligomer.

As the high ionic conductivity was obtained in the case of gel electrolyte with the GEMA oligomer, we measured a conductive dependence due to the difference of concentration of LiN(CF₃SO₂)₂ salt under the same condition. The conductivity increased with increasing the concentration of LiN(CF₃SO₂)₂ salt, and saturated more than 2.7 mmol/g as shown in Fig.3. In this case the maximum value of conductivity was obtained by utilizing LiN(CF₃SO₂)₂ salt and GEMA oligomer. The maximum ionic conductivity was 4.5×10^{-3} S/cm.

For the next step, to obtain a more high ionic conductivity, we synthesised the novel GEMA oligomer contained vinyl phosphoric acid (VPA). Figure 4 shows the ionic conductivity of GEMA oligomer contained VPA on the different kinds of lithium salt. This gel electrolyte also had very high conductivity for LiN(CF₃SO₂)₂ salt compare

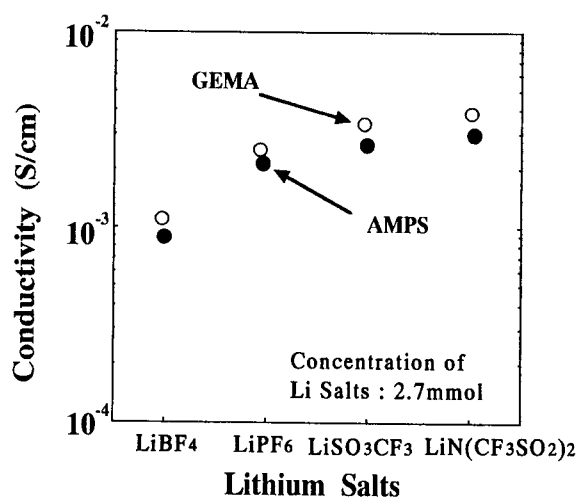


Fig.2 Dependence of ionic conductivity on the difference of lithium salts about AMPS oligomer and GEMA oligomer.

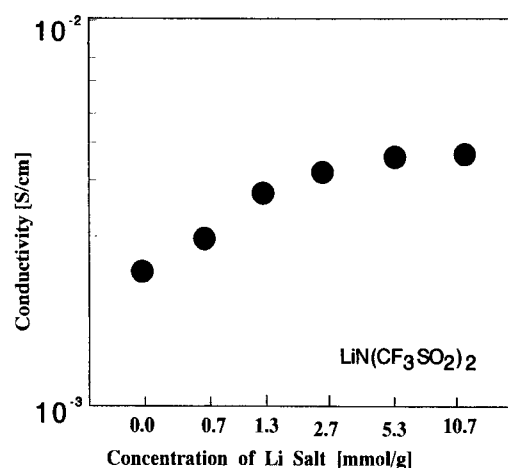


Fig.3 Dependence of ionic conductivity on the concentration of LiN(CF₃SO₂)₂ salt.

with another lithium salt. The highest conductivity of 7×10^{-3} S/cm could be obtained in this gel material. It is considered that the high conductivity is affected by phosphoric acid introduced into GEMA oligomer. Because of the phosphoric acid change a cation in the GEMA molecule chain, the positive lithium ion can smoothly move with hopping transport by repulsion based on the cation of phosphoric acid.

Then, in order to obtain the large ionic conductivity more than 10^{-3} S/cm, we are synthesizing the gel electrolytes using an ionic solution such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

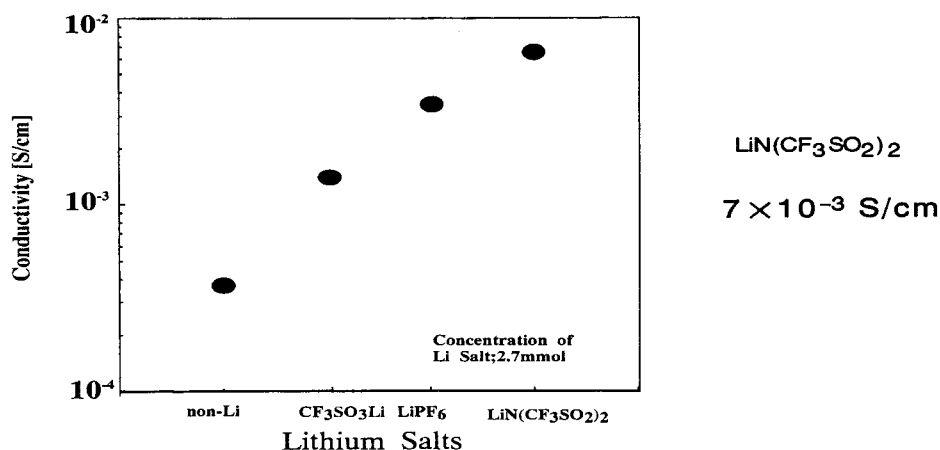


Fig.4 Ionic conductivity of GEMA oligomer contained vinyl phosphoric acid (VPA) on the different kinds of lithium salt.

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