Characteristics of gel alkylene oxide polymer electrolytes containing γ-butyrolactone

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Abstract

Gel polymer electrolytes consisted of poly(alkylene oxide) (PAO), $LiBF_4$ or $LiClO_4$, and aprotic solvents (γ-butyrolactone (GBL) and/or ethylene carbonate (EC)) were prepared and the conductivity was measured. The conductivity was very high and similar to that of the organic liquid electrolytes. The performance of Li | gel polymer electrolyte | $LiCoO_2$ cell was measured and compared to that of the cell with the liquid electrolyte corresponded. The cell with the gel electrolyte showed a decrease of capacity at high-rate discharge and low temperature owing to concentration polarization.
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1. Introduction

The ionic conductance of solid polymer electrolytes represented first by Wright et al. in 1973 [1]. Then Armand et al. suggested that the complexes of poly(ethylene oxide) (PEO) and alkali isothiocyanates could be used as solid electrolytes in light weight rechargeable batteries in 1979 [2]. However, the concentration of lithium salts in the solid electrolytes was not high and the highest conductivity was obtained at rather low concentration ratio of [Li]:[O in PEO], 1:20, because the conductivity connects with the segment motion of base polymers [3]. For the purpose of development of advanced rechargeable batteries, gel polymer electrolytes consisted of plasticizers and lithium salts have been studied. Rechargeable lithium batteries with gel polymer electrolyte have been expected in view of no liquid leak, prevention of dendrite formation, flexibility, etc. In these works base polymers were PEO [4,5], PEO-poly(methyl-methacrylate) [6,7], poly(vinylidene fluoride) [8,9], poly(urethane) [10], poly(acrylonitrile) [11,12], poly(N-vinylpyrrolidone) [13], etc. In a same view, inorganic solid plasticizers were reported as the effective additives for solid polymer electrolytes [14,15].

Poly(alkylene oxide) (PAO) which is a cross-linked random copolymer of ethylene oxide (EO) and propylene oxide (PO) showed excellent mechanical structure and retainment of a large amount of liquid electrolyte [16–19]. The conductivity of the gel alkylene oxide polymer was very high, but the performance of rechargeable lithium batteries has not been reported.

In this work, the conductivity of gel PAO electrolytes was measured for a wide temperature range and the performance of Li | gel PAO electrolyte | $LiCoO_2$ cell was investigated in comparison to a cell with organic electrolyte at the corresponding low and ambient temperatures. Then gel polymer electrolytes were prepared from macromonomer of alkylene oxide, lithium salts, $LiClO_4$ or $LiBF_4$, and γ-butyrolactone (GBL) or ethylene carbonate (EC)-GBL. The ionic conductance of the gel polymer electrolytes was investigated precisely in wider ranges of temperature and mixing ratio of the materials than that reported in a previous paper [20]. The maximum retention of liquid in the gel polymer electrolytes was ca. 94 wt.% in stable state rechargeable lithium test cells assembled with the gel polymer electrolyte and their performance was estimated at different temperatures. At lower temperature, $-20\,°C$, the capacity of the cell with the gel electrolyte decreased more than that of the cell with the organic electrolyte solution corresponded. However the relations between the composition of the gel electrodes

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and the performance of Li | gel PAO electrolyte | LiCoO$_2$ cells were investigated at −20 and 20 °C.

2. Experimental

The chemical structure of macromonomer of alkylene oxide studied in this report was a random copolymer of ethylene oxide/propylene oxide (80:20 by weight) having trifunctional cross-linkable acrylic groups at the macromonomer chain ends. It was a commercial product by Dai-ichi Kogyo Seiyaku. The average molecular weight was 8000 and it was the best for mechanical properties of gel poly-(alkylene oxide) electrolytes. GBL and EC were solvents for lithium batteries by Ube Industry and lithium salts, LiClO$_4$ and LiBF$_4$, were products by Morita.

Gel polymer electrolytes were prepared as follows. At first lithium salt, LiClO$_4$ or LiBF$_4$, dissolved completely in GBL or EC-GBL. The macromonomer was dissolved in the solvent containing lithium salt, then a small amount of the initiator, bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, was added into the solution. The homogeneous solution resulting from mixing the above solution was admitted into a space between two glass plates sandwiching with a silicon rubber frame. The thickness of the silicon rubber frame was 0.5 mm. Then the solution was polymerized by heating at 50 °C for 24 h.

