

Behavior of interfacial resistance at lithium electrode for gel electrolyte using novel three-dimensional network polymer host

Michiyuki Kono ^{*}, Masahito Nishiura, Eriko Ishiko

R & D Center, Dai-Ichi Kogyo Seiyaku, 55 Higashikubo-cho, Nishi-shichijo, Simogyo-ku, Kyoto 600-8873, Japan

Abstract

A novel macromonomer based on tri-functional poly (alkylene oxide) main chain with acrylate chain ends was specially designed and synthesized for gel electrolyte purpose. Various kinds of gel electrolyte, based on the crosslinked macromonomer, were prepared. Interfacial resistance between lithium electrodes and the gel electrolytes was measured. The significant decrease in interfacial resistance was observed during 4–6 h after assembling the cell. The discharge capacity of secondary cells with the gel electrolyte depended on the kind of liquid electrolyte incorporated in the gel electrolyte. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Gel electrolyte; Interfacial resistance; Lithium; Macromonomer

1. Introduction

Various kinds of gel polymer electrolytes have been studied to improve safety, reliability, and energy density of lithium and lithium ion batteries. Among them, the thermoplastic polymers such as PEO, PAN, PVdF, and PVdF-HFP will be promising hosts for gel electrolytes. Crosslinked acrylate or methacrylate monomers could be one of the better candidates for the polymer host of gel polymer electrolyte. Though the gel polymer electrolytes obtained from the latter polymer hosts *do not show flowing* property even at higher temperature, their mechanical strength has not been satisfactory [1].

A novel macromonomer having a structure of poly (alkylene oxide) main chain with acrylate chain end has been specially prepared for gel electrolyte purpose [2,3]. A gel electrolyte consisting of the crosslinked macromonomer and a liquid electrolyte showed excellent physical property due to the formation of three-dimensional polymer network. The ionic conductivity of the gel electrolyte depended on the kind and quantity of the liquid electrolytes incorporated. However, the interfacial resistance between lithium electrodes and gel electrolyte showed specific dependence on the liquid electrolyte incorporated [4].

In this study, various kinds of gel electrolytes were prepared based on the photo-crosslinked macromonomer. Electrochemical property of the resulting gel electrolytes

was studied, specially focused on the interfacial phenomenon between lithium electrodes and gel electrolytes.

2. Experimental

A random alkylene oxide copolymer was synthesized by ring opening polymerization of ethylene oxide (EO) and propylene oxide (PO) in an autoclave. The ratio of EO/PO in weight was controlled to 80/20. Glycerol was used as a starting substance for polymerization, resulting in a triol-type polyether. The molecular weight of the polyether triol was found to be 8140 by the titration of terminal OH groups. A crude macromonomer was obtained from esterification reaction of the triol's terminal hydroxyl groups with acrylic acid. The macromonomer was purified by neutralization and desalting, followed by dehydration over molecular sieves (4 Å). The conversion to acrylic ester was 95% as determined by nuclear magnetic resonance (NMR). The residual water content was below 15 ppm as determined by Karl–Fisher coulometric analyzer.

The solvents used for preparing the liquid electrolytes were; ethylene carbonate (EC)–propylene carbonate (PC) (= 1/1 in volume ratio), EC- γ -butyrolactone (GBL) (= 1/1 in volume ratio), PC neat, PC–GBL (= 1/1 in volume ratio), and GBL neat. LiBF₄ was dissolved in the above solvents in a concentration of 1 M. All liquid electrolytes were dried over molecular sieves (4 Å) to reduce the moisture content below 10 ppm.

^{*} Corresponding author

The macromonomer was mixed with the dried liquid electrolyte prepared above. The weight ratio of macromonomer/liquid electrolyte was 25/75 for all gel electrolytes studied here. 2,2-Dimethoxyphenylacetophenone (DMPA), a photo-initiator, was dissolved in the mixture in a concentration of 0.1%. The gel electrolyte was prepared by pouring the mixture into a gap of 2 quartz glass plates followed by exposing to UV light (7 mW/cm², 365 nm) for 10 min in an argon-filled glove box (moisture < 1 ppm). The film thickness was controlled by using spacers between the glass plates.

