Short communication

Effect of the cross-linking agent on cycling performances of lithium-ion polymer cells assembled by in situ chemical cross-linking with tris(2-(acryloyloxy)ethyl) phosphate

Ji-Ae Choi [a], Yongku Kang [b], Hyojin Shim [b], Dong Wook Kim [b], Hyun-Kon Song [c], Dong-Won Kim [a],*

[a] Department of Chemical Engineering, Hanyang University, Seungdong-Gu, Seoul 133-791, Republic of Korea
[b] Advanced Materials Divisions, Korea Research Institute of Chemical Technology, Yusung-Gu, Daejeon 305-600, Republic of Korea
[c] Batteries R&D, LG Chemical Ltd., 104-1 Munji-Dong, Yusung-Gu, Daejeon 305-380, Republic of Korea

ARTICLE INFO

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 tris(2-(acryloyloxy)ethyl) phosphate enhanced the electrochemical stability of the electrolyte and also promoted strong interfacial adhesion between the electrodes and the membrane. Lithium-ion polymer cells composed of a carbon anode and a lithium–cobalt oxide cathode were assembled by in situ chemical cross-linking, and their charge/discharge cycling performances were evaluated. Effect of the cross-linking agent on cycling performances of the cells has been investigated.

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1. Introduction

Rechargeable lithium-ion polymer batteries have been considered to be one of the most important next-generation power sources for portable electronic devices and electric vehicles. 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 [1–4]. It was found that the addition of polar solvents could significantly increase the ionic conductivity of those materials [4–7]. Such gel polymer electrolytes encapsulate high amount of an electrolyte solution, and their ionic conductivities usually exceed 10^{-3} S cm^{-1} at room temperature. However, their mechanical strength is not good, which is one of the most important deficiencies preventing them from being used in practical lithium batteries. 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 mechanical strength of the gel polymer electrolytes [8–13]. 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 [8]. 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 [9]. 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 [10–12]. In all of referred works, the inclusion of the polyolefin membrane overcame the aforementioned problems of the gel polymer electrolytes. The membranes can provide the shutdown capability and have the mechanical strength to withstand the rigors of the battery manufacturing process.

In our recent work, the cross-linked gel polymer electrolytes supported by the microporous polyethylene membrane have been prepared for application in lithium-ion polymer batteries [13]. In order to induce in situ chemical cross-linking reaction in the cell, a star-shaped siloxane-based cross-linking agent with oligo (ethylene oxide) acrylate functional group has been used. In the quest for improving the cycling performances of the cells, we synthesized phosphorous-based cross-linking agents and applied them
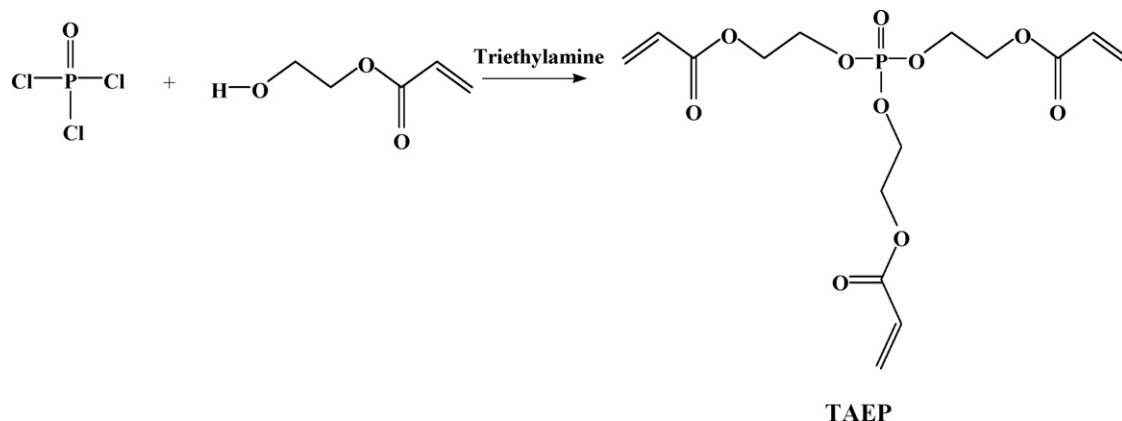
Scheme 1. Synthetic scheme of tris(2-(acryloyloxy)ethyl) phosphate (TAEP).

