Short communication

Study on cycling performances of lithium-ion polymer cells assembled by in situ chemical cross-linking with star-shaped siloxane acrylate

Wanju Kim[a], Jeong-Ju Cho[b], Yongku Kang[c], Dong-Won Kim[a,*]

[a] Department of Applied Chemistry, Hanbat National University, San 16-1, Dukmyung-Dong, Yusung-Gu, Daejeon 305-719, Republic of Korea
[b] Batteries R&D, LG Chemical Ltd., 104-1 Munji-Dong, Yusung-Gu, Daejeon 305-380, Republic of Korea
[c] Advanced Materials Divisions, Korea Research Institute of Chemical Technology, Yusung-Gu, Daejeon 305-600, Republic of Korea

Abstract

The chemically cross-linked gel polymer electrolytes supported by the microporous polyethylene membrane were prepared for application in lithium-ion polymer cells. The chemical cross-linking by star-shaped siloxane acrylate allowed to encapsulate an electrolyte solution in the porous membrane and also promote strong interfacial adhesion between the electrodes and the membrane. Lithium-ion polymer cells composed of a mesocarbon microbead anode and a lithium–cobalt oxide cathode were assembled by using in situ chemical cross-linking method, and their charge/discharge cycling performances were evaluated. Effect of the cross-linking agent content on cycling performances of the cells has been investigated.
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1. Introduction

Polymer electrolytes have been actively studied and developed for application in rechargeable lithium batteries. Attempts to obtain solid polymer electrolytes, consisting of a matrix polymer and a lithium salt, so far have been producing materials with limited ionic conductivity at ambient temperature [1–3]. It was found that the addition of polar solvents could significantly increase the ionic conductivity of those materials [4–6]. Such gel polymer electrolytes encapsulate high amounts of an electrolyte solution, and their ionic conductivities usually exceed $10^{-3}\ S\ cm^{-1}$ at room temperature, which is necessary for battery application. However, their mechanical properties are often very poor, which is one of the most important deficiencies preventing them from being used in practical lithium cells. For example, the poor mechanical strength of gel polymer electrolytes can lead to internal short-circuits and safety hazards. In order to overcome this problem, the microporous polyolefin membrane has been employed as a dimensional support to enhance the mechani-

cal strength of the gel polymer electrolytes [7–11]. Abraham et al. first reported the impregnation of gel polymer electrolyte by UV-irradiation of the porous polyolefin membrane soaked with a solution consisting of ethylene carbonate, propylene carbonate, tetraethylene glycol dimethyl ether, tetraethylene glycol diacrylate, LiAsF$_6$ and a small amount of a photopolymerization initiator [7]. In another approach, the gel polymer electrolyte consisting of polymer, a lithium salt and non-aqueous organic solvents has been directly applied to both sides of a microporous polyolefin separator [8]. To improve the interfacial contacts, a thin polymer layer that can be gelled by liquid electrolyte has been also proposed to coat the surface of the microporous membrane [9–11]. Such membrane-supported gel polymer electrolytes show excellent mechanical strength for the fabrication of lithium-ion polymer batteries and can therefore help in reducing the overall thickness of the electrolyte when compared to conventional gel polymer electrolytes.

In this work, the cross-linked gel polymer electrolytes supported by the microporous polyethylene membrane were prepared for application in lithium-ion polymer batteries. In order to induce in situ chemical cross-linking reaction in the cell, a new star-shaped siloxane-based cross-linking agent with oligo(ethylene oxide) acrylate functional group was used.