An interfacial resistance and a double-layer capacitance between electrolyte and lithium (Li) electrode was measured by AC impedance method using computer-controlled LF impedance analyzer (Hewlett Packard, Model 4192A) for a Li/electrolyte/Li symmetrical cell. A bulk resistance for electrolyte was also measured by the above method. The cell was assembled by sandwiching the gel electrolyte (500 μm in thickness) between Li electrodes (Honjo Metal, 0.21 mm in thickness and 1.767 cm² in surface area) and was sealed in a moisture-tight metallized plastic package. The liquid electrolyte was immersed into nonwoven textile (250 μm in thickness) to enable the similar cell assembly described above. Those cells in the packages were sandwiched between two stainless steel plates to ensure a good contact and were stored at 25°C under open circuit conditions.

A Li/gel electrolyte/LiCoO₂-C-PVdF secondary cell was assembled by sandwiching the gel polymer electrolyte membrane (100 μm in thickness) between a Li negative electrode and a LiCoO₂ composite positive electrode. The composition of the positive electrode was fixed to LiCoO₂:C:PVdF = 87:10:3 in weight ratio. The positive composite dispersed in *N*-methyl pyrrolidinone (NMP, Aldrich) was coated on an aluminum foil and NMP was finally removed at elevated temperature in vacuo. The apparent surface area of the positive electrode was normalized to 1.327 cm². The thickness of the positive electrode was controlled to include 10 mg of LiCoO₂. Thus, a theoretical capacity of the cells was estimated to 1.3 mA h based on the positive electrode. The Li negative electrode (0.785 cm² in area and 0.21 mm in thickness) was pressed onto stainless steel foil. Charge–discharge measurement was performed at the current density of 0.490 mA/cm² (0.5 C) to the positives. Cut-off voltages were 4.2 V on charging and 2.5 V on discharging. Cells were operated at 25°C. The first discharge was performed at 2 h after assembling the cell.

3. Results and discussion

3.1. Interfacial resistance

Fig. 1 shows the impedance spectrum of a symmetrical Li/GBL–LiBF₄ incorporated gel/Li cell measured at various times. Double-layer capacitance (C_{dl}) of the interface

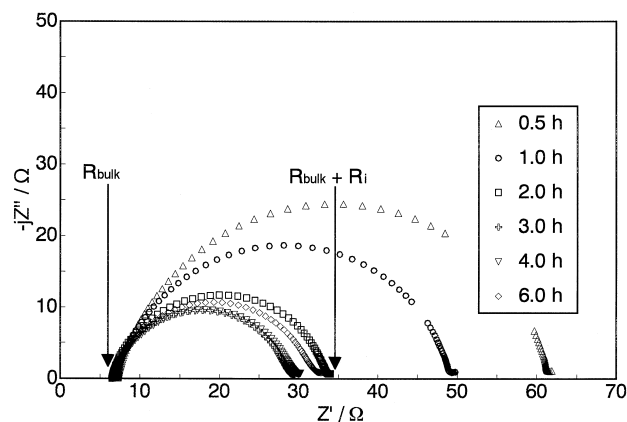


Fig. 1. Typical time dependence of impedance for the Li/electrolyte/Li cell stored at 25°C using gel electrolyte consisting of crosslinked macromonomer and GBL–LiBF₄.

between Li electrode and electrolyte (Li/electrolyte interface) was estimated by assuming that a simple equivalent circuit for the interfacial process can be expressed by the parallel combination of charge transfer resistance and C_{dl} . Thus, it should be noted that $R_i + R_{bulk}$ indicated in Fig. 1 is internal resistance of the cell and interfacial resistance (R_i) is the sum of two resistances between Li and electrolyte.

