Application of gel alkylene oxide electrolytes to rechargeable lithium batteries

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Abstract

Advanced gel polymer electrolytes of alkylene oxide system were prepared. The base polymer was random copolymer of alkylene oxide system (MW: 8000, ethylene oxide (EO): ca. 80%, propylene oxide (PO): ca. 20%, end functional group: acrylic group). The gel polymer electrolyte was prepared by mixing the base polymer, a solvent, a lithium salt and an initiator followed by UV irradiation. Ionic conductivity of gel polymer electrolyte was measured with ac method at temperature range between -20 and $+60°C$. The ionic conductivity reached over 2.5 mS cm^{-1} at 20°C when LiBF$_4$/γ-butyrolactone (GBL) solution was incorporated as an electrolyte. The discharge capacity with charge-discharge cycle of test cells, C$_n$-Li/LiCoO$_2$, with the gel polymer electrolyte was more stable during cycling than that with liquid organic electrolyte solution. It was affected by the kind of plasticizer in the gel electrolyte. The capacity of the test cell was limited by the weight of cathode active material (1.3 mAh). The highest discharge capacity was attained using C$_n$-Li/the base polymer–GBL–LiBF$_4$/LiCoO$_2$ and its utilization rate of the cathode material was 83%. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Rechargeable lithium batteries; Gel alkylene oxide; Electrolytes

1. Introduction

Gel polymer electrolytes have been investigated in connection with development of lithium ion plastic batteries [1–11]. Recently poly(acrylonitrile) (PAN) and poly(vinyldene fluoride) (PVdF) have been investigated mostly as the base networks of such gel polymer electrolytes [11–15]. However, poly(ethylene oxide) (PEO) based polymers such as poly(ethylene glycol)ethers have been reported as the additive in the electrolyte solution of rechargeable lithium metal batteries [16]. In the present work, advanced gel polymer electrolytes of alkylene oxide system were prepared, and its ionic conductivity as well as the application to rechargeable lithium batteries were investigated.

2. Experimental

The base polymer was a random copolymer of EO/PO ($= 80/20$ by weight) having trifunctional cross-linkable acrylic groups at the macromonomer chain end (average MW = 8000). Gel polymer electrolyte membranes are prepared by UV irradiation to the gel electrolyte precursors consisting of the macromonomer, various liquid electrolytes and photopolymerization initiator.

Ionic conductivity of the gel polymer electrolyte membranes was measured using a sandwich type cell with stainless steel electrodes by ac method in the temperature range from -20 to $+60°C$. On the measurement of conductivity, the frequency of 10 kHz and voltage amplitude of 50 mV were applied. Two sandwich type electrochemical cells with two electrodes were used. Cell A had a lithium negative electrode (apparent surface area: 0.785 cm^2) and a LiCoO$_2$ composite positive electrode (apparent surface area: 1.327 cm^2) consisting of LiCoO$_2$, carbon, and PVdF in 87:10:3 weight ratio. Cell B had two lithium electrodes (apparent surface area: 1.131 cm^2). LCR meter, Ando AG-4306, was used for measurement of the conduc-
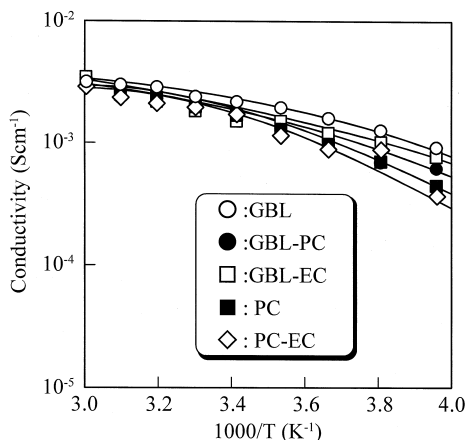
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Fig. 1. Temperature dependence of ionic conductivity of gel polymer electrolytes containing 1.0 M LiBF$_4$ (polymer content: 25 wt.%).

Fig. 3. Variation of discharge capacity with cycle number for Li/LiCoO$_2$ cells with gel polymer and liquid electrolytes containing 0.5 M LiBF$_4$ (polymer content: 25 wt.%).

tance and potentio-galvanostat, Hokuto Denko HAB-151, was applied to evaluate the electrochemical characteristics. On polarization measurement, current density increased step by step from 0 to 0.2 mA cm^{-2} and to reverse direction, keeping at a fixed current density for 3 min.