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* Corresponding author. Tel.: +82 42 821 1550; fax: +82 42 822 1562.
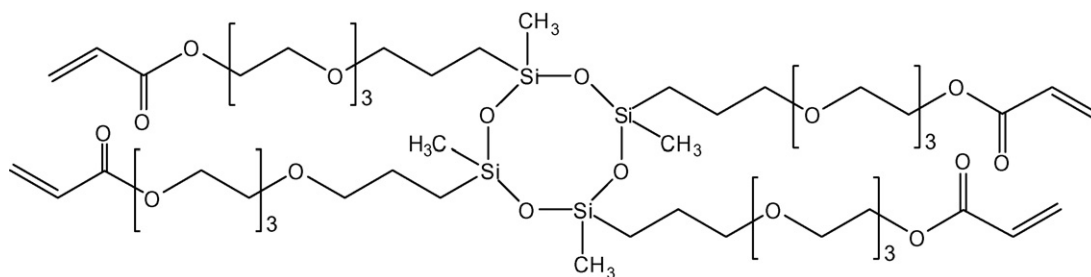 E-mail address: dwkim@hanbat.ac.kr (D.-W. Kim).

Fig. 1. Chemical structure of the star-shaped siloxane crylate cross-linker.

The electrochemical characteristics of the gel polymer electrolytes cured by the cross-linking agent are reported, and the electrochemical performances of lithium-ion polymer cells composed of a mesocarbon microbead (MCMB) anode and a lithium–cobalt oxide cathode are presented. More attention will be paid to the influences of the content of cross-linking agent on cycling performances of the lithium-ion polymer cells.

2. Experimental

2.1. Preparation of gel polymer electrolytes and electrodes

The star-shaped siloxane acrylate cross-linking agent (Fig. 1) was synthesized by hydrosilylating poly(ethylene glycol) monoallyl ether with 2,4,6,8-tetramethyl cyclotetrasiloxane and followed by acryloylation, as previously reported in detail [12,13]. Gel polymer electrolyte was prepared by radical initiated reaction of the microporous polyethylene membrane (Asahi Kasei, thickness: 25 μm, porosity: 40%) soaked with a homogeneous precursor electrolyte solution consisting of cross-linking agent, liquid electrolyte (1.0 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate, 1/1 (v/v), Samsung Cheil Industries, battery grade) and *t*-butyl peroxyprivalate as a thermal radical initiator, which was cured at 80 °C for 20 min. During the cross-linking reaction with the radical initiator, no gaseous products were formed. In order to control the cross-linking density, a cross-linking agent was dissolved with different concentration (0, 5, 10 wt.%) in the liquid electrolyte. The carbon anode was prepared by coating the *n*-methyl pyrrolidinone (NMP)-based slurry containing 92 wt.% of MCMB(Osaka gas), 7 wt.% of PVdF and 1 wt.% of super-P carbon (MMM Co.) on a copper foil. The cathode was made from 94 wt.% of $LiCoO_2$ (Japan Chemical), 3 wt.% of PVdF and 3 wt.% of super-P carbon in NMP, which was cast on aluminum foil. Electrodes were roll pressed to enhance particulate contact and adhesion to foils. The thickness of electrodes ranged from 50 to 65 μm after roll pressing, and their active mass loading corresponded to capacity of about 2.84 mAh cm^{-2} for the cathode.

2.2. Electrical measurements

A linear sweep voltammetry was performed to evaluate the electrochemical stability of the gel polymer electrolyte on a stainless steel (SS) working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0 mV s^{-1}. ac

impedance measurements were carried out in order to measure the interfacial resistances using an impedance analyzer over the frequency range of 1 mHz–100 kHz with an amplitude of 10 mV. Lithium-ion polymer cell was assembled by sandwiching the microporous polyethylene membrane between MCMB anode and $LiCoO_2$ cathode, which have been previously immersed in the liquid electrolyte solution containing cross-linking agent and initiator. The cell was enclosed in 2032-type coin cell and aged at 80 °C for 20 min in order to induce the in situ thermal curing. All assemblies of the cells were carried out in a dry box filled with argon gas. The charge and discharge cycling tests of lithium-ion polymer cells were conducted using Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