The time dependence of R_i , C_{dl} , and R_{bulk} of the symmetrical Li/electrolyte/Li cell with liquid electrolytes and with gel electrolytes measured at 0.5 h to 24 h after assembling the cell are shown in Fig. 2a, b and c, respectively. The trend of the change in R_i and C_{dl} for the Li/liquid electrolyte interface and Li/gel electrolyte interface showed quite a different manner. R_i of the Li/liquid electrolytes interface showed minimum value at 1 h after assembling the cell then increased. C_{dl} of the Li/liquid electrolyte interface showed the maximum value after 1 h then decreased. It is well-known that the liquid electrolytes react with Li to form many kinds of passivation layers depending on the kinds of electrolyte solvents and salts [5,6]. Thevenin and Muller [7] studied the change in R_i of the Li/PC–LiClO₄ interface, and reported that R_i changed to 27, 33, 43 Ω cm² after 0.5, 2, 6 h, respectively. This tendency agreed with our result of R_i for the Li/liquid electrolytes interface. The decrease in C_{dl} with increasing R_i of Li/liquid electrolyte interface suggested that the thickness of the passivation layer increased as a function of time.

R_i of the Li/gel electrolytes interface continued to decrease until 4 to 6 h after cell preparation, then increased gradually in contrast to that of Li/liquid electrolyte interface. In addition, a magnitude of the decrease in R_i of Li/gel electrolyte interface largely depended on the kind of liquid electrolyte incorporated in the gel. R_i of Li/PC–LiBF₄-incorporated gel electrolyte interface showed significant decrease compared to that of Li/GBL–LiBF₄-incorporated gel electrolyte interface. The

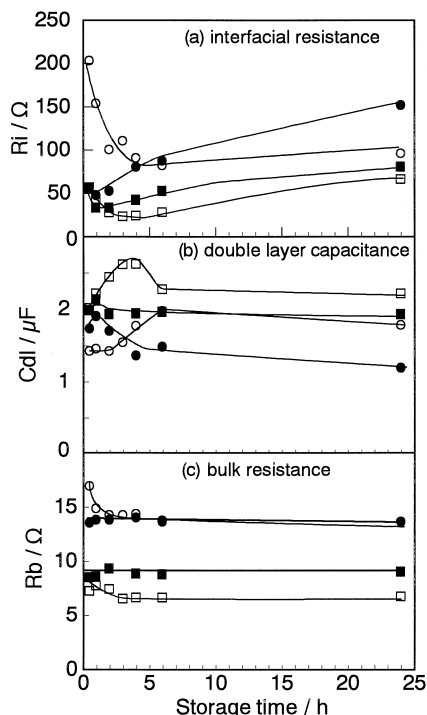


Fig. 2. Time dependence of impedance for Li/electrolyte/Li cell with liquid electrolyte and gel electrolyte: (○) gel electrolyte of PC-LiBF₄; (□) gel electrolyte of GBL-LiBF₄; (●) liquid electrolyte of PC-LiBF₄; (■) liquid electrolyte of GBL-LiBF₄.

trend of change in C_{dl} for Li/gel electrolytes interface well-corresponded to the trend of R_i , i.e., C_{dl} increased with decreasing of R_i . These results suggested that the contact area of the interface between gel electrolyte and Li electrodes spreads during 4 to 6 h storage, in contrast to the liquid electrolytes. Fig. 2c well-confirmed the above suggestion, because R_{bulk} of the gel electrolytes gradually decreased with time evolution during 4 to 6 h storage then remained constant, while R_{bulk} of the liquid electrolyte remained constant during storage. Though the passivation of Li electrodes by the gel electrolyte may proceed in this period, the interfacial process would be governed by the spread of the contact area. The spread of the interfacial contact area between Li and gel electrolyte would be attributed to the slight exudation of the liquid electrolyte from the gel electrolyte bulk to the interface by a pressure given to the cell or by an elasticity of the polymer network. Consequently, a microscopic gap of the Li/gel electrolyte interface would be gradually filled with liquid electrolyte during initial storage period.