3. Results and discussion

Temperature dependence of ionic conductivity of gel polymer electrolytes containing various solvents (plasticizers) with LiBF$_4$ are shown in Figs. 1 and 2. In these figures, the relationships between the conductivity and 1000/T are not distinct strait lines and the data seem to exhibit Vogel–Tamman–Fulcher type behabior. The highest conductivity was obtained for the gel electrolyte containing GBL. In Fig. 2, the effect of LiBF$_4$ concentration in the solution contained in the gel polymer electrolyte on the conductivity is shown, and the conductivity increased with increase of LiBF$_4$ concentration in the gel electrolyte. The
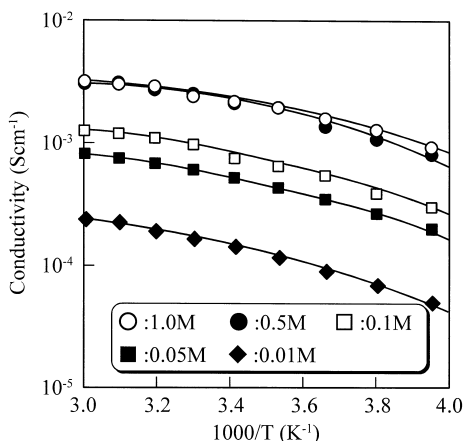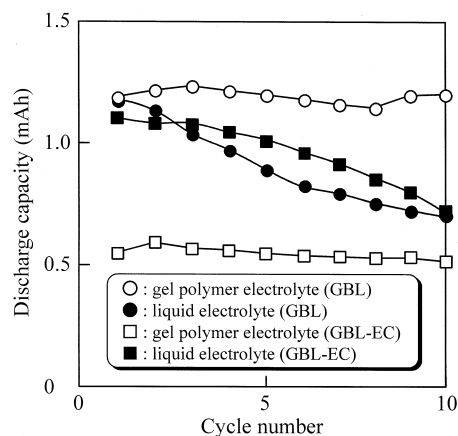
highest conductivity was obtained at the gel electrolyte with 1.0 M LiBF$_4$.

Using cell A, the influence of the type of electrolytes, gel polymer electrolytes or liquid electrolytes, on the discharge capacity with charge-discharge cycling were evaluated. The results are shown in Fig. 3. Discharge capacity of the cells with gel polymer electrolyte was stable with charge–discharge cycling, but that of the cells with liquid electrolyte decreased with cycling. The highest discharge capacity, 1.3 mAh, was obtained on the cell with gel polymer electrolyte containing GBL/1.0 M LiBF$_4$. Discharge capacity of the cell with gel electrolyte containing GBL-EC/1.0 M LiBF$_4$ was small, but the cycling performance was very stable. These results suggested that the cells with gel polymer electrolytes show more stable cycling performance. Among these cells, a cell with gel polymer electrolyte containing LiBF$_4$/GBL showed the best performance.

Fig. 2. Temperature dependence of ionic conductivity of gel polymer electrolytes containing LiBF$_4$/GBL (polymer content: 25 wt.%).
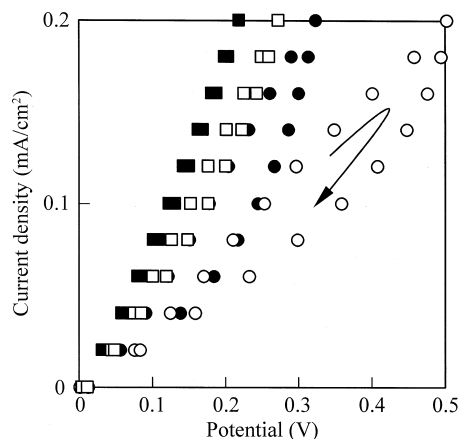

Fig. 4. Polarization curves of test cells with gel polymer electrolytes containing LiBF$_4$/GBL. Cycle number ○:2 ●:3 □:4 ■:5.
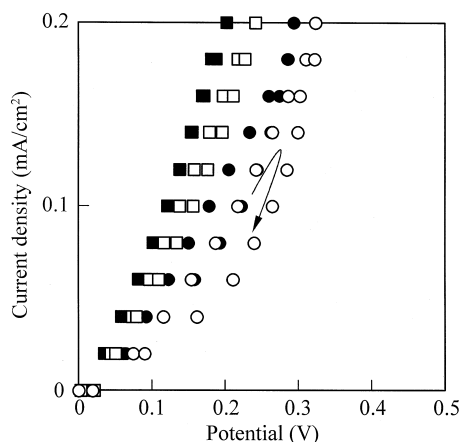
Fig. 5. Polarization curves of test cells with gel polymer electrolytes containing LiBF$_4$/GBL-PC. Cycle number ○:2 ●:3 □:4 ■:5.
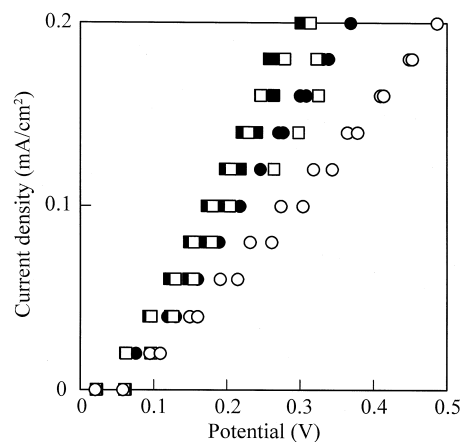