The electrochemical stability of the chemically cross-linked gel polymer electrolyte supported by the microporous membrane was evaluated by linear sweep voltammetric measurement. The voltage was swept from the open circuit potential of cell towards more anodic value until a large current due to the electrolyte decomposition at the inert electrode interface occurred. Fig. 2 shows the linear sweep voltammetry curves of the cells prepared with liquid electrolyte ($LiClO_{4-}$ EC/DMC) and chemically cross-linked gel polymer electrolytes. It should be noted that the small oxidation peak is observed for the chemically cross-linked gel polymer electrolyte around at 4.5 V. The origin for this oxidation peak is not clear at this time, but it may be thought
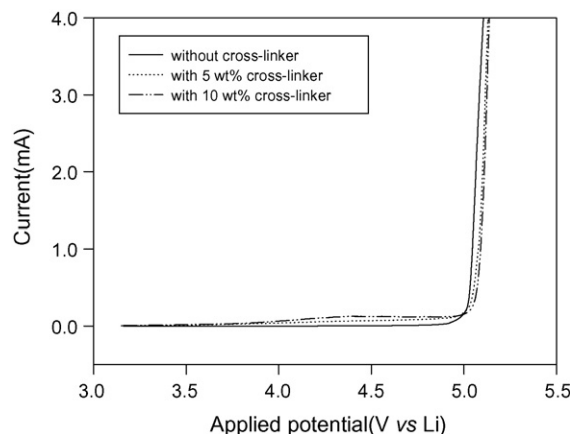

Fig. 2. Linear sweep voltammetry curves of the cells prepared with the liquid electrolyte and gel polymer electrolytes (scan rate: 1 mV s^{-1}).

to correspond to the oxidative breakdown of ethylene oxide unit ($-CH_2CH_2O-$) in the cross-linking agent. This presumption is well consistent with previous reports that the decomposition potential of poly(ethylene oxide) (PEO)-based solid polymer electrolyte was about 4.5 V *versus* Li/Li$^+$ [14,15]. A rapid rise in current was observed at about 5.0 V *versus* Li/Li$^+$ for all the electrolyte systems and continued to increase as the potential was swept, which was associated with the oxidative decomposition of the liquid electrolyte. Ionic conductivity of liquid electrolyte was measured to be 7.9×10^{-3} S cm^{-1}. When comparing the ionic conductivities of two gel polymer electrolytes, the gel polymer electrolyte cured by 5 wt.% cross-linking agent (1.3×10^{-3} S cm^{-1}) exhibited higher ionic conductivity than that of gel polymer electrolyte cured by 10 wt.% cross-linker (7.4×10^{-4} S cm^{-1}). Decrease of ionic conductivity with content of cross-linking agent is due to the fact that the ionic motion is more restricted with increasing cross-linking density.

In order to evaluate the electrochemical performance of lithium-ion polymer cell assembled with chemically cross-linked gel polymer electrolyte, we fabricated the carbon/LiCoO$_2$ cell with the gel polymer electrolyte. The assembled cell was initially subjected to the preconditioning cycle with cut-off voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at 0.05 C rate (0.14 mA cm^{-2}). After preconditioning cycle, the cell was charged at a current density of 1.42 mA cm^{-2} (0.5 C rate) up to a target voltage of 4.2 V. This was followed by a constant voltage charge with a decline of current until the final current was reached to 20% of charging current and then it was discharged down to a cut-off voltage of 2.8 V at the same current density (0.5 C rate). Fig. 3 compares the charge–discharge curves of the 1st, 10th, 20th, 50th and 100th cycle of the lithium-ion polymer cell using gel polymer electrolyte cured by 5 wt.% cross-linker. The discharge capacity of the cell declines from the initial value of 137 to 115 mAh g^{-1} after 100 charge/discharge cycles. Decline in the capacity is related with the gradual growth of internal resistance of the cell during the cycling. Coulombic efficiency is steadily increased with cycle number and it reaches a value of 99.2% at the 100th cycle.
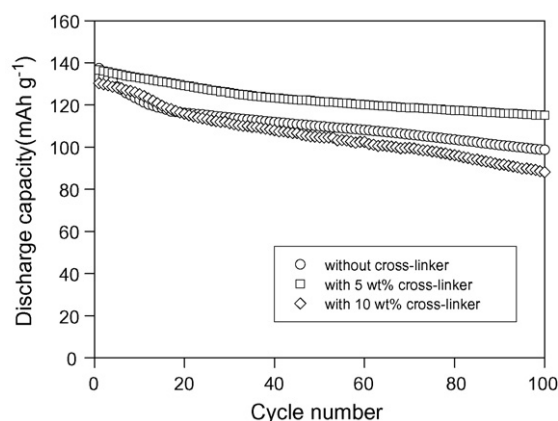
Fig. 4. Discharge capacities as a function of cycle number in the cells assembled with and without cross-linking agent (cut-off: 2.8–4.2 V, 0.5 C rate).