For conductivity measurements, a sandwich type screw cell with stainless steel electrodes was used. The gel polymer electrolytes which were prepared with above procedure were cut to 10 mm diameter disk and were set in the cell. Then silicon rubber spacer (0.5 mm thickness) was sandwiched between two electrodes for keeping the form of the gel polymer electrolyte. The conductivity was measured using ac method (10 kHz, 10 mVp-p) in the temperature range between −10 and 60 °C.

For the measurement of charge–discharge performance, a beaker type cell (diameter 2.5 cm, height; 3.0 cm) was used. A negative electrode was lithium foil (apparent surface area: 1.5 cm^2) and a positive electrode was LiCoO$_2$ (LiCoO$_2$ 35 mg + binder 1 mg + carbon 1 mg, apparent surface: 0.25 cm^2) coated on an aluminum current collector. The gel polymer electrolytes were prepared in the cell by heat treatment of the mixed solution of the macromonomer; LiBF$_4$, EC-GBL (3:7 (v/v)), and a small amount of an initiator. The initiator was bis(4-*tert*-buthylcyclohexyl) peroxydicarbonate. The cell performance was usually estimated at the first cycle. The current collector of the negative electrode was a nickel mesh. The charge–discharge test was controlled by a charge–discharge system, Toyo-System TYS-31TU01. All measurements were performed under argon atmosphere.

3. Results and discussion

The proper mechanical stability of the gel polymer electrolyte was observed in the range of mole ratio of [GBL]:[O

in polymer] between 8.3:1 and 8.3:45. In the case of low concentration of PAO in the gel electrolytes below 6 wt.% the mechanical strength was too weak to restrain large amounts of liquid electrolyte. In Fig. 1 the conductivity increased with increase of GBL content in the gel polymer electrolytes. For the gel polymer electrolytes in which PAO content was higher than 8.3:10 of the mole ratio of [GBL]:[O in polymer], the curves in the figure were convex. These phenomena followed the Vogel–Tamman–Fulcher (V–T–F) relation. Therefore the ionic conductance of the gel polymer electrolytes containing PAO in high content connects significantly to the segment motion of the polymer chains. The relation between the reciprocal of temperature and the logarithm of conductivity was almost linear for the gel polymer electrolytes whose PAO content was low, e.g. [GBL]:[O in polymer] was 8.3:1 and 8.3:2. The conductivity of these gel polymer electrolytes was similar to that of organic liquid electrolytes. These results suggested that the conductance would be connected mainly to the transfer of ions in the GBL phase. Therefore the contribution of V–T–F relation was weak for such gel polymer electrolytes. As mentioned above, for the limitation of the mechanical stability of the gel polymer electrolyte was 8.3:1 of the mole ratio of [GBL]:[O in polymer], the maximum retention of liquid electrolyte was ca. 94 wt.%. The gelled polymer electrolyte prepared in this work has a three-dimensional network structure such that it is difficult to obtain T_g within the temperature range due to the fact that cross-linked polymers may decompose before the transition temperature is reached. In general, chemically cross-linked PAO electrolyte without plasticizer does not show high conductivity of above 10^{-4} S/cm at 30 °C. Therefore the liquid electrolyte is the major contributor of the ionic conductivity regardless of the content. As the cross-linked PAO is mainly used as frame for the content of liquid electrolyte and mobility change of ionic species though those channels would be considerable reason for the result.
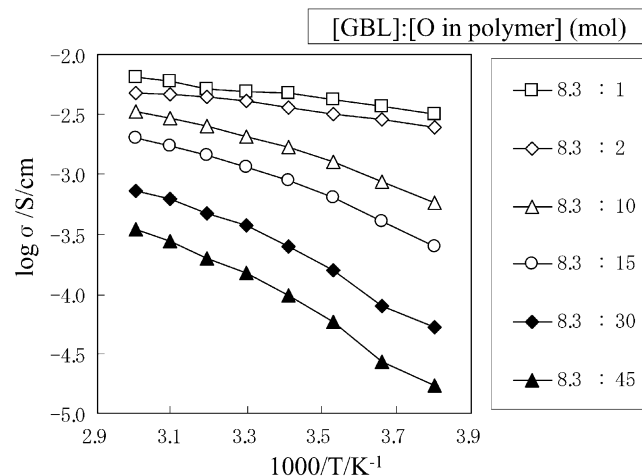