for assembling the lithium-ion polymer cells. In this work, the electrochemical performances of lithium-ion polymer cells assembled by in situ chemical cross-linking with tris(2-(acryloyloxy)ethyl) phosphate 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. Synthesis of tris(2-(acryloyloxy)ethyl) phosphate (TAEP)

Phosphorous oxychloride (99%) and 2-hydroxyethylacrylate (96%) were purchased from Aldrich Chem. Co. and were purified by a vacuum distillation before use. Tris(2-(acryloyloxy)ethyl) phosphate (TAEP) was synthesized by the reaction of phosphorous oxychloride with 2-hydroxyethylacrylate, as shown in Scheme 1. 2-Hydroxyethylacrylate (34 g, 0.29 mol) and triethylamine (29.54 g, 0.29 mol) were dissolved in anhydrous dichloromethane (100 ml) at 0 °C under nitrogen flow. Phosphorous oxychloride (13.56 g, 0.089 mol) was added slowly for 6 h using a syringe pump. After stirring at room temperature for 12 h, the resulting reaction mixture was filtered off the precipitate. The solvent was removed by evaporating and the residue was purified by silica gel column chromatography using ethyl acetate as an eluent (yield: 83%). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were obtained to analyze the chemical structure and purity of TAEP in CDCl$_3$ solvent on Bruker DPX-300 spectrometer.

2.2. Preparation of gel polymer electrolytes and electrodes

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) and t-butyl peroxy-2-ethyl haxanoate as a thermal radical initiator, which was cured at 80 °C for 20 min. In order to control the cross-linking density, a cross-linking agent was dissolved with different concentration (0, 2.5, 5.0, 7.5 and 10.0 wt.%) in the liquid electrolyte. The carbon anode was prepared by coating the n-methyl pyrrolidinone (NMP)-based slurry of mesocarbon microbeads (MCMB, Osaka gas), poly(vinylidene fluoride) (PVdF) and super-P carbon (MMM Co.) on a copper foil. The cathode contained the same binder and super-P carbon along with LiCoO$_2$ (Japan Chemical) cathode material, which was cast on aluminum foil. Electrodes were roll pressed to enhance particulate contact and adhesion to foils. The thickness of electrodes ranged from 55

to 70 μm after roll pressing, and their active mass loading corresponded to capacity of about 2.9 mAh cm^{-2}.

2.3. Electrical measurements

A linear sweep voltammetry was performed on a stainless steel (SS) working electrode, with counter and reference electrodes of lithium metal, at a scanning rate of 1.0 mV s^{-1}. AC impedance measurements were performed in order to measure the interfacial resistances using an impedance analyzer over the frequency range of 1 mHz to 100 kHz with an amplitude of 10 mV. Lithium-ion polymer cell was assembled by sandwiching the microporous polyethylene membrane between carbon anode and LiCoO$_2$ cathode, which have been previously immersed in the liquid electrolyte containing cross-linking agent and initiator. The cell was enclosed in a metallized plastic bag, vacuum-sealed 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

Tris(2-(acryloyloxy)ethyl) phosphate was synthesized by the coupling reaction between phosphorous oxychloride and 2-hydroxyethylacrylate. Since the starting materials and solvent were fairly pure, the reaction yields were high (higher than 80%). The product was purified by column chromatography to obtain a colorless liquid. The structure and purity of the TAEP were confirmed by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, as shown in Fig. 1. ^{1}H NMR spectrum shows multiplet of the aliphatic protons of ethyloxy at 3.95–4.05 ppm and acrylate group at 5.56, 5.82, and 6.10 ppm. The integral ratio was in a good agreement with the theoretical one and there were no impurity peaks. ^{13}C NMR spectrum shows the ethyloxy carbons at 63 and 66 ppm, acryl carbons at 129 and 133 ppm, and carbonyl carbon at 166 ppm. In ^{31}P NMR spectrum, the peak due to P–Cl of phosphorous oxychloride was completely disappeared at −11.5 ppm and a new singlet peak was observed at −1.29 ppm due to P–O–CH$_2$– of TAEP, indicating successful preparation of the compound.