Fig. 4 shows the discharge capacities as a function of cycle number in the cells prepared with the liquid electrolyte and the chemically cross-linked gel polymer electrolytes, respectively. The cycling characteristics of the cells were found to depend on the content of cross-linking agent. As can be seen in the figure, the use of the gel polymer electrolyte cured by 5 wt.% cross-linker allowed the best cycling characteristics to be reached. Upon gelling liquid electrolyte by thermal curing with cross-linking agent, it becomes a gel polymer electrolyte and it serves as a strong adhesive to bond the membrane and electrodes together, which result in good capacity retention. In fact, it was obviously found that the membrane could not be separated from the both electrodes after the cross-linking reaction, which means that in situ thermal curing enables to the membrane firmly bond both electrodes together in the cell. However, an excessive cross-linking by 10 wt.% cross-linker may inevitably block the penetration of liquid electrolyte into the pores of microporous membrane and electrodes, which results in an increase of resistances for ion migration in both electrolyte and electrodes. It can give rise to a significantly uneven current distribution, which can cause the formation of dendritic lithium on the carbon electrode and the electrolyte decomposition at the active sites on the cathode surface. Thus, they could further increase the impedance of the cell, as charge–discharge cycles progress. These results imply that the proper control of cross-linking density in the cell is important to achieve good capacity retention.

To understand the cycling behavior of lithium-ion polymer cells, we obtained ac impedance spectra of the cells, before cycling and after 100 cycles. Fig. 5 shows the ac impedance spectra of the lithium-ion cells prepared with the liquid electrolyte or the gel polymer electrolytes, which are obtained at fully discharged state. It has been known that ac impedance spectrum of lithium-ion cell depends on the state of charge [16,17]. For a fair comparison, we tried to investigate at fully discharged state of the cell in this work. Before charge and discharge cycles, ac impedance spectra showed a poorly separated semicircle. By previous works [16,18], the overlapped semicircle observed from high to low frequency regions corresponds to solid electrolyte interphase (SEI) film impedance and charge transfer process. Of particular our interest in the
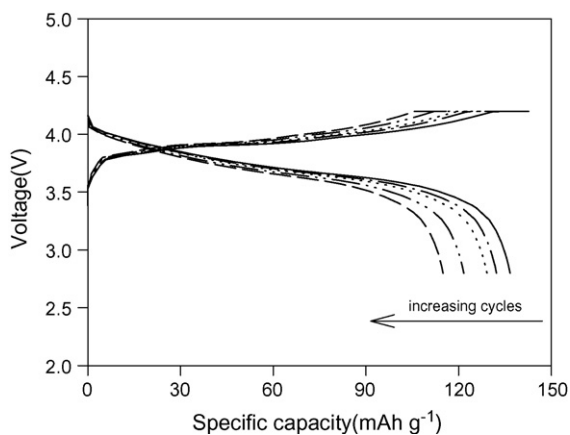