Fig. 3 also shows R_i of Li/gel electrolyte interface as a function of storage time for relatively long period. The trend of the change in R_i was also affected by the kind of incorporated liquid electrolyte in the gel electrolyte. Especially, the cells with PC-LiBF₄- and EC-PC-LiBF₄-incorporated gel electrolytes showed significant increase in R_i during storage as compared with others. The continuous increase in R_i with time was observed for Li/PC-based liquid electrolyte interface [7]. Their data well corresponds

to the time dependence of R_i for the Li/PC-LiBF₄-incorporated gel electrolyte interface of this study. They assumed the formation of a compact-stratified layer [CSL] or a solid-polymer layer [SPL] as a possible cause of the increase in R_i . Similar process may occur for the interface between Li and PC-LiBF₄-incorporated gel electrolyte. The other possible cause of the increase in R_i for the Li/gel electrolyte interface mentioned above could be the contact problem. With changing the morphology of the passive layer, it is likely that the gel electrolyte could be partly peeled off from the Li electrodes. Physical properties of the gel electrolytes studied here were varied by the nature of the incorporated liquid electrolytes. For example, a swelling ratio of the network polymer to the liquid electrolytes was varied by the kind of liquid electrolyte [4]. Thus, the degree of exudation of the liquid electrolyte could be influenced by the kind of liquid electrolyte, and the higher degree of exudation may cause liquid-like gel electrolyte surface.

R_i of the interface between gel electrolyte involving GBL-LiBF₄ and Li appeared to be stable over the entire period of storage. Instability of R_i for Li/gel electrolytes interface during storage have been reported by several workers. For example, Appetecchi et al. [8] reported the significant increase in R_i during storage for various gel electrolytes. However, R_i of Li/gel electrolyte interface of the present study showed a good storage stability by choosing adequate liquid electrolyte such as GBL-LiBF₄ and EC-GBL-LiBF₄. This fact provides a possibility of an application of the gel electrolyte to the cells with Li metal anode.

3.2. Li secondary cell preliminary result

The gel electrolytes incorporating various liquid electrolytes were applied to the Li/gel electrolyte/LiCoO₂ secondary cells. Though all the cells showed good cycling stability for the 10th cycle, the discharge capacity was varied by the kind of liquid electrolyte used in gel electrolyte. Fig. 4 shows the discharge capacities of the cells

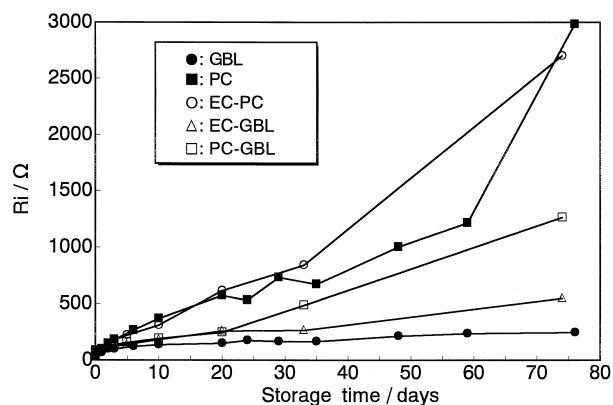


Fig. 3. Time dependence of the interfacial resistance (R_i) between gel electrolyte and lithium electrode at 25°C. Liquid electrolytes incorporated in the gel were indicated in the figure.