The electrochemical stability of the chemically cross-linked gel polymer electrolyte prepared with tris(2-(acryloyloxy)ethyl) phosphate 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 oxidation at the inert electrode interface occurred. Fig. 2 shows the linear sweep voltammetry curves of the cells
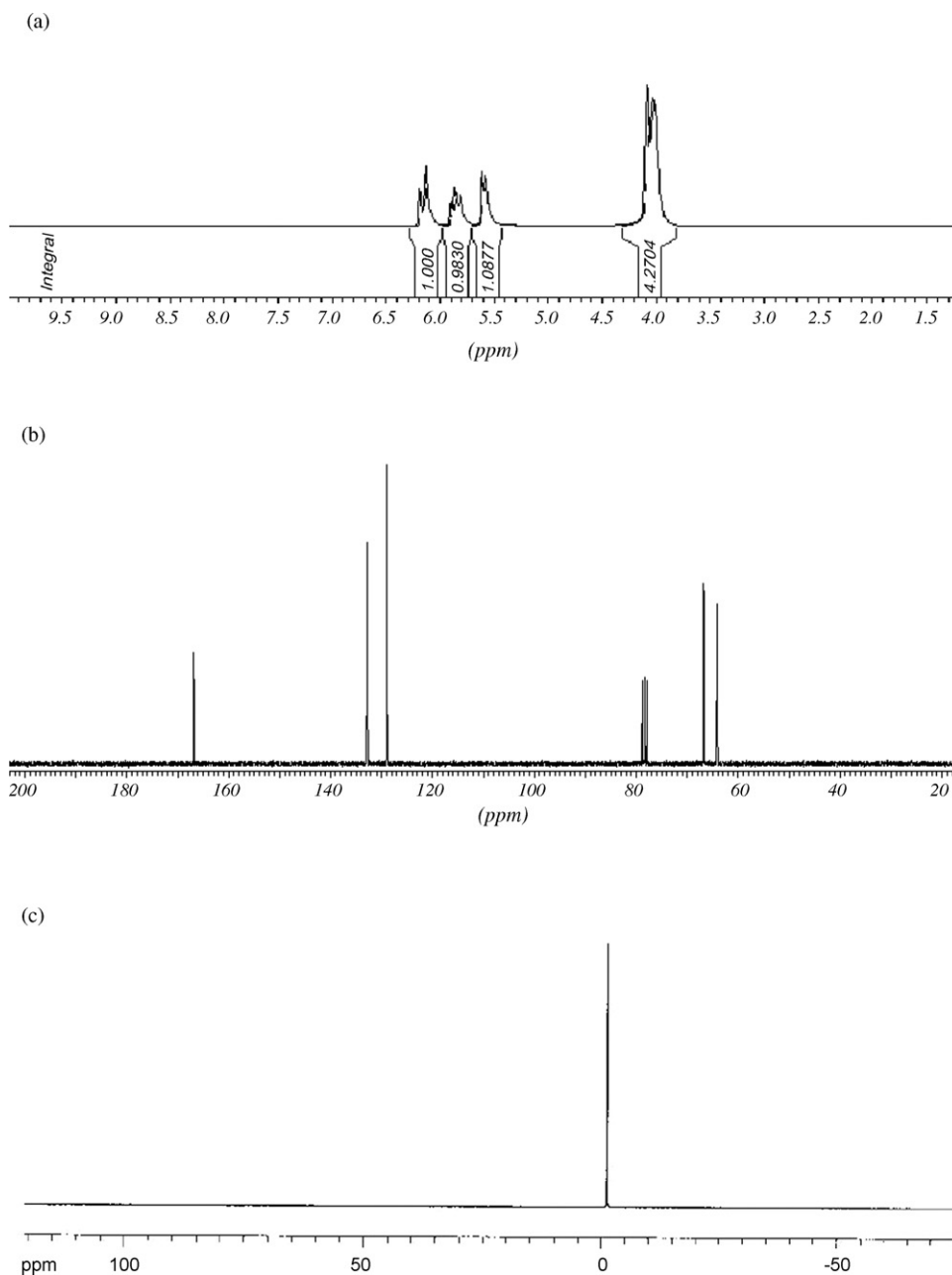
(a)

(b)

(c)

Fig. 1. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{31}P NMR spectrum of TAEP.