Fig. 7. Polarization curves of test cells with gel polymer electrolytes containing LiBF$_4$/PC. Cycle number ○:2 ●:3 □:4 ■:5.

Polarization characteristics of cell B with gel polymer electrolytes containing various plasticizers are shown in Figs. 4–7. In all cases, polarization was plotted from 2nd to 5th measurement because 1st measurement was unstable. The polarization of a lithium electrode decreased with charge–discharge cycling and it was relatively small in the gel electrolytes containing GBL. The polarization of cell B with gel polymer electrolytes containing LiBF$_4$/PC-EC showed similar behavior to that containing LiBF$_4$/PC (Fig. 8). This phenomenon would connect to the stable charge–discharge performance of the cells with gel polymer electrolytes. The reason for the different behavior of gel vs. liquid electrolyte in case of GBL and EC structure seems to be the difference of the interface between lithium and the electrolyte. At the interface between lithium and the gel electrolyte, some oxygen atoms in poly alkylene oxide would coordinate lithium metal. These coordinated parts and reduced products of the plasticizer and LiBF$_4$ would form a stable lithium ion permeable film on lithium elec-

trode. Further, the difference of reduction reactions of GBL, PC, and EC would affect the polarization behavior of lithium electrode. The reduced product of GBL on lithium electrode are mainly lithium butylate, a compound shown in Chemical structure 1, and LiF [16] and that of PC and EC consist of corresponding ROLi, ROCO$_2$Li, LiF and Li$_2$CO$_3$ [17–19]. These differences of the reaction products would affect polarization of the cells B.
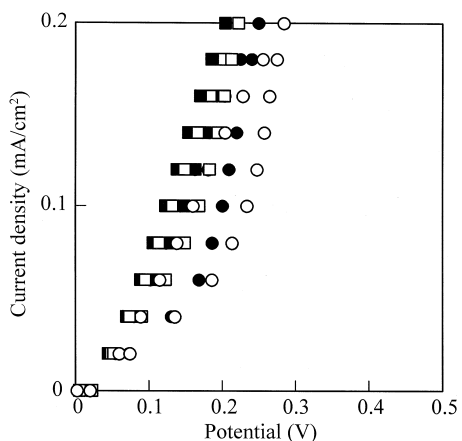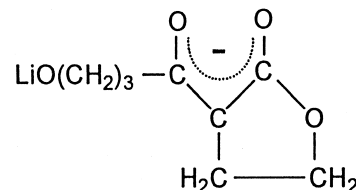

Fig. 6. Polarization curves of test cells with gel polymer electrolytes containing LiBF$_4$/GBL-EC. Cycle number ○:2 ●:3 □:4 ■:5.

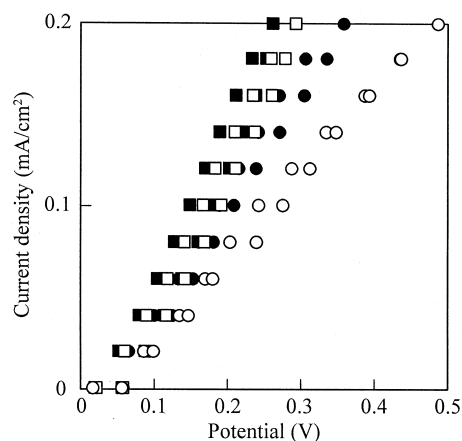Fig. 8. Polarization curves of test cells with gel polymer electrolytes containing LiBF$_4$/PC-EC. Cycle number ○:2 ●:3 □:4 ■:5.

4. Conclusion

Gel polymer electrolytes of the alkylene oxide system containing GBL/LiBF4 showed excellent suitability and cycling performance of Li/gel polymer electrolyte/LiCoO$_2$ cell was very stable. Cycling performance of a Li anode with gel polymer electrolyte of alkylene oxide system was very stable. Among the plasticizers, GBL was the most suitable for gel polymer electrolytes of alkylene oxide system, to be used in rechargeable lithium batteries.

Acknowledgements

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