Fig. 1. Temperature dependence of ionic conductivity of LiClO$_4$/GBL gel polymer electrolyte ([LiCl$_4$]:[GBL] = 0.48:8.3 (mol/mol), −10 to 60 °C).
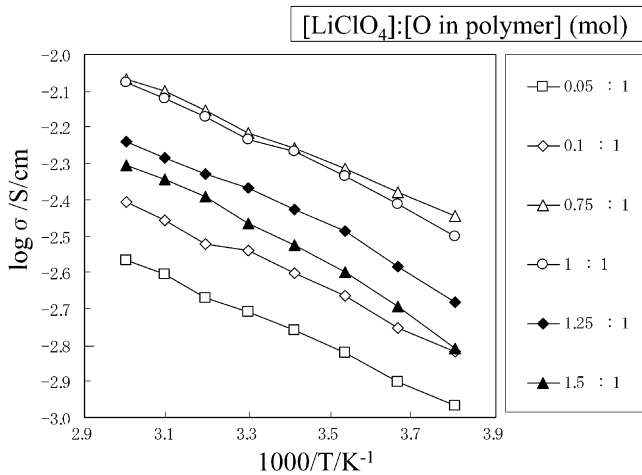
Fig. 2. Temperature dependence of ionic conductivity of LiClO$_4$/GBL gel polymer electrolyte ([GBL]:[O in polymer] = 8.3:1 (mol/mol), −10 to 60 °C).

The temperature dependence of ionic conductivity of the gel polymer electrolytes are shown in Fig. 2, where the amount of LiClO$_4$ in the gel electrolytes was changed for [O in polymer] step by step. The ionic conductivity increased with increase of LiClO$_4$ concentration in the gel electrolyte of which LiClO$_4$ concentration was low because the addition of LiClO$_4$ caused the increase of the concentration of ionic carriers. Contrarily in the gel electrolytes of which LiClO$_4$ concentration was high the conductivity decreased with increase of the concentration due to the ionic association and the increase of viscosity. Among the gel polymer electrolytes, the one whose mole ratio of [LiClO$_4$]:[GBL]:[O in polymer] was 0.75:8.3:1 showed the highest ionic conductivity which was similar to that of liquid electrolytes over 10^{-3} S/cm.

The ionic conductivity of the gel polymer electrolyte containing LiBF$_4$ instead of LiClO$_4$ was measured and
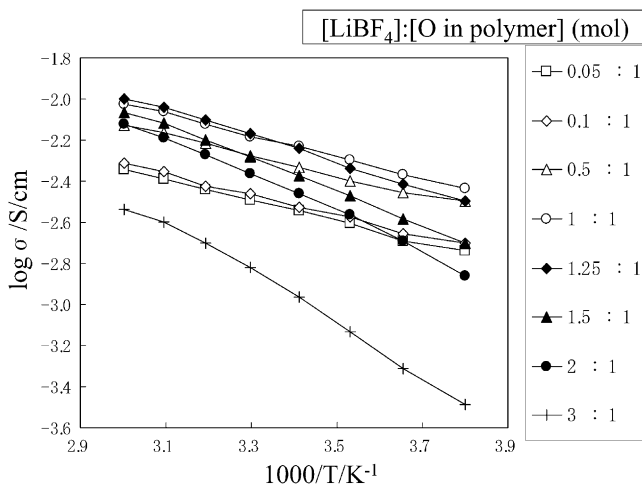