Fig. 3. Charge and discharge curves of the lithium-ion polymer cell cured by 5 wt.% cross-linking agent, which are corresponding to 1st, 10th, 20th, 50th, 100th cycle. Cycling was carried out between 2.8 and 4.2 V at current rate of 0.5 C.
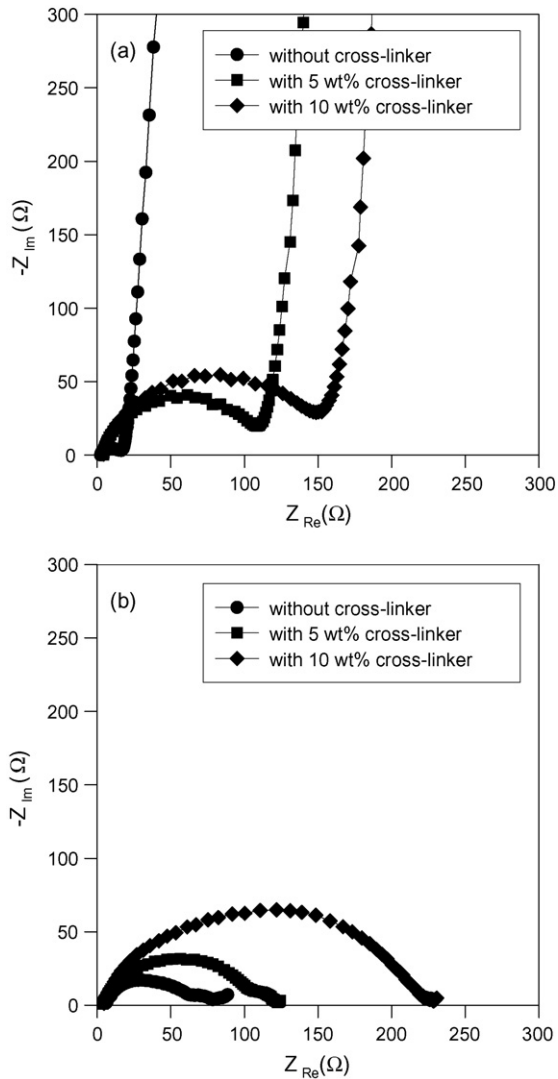
Fig. 5. ac impedance spectra of the lithium-ion cells assembled with and without cross-linking agent, which are measured before (a) and after (b) the repeated 100 cycles.
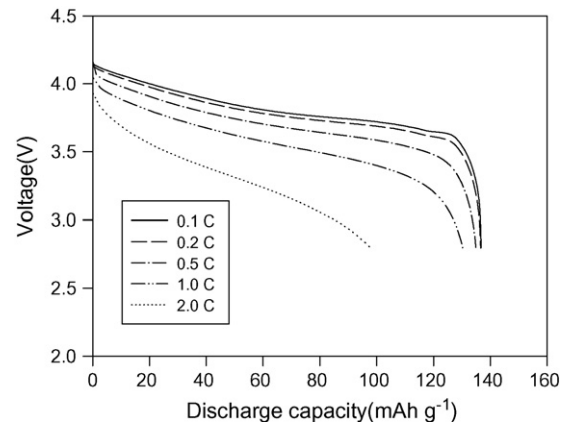

Fig. 6. Discharge profiles of a lithium-ion polymer cell cured by 5 wt.% cross-linking agent, which are obtained at different current rate. Charge rate is 0.2 C with 4.2 V cut-off.