prepared with liquid electrolyte (LiClO$_4$–EC/DMC) and chemically cross-linked gel polymer electrolytes cured by different amount of cross-linking agent. A rapid rise in current was observed at about 5.0 V *vs.* Li/Li$^+$ for liquid electrolyte systems and continued to increase as the potential was swept, which was associated with the oxidative decomposition of the liquid electrolyte. On the other hand, the electrolyte decomposition occurred around 5.1 V *vs.* Li/Li$^+$ for the chemically cross-linked gel polymer electrolytes. This result suggests that the electrochemical stability of the electrolyte could be enhanced by chemically cross-linking the liquid electrolyte. However, the enhancement of the electrochemical stability was little dependent on the content of cross-linking agent, i.e., degree of cross-linking. Ionic conductivity of liquid electrolyte was measured to be 7.9×10^{-3} S cm^{-1}. When comparing the ionic conductivities of cross-linked electrolytes, the gel polymer electrolyte cured by 10.0 wt.% cross-linking agent (1.7×10^{-4} S cm^{-1}) exhibits

lower ionic conductivity than that of gel polymer electrolyte cured by 2.5 wt.% cross-linker (4.9×10^{-4} S cm^{-1}). Decrease of ionic conductivity with content of cross-linking agent is due to the fact that the ionic motion is restricted with increasing cross-linking density.

In order to evaluate the electrochemical performance of lithium-ion polymer cell assembled chemically cross-linked gel polymer electrolyte, we fabricated the carbon/LiCoO$_2$ cell by in situ chemical cross-linking. 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 0.05C rate (0.145 mA cm^{-2}). After preconditioning cycle, three cycles were performed in the voltage range of 2.8–4.2 V at constant current of 0.1C, 0.2C and 0.5C rate. After three cycles, the cell was charged at a current density of 1.45 mA cm^{-2} (0.5C 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
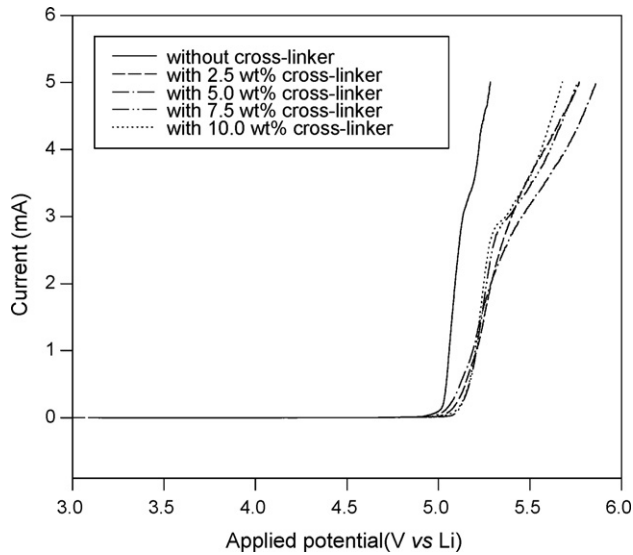
Fig. 2. Linear sweep voltammetry curves of the cells prepared with liquid electrolyte and cross-linked gel polymer electrolytes (scan rate: 1 mV s^{-1}).

Fig. 4. Discharge capacities as a function of cycle number in the lithium-ion polymer cells assembled with different amount of cross-linking agent (cut-off: 2.8–4.2 V, 0.5C rate).

current and then it was discharged down to a cut-off voltage of 2.8 V at the same current density (0.5C rate). Fig. 3 compares the charge–discharge curves of the 1st, 10th, 50th, 100th and 250th cycle of the lithium-ion polymer cell using gel polymer electrolyte cured by 5 wt.% cross-linker. The cell has a first discharge capacity of 122.3 mAh g^{-1} based on LiCoO$_2$ active cathode material. The discharge capacity of the cell declines from the initial value of 122.3–115.7 mAh g^{-1} after 250 charge/discharge cycles. Although the initial discharge capacity of the cell was rather low, the capacity retention was fairly good, i.e., 95% of the initial discharge capacity after 250 cycles. This result is due to the fact that the in situ chemical cross-linking allows to maintain good interfacial contact between electrodes and membrane during the repeated cycling. Coulombic efficiency is steadily increased with cycle number and it is maintained to be higher than 99.0% through cycling after the initial few cycles.