Fig. 3. Temperature dependence of ionic conductivity of LiBF$_4$/GBL gel polymer electrolyte ([GBL]:[O in polymer] = 8.3:1 (mol/mol), −10 to 60 °C).
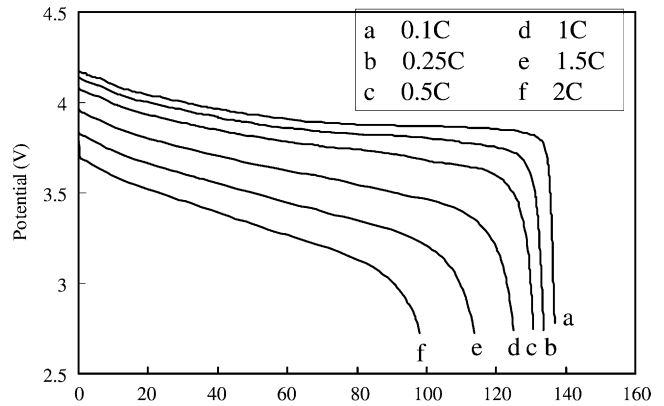

Fig. 4. Discharge profiles of Li | gel electrolyte | LiCoO$_2$ cell; liquid electrolyte: 2 M LiBF$_4$/EC-GBL (3:7 (v/v)); gel electrolyte contains 95 wt.% of liquid electrolyte; Cut off voltage 4.2–2.75 V at 20 °C.

the results are shown in Fig. 3. The mole ratio of [GBL]:[O in polymer] was a constant value of 8.3:1. The gel electrolyte whose mole ratio of [LiBF$_4$]:[GBL]:[O in polymer] was 1:8.3:1 showed the highest ionic conductivity. The conductivity of the gel electrolytes with LiBF$_4$ was a little higher than that of the gel electrolytes with LiClO$_4$. These phenomena would suggest that the ionic association was suppressed a little in the gel electrolytes with LiBF$_4$ compared to LiClO$_4$ or the affinity among solvated lithium ions, anion, EO and PO in the base polymer varied slightly.

The first discharge capacity of Li | gel PAO electrolyte | LiCoO$_2$ cell at different discharge rate at 20 °C is shown in Fig. 4. The gel electrolytes contained 95 wt.% liquid electrolyte and operating potential range was between 4.2 and 2.75 V. The theoretical capacity was estimated depending on the active material of the positive electrode, LiCoO$_2$ (273.8 mAh/g). The results show that the discharge terminated owing to the concentration polarization and the discharge capacity decreased with increase of discharge rate.

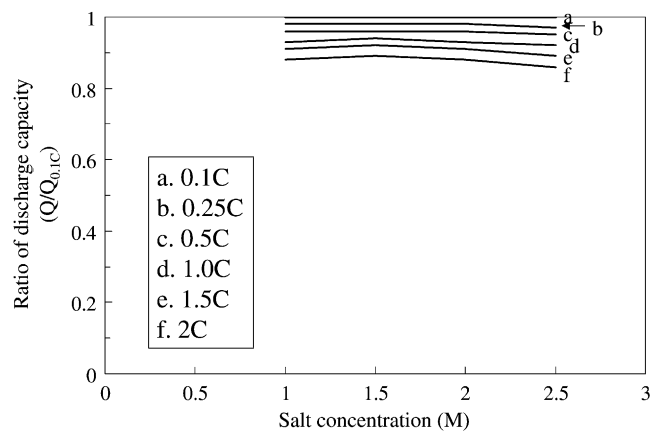Fig. 5 shows discharge performance of Li | gel PAO electrolyte | LiCoO$_2$ cell. The liquid electrolyte contained

Fig. 5. Discharge performance of Li | gel electrolyte | LiCoO$_2$ cell; liquid electrolyte: 2 M LiBF$_4$/EC-GBL (3:7 (v/v)); gel electrolyte contains 95 wt.% of liquid electrolyte; Cut off voltage 4.2–2.75 V at 20 °C.
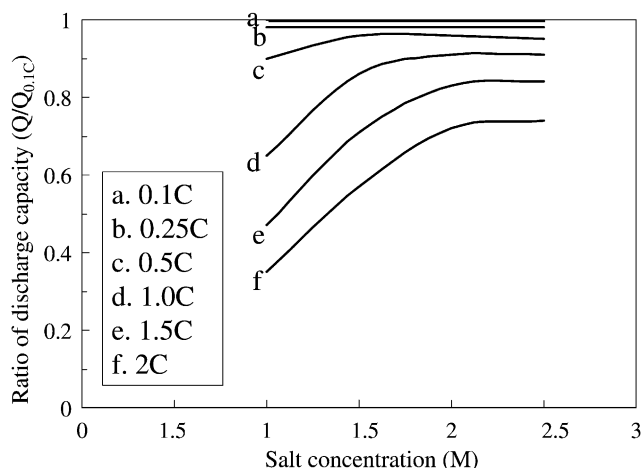
Fig. 6. Discharge performance of Li | x M LiBF$_4$/EC-GBL (3:7 (v/v)) | LiCoO$_2$ cell; Cut off voltage 4.2–2.75 V at 20 °C.