depressed semicircles is the total interfacial resistance, which is sum of the resistance of SEI and charge transfer resistance. When comparing the interfacial resistance among three systems, the cell prepared with liquid electrolyte has the lowest interfacial resistance. An increase in interfacial resistance of the cell with increasing cross-linking density is due to the fact that the formation of cross-links reduces both the diffusion of lithium ions and the charge transfer reaction in the electrode. After the repeated cycling, the interfacial resistances of all the cells are found to be increased. An increase in interfacial resistances after cycling is observed to be minimum in the cell cured by 5 wt.% cross-linking agent. For the cell assembled with gel polymer electrolyte cured by 5 wt.% cross-linking agent, the interfacial resistance increases from the initial value of 104 to 119 Ω after 100 charge/discharge cycles. It is because that the proper chemical cross-linking allows to encapsulate an electrolyte solution in the porous membrane and the electrodes, and further to maintain good interfacial contact between electrodes and membrane during the repeated cycling. These results are

quite consistent with the cycling characteristics, as shown in Fig. 4. However, it is thought that, from the interfacial resistances measured after 100 cycles for all the cells, their discharge capacity values at the 100th cycle may not be directly correlated with interfacial resistance, because the liquid electrolyte-based cell shows lower resistance than those of the cells with gel polymer electrolytes.

Voltage profiles of the lithium-ion polymer cell prepared with the gel polymer electrolyte cured by 5 wt.% cross-linking agent are presented in Fig. 6, which are obtained at different current rate. It is found that both average discharge voltage and discharge capacity are decreased on increasing the current rate from 0.1 to 2.0 C rate. It showed a good performance at 1.0 C rate (2.84 mA cm^{-2}), whose discharge capacity was 130 mAh g^{-1} based on LiCoO$_2$ material in the cathode. However, the discharge capacity is found to drop to 98 mAh g^{-1} at 2.0 C rate, which corresponds to 71% of the capacity as delivered at 0.1 C rate. This result is not sufficient as a high rate performance of the lithium-ion polymer cell, and has to be improved. Fig. 7 shows the relative capacities of lithium-ion cells prepared with the liquid electrolyte and the chemically cross-linked gel polymer electrolytes, as a function of current rate. In the figure,
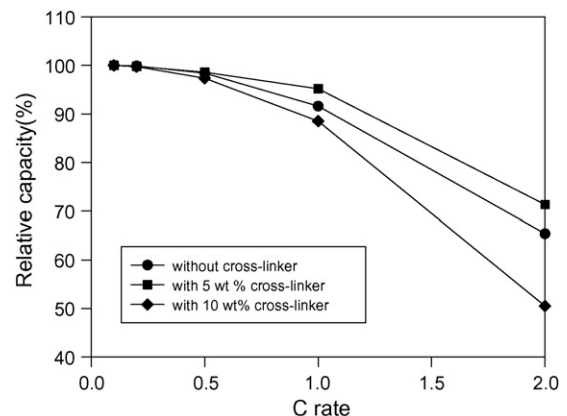

Fig. 7. Relative capacities of lithium-ion cells assembled with and without cross-linking agent, as a function of current rate.

the relative capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge capacity delivered at 0.1 C rate. It is clearly seen that the cell prepared with gel polymer electrolyte cured by 5 wt.% cross-linking agent has the best high rate performance. As discussed above, increasing the content of cross-linking agent over 5 wt.% may suppress the ionic migration and the charge transfer reaction, though it can promote strong interfacial adhesion between the electrodes and the membrane. From these results, the optimum content of cross-linking agent to ensure both good capacity retention and good rate performance is thought to be about 5 wt.% in our system.

4. Conclusions

The chemically cross-linked gel polymer electrolytes supported by the microporous membrane were prepared with star-shaped siloxane acrylate. It could adapt to encapsulate an electrolyte solution in the porous membrane and promote strong interfacial adhesion between the electrodes and the membrane. Lithium-ion polymer cells composed of MCMB anode and $LiCoO_2$ cathode have been assembled by it situ chemical cross-linking of liquid electrolyte with the cross-linking agent. The optimum content of cross-linking agent to ensure both good capacity retention and good rate performance was about 5 wt.% in this work. Further studies are being conducted in order to improve the cycling performance of the lithium-ion polymer cells by optimizing the type and quantity of a cross-linking agent.

Acknowledgement

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