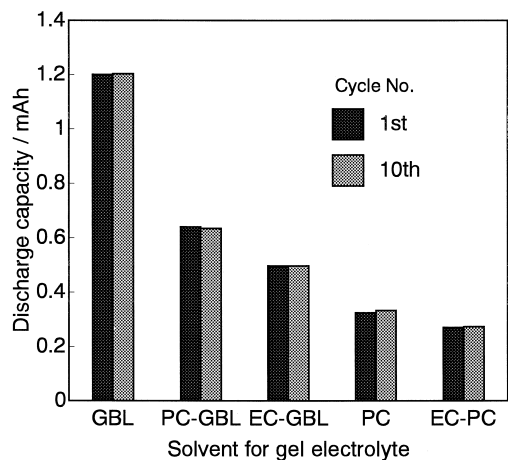


Fig. 4. Variations in discharge capacity at 1st and 10th cycles for various Li/gel electrolyte/LiCoO₂ cells. The solvents of liquid electrolyte incorporated in the gel were varied as shown in figure.

with various kinds of gel electrolytes at 1st and 10th cycles. The discharge capacity of the cell with GBL–LiBF₄-incorporated gel electrolyte showed excellent value. On the other hand, the cell with PC–LiBF₄-incorporated gel exhibited poor discharge capacity. Such a variation in discharge capacity would be attributed to the difference of the internal resistance for the secondary cells. A bulk resistance of the gel electrolyte and two interfacial resistances between electrodes and gel electrolyte are considered to be the significant component of the internal resistance of the cell. R_i of Li/gel electrolytes interface measured at 2 h after assembling the Li/gel electrolyte/Li cells were 27, 41, 49, 100, and 98 Ω for GBL–LiBF₄-, PC–GBL–LiBF₄-, EC–GBL–LiBF₄-, PC–LiBF₄-, and EC–PC–LiBF₄-incorporated gel electrolytes, respectively. It was clearly shown that the magnitude of R_i was inversely proportional to the magnitude of discharge capacities of the secondary cells. The bulk resistance of the gel electrolyte for secondary cells seemed to be negligible in comparison with R_i , because the ionic conductivities of gel electrolytes used in the secondary cells were as high as 1 to 3 mS/cm (see Fig. 2c) and the thickness of the gel membrane in the cells was 100 μ m. Though the interfacial resistance between cathode and the gel electrolyte has not

been estimated yet, lowering the interfacial resistance between gel electrolyte and electrodes was ascertained to be one of the important criteria for increasing the discharge capacity of Li polymer batteries.

Nevertheless, the optimization of the cell assembly has not finished in this stage; the preliminary cell showed a good cyclability and a high capacity by selecting an appropriate liquid electrolyte. And the compatibility of the gel electrolyte with high potential cathodes such as LiCoO₂, LiNiO₂, and LiMn₂O₄ was expected.

4. Conclusion

The interfacial resistance of the Li/gel electrolyte studied here showed significant decrease during early storage period. This behavior will be important for the evaluation of secondary cells with the gel electrolyte, since the interfacial resistance will largely affect the resulting cell performance. The gel electrolyte studied here showed a good electrochemical stability and a high compatibility with high potential cathode material such as LiCoO₂.

Acknowledgements

The authors would like to thank Dr. Yoshiharu Matsuda of Kansai University and Dr. Masayoshi Watanabe of Yokohama National University for helpful discussions.

References

- [1] M. Alamgir, K.M. Abraham, in: G. Pistoia (Ed.), *Lithium Batteries*, Elsevier, Amsterdam, 1994, p. 102.
- [2] M. Nishiura, M. Kono, N. Namegaya, Y. Matsuda, *Electrochemical and Solid-State Letters* 6 (1998) 1.
- [3] M. Kono, E. Ishiko, M. Watanabe, *J. Electrochem. Soc.* (in press).
- [4] M. Kono, E. Ishiko, M. Watanabe, Ext. Abstr. 74th Meet. Chem. Soc. Jpn. Kyoto, 1998, p. 137.
- [5] D. Aurbach, *J. Electrochem. Soc.* 136 (1989) 1606.
- [6] F.P. Dousek, J. Jansta, *J. Electroanal. Chem.* 74 (1976) 195.
- [7] J.G. Thevenin, R.H. Muller, *J. Electrochem. Soc.* 134 (1987) 273.
- [8] G.B. Appetecchi, G. Dautzenberg, B. Scrosati, *J. Electrochem. Soc.* 143 (1996) 6.