in the gel electrolyte was LiBF$_4$/EC-GBL. The discharge capacity ratio of the chosen rate to that at 0.1 C rate, changed depending on the lithium salt concentration of the liquid electrolyte. The ratios for the cells with the gel electrolyte containing the liquid electrolyte of lower salt concentration decreased on a large scale. Therefore the cell with the gel electrolyte whose content of LiBF$_4$ was rather low, e.g. 1 and 1.5 M, would cause large concentration polarization. On the contrary, the cells with the liquid electrolyte corresponding to that in the gel electrolyte showed different results as shown in Fig. 6. The capacity change was small for the change of discharge rate because the diffusion of the ions in the liquid electrolytes would be faster than that in the gel electrolytes.

In Fig. 7, the discharge capacity changes of the cells with the gel polymer electrolyte and corresponding liquid electrolyte at −20 °C are observed. For the cell with the gel electrolyte, the ratio of discharge capacity at 0.5 C to that at 0.1 C was much lower than that of the cell with the liquid electrolyte. The highest ratio of $Q_{0.5C}$ to $Q_{0.1C}$ for the cells
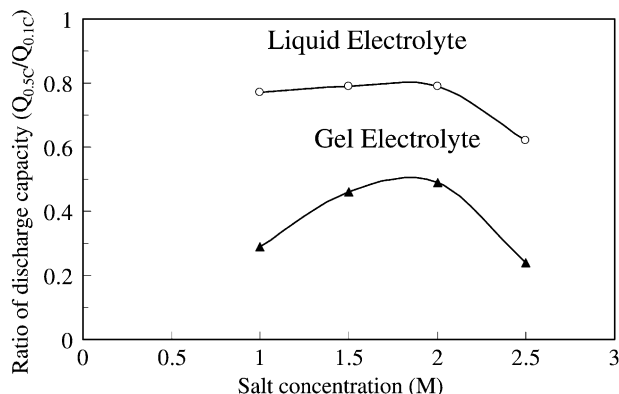
with the gel electrolytes appeared for the cell with the gel electrolyte with 2 M LiBF$_4$. In the cell with such a gel electrolyte with 2 M LiBF$_4$ the concentration polarization would decrease relatively due to high concentration of lithium salt in the gel electrolyte. The gel polymer electrolytes with rather highly concentrated lithium salt are suitable for the cell performance though these electrolytes do not show the best conductivity. The results suggest that proper concentration of lithium salt of the gel polymer electrolytes is different for the conductivity and the lithium cell performance.

4. Conclusions

Gel polymer electrolytes consisted of poly(alkylene oxide), GBL or EC-GBL, and LiBF$_4$ or LiClO$_4$ have been investigated. The gel polymer electrolytes showed excellent conductivity and retained ca. 94 wt.% of the liquid electrolyte. The gel electrolyte whose mole ratio of [LiBF$_4$]:[G-BL]:[O in polymer] was 1:8.3:1 showed the highest ionic conductivity like liquid organic electrolyte solutions.

Rechargeable lithium cells with gel poly(alkylene oxide) containing LiBF$_4$/EC-GBL were assembled and their performance was estimated at 20 and −20 °C. The cells with gel polymer electrolyte showed the decrease of discharge capacity at high-rate discharge and low temperature owing to the concentration polarization comparing to the cells with the liquid electrolyte corresponded. The proper concentration of the gel polymer electrolytes for the cell performance is higher than the best concentration for the highest conductivity.

Fig. 7. Discharge performance of Li | gel polymer electrolyte | LiCoO$_2$ cell at 20 and −20 °C; liquid electrolyte: x M LiBF$_4$/EC-GBL (3:7 (v/v)); gel electrolyte contains 95 wt.% of liquid electrolyte; Cut off voltage 4.2–2.75 V; discharge rate 0.1, 0.5 C.

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