Fig. 4 shows the discharge capacities as a function of cycle number in the cells prepared with the liquid electrolyte and the
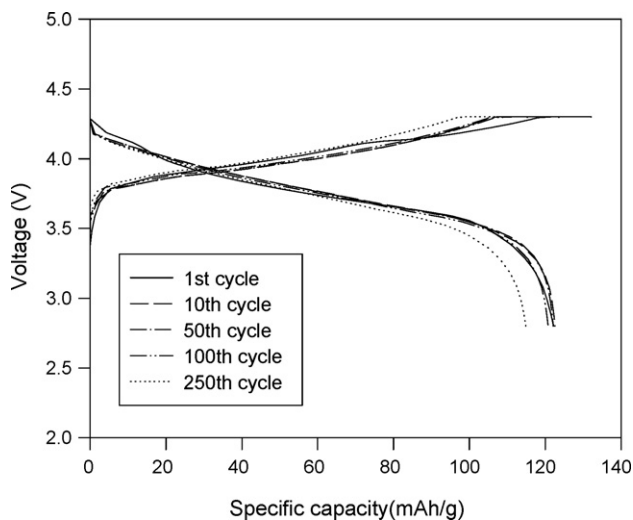
chemically cross-linked gel polymer electrolytes, respectively. The cycling characteristics of the cells were found to depend on the content of cross-linking agent. As can be seen in the figure, an initial discharge capacity of the cell was decreased with increasing the degree of cross-linking. A cross-linking reaction 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 reduction of discharge capacity. On the other hand, the capacity retention is improved with increasing degree of cross-linking. Upon gelling liquid electrolyte by thermal curing with cross-linking agent, it becomes a gel polymer electrolyte and it serves as an adhesive to bond the membrane and electrodes together, which result in good capacity retention. In the lithium-ion polymer cell cured by 10 wt.% cross-linker, the discharge capacity

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, 50th, 100th and 250th cycle. Cycling was carried out between 2.8 and 4.2 V at current rate of 0.5C.
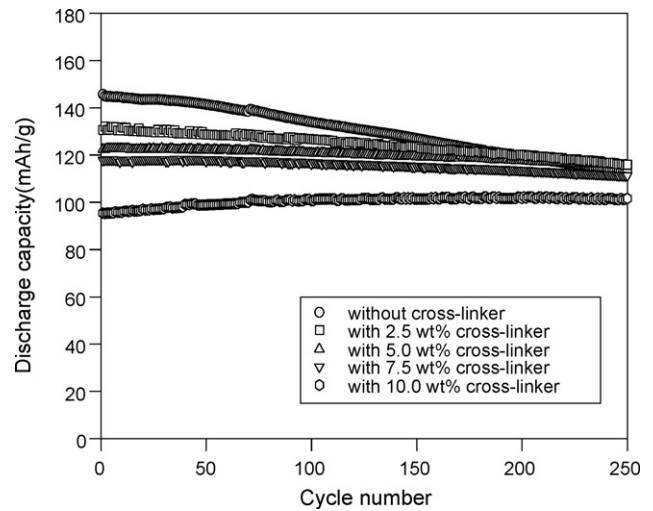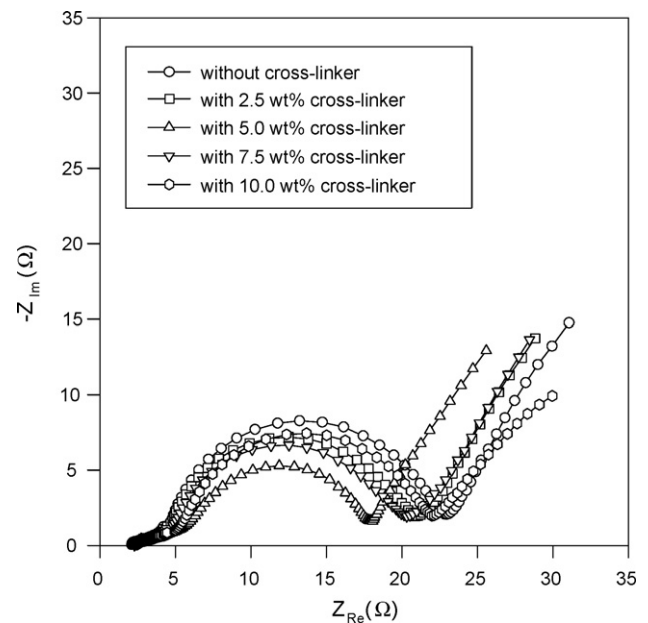

Fig. 5. AC impedance spectra of the lithium-ion polymer cells assembled with different amount of cross-linking agent, which are measured after the repeated 250 cycles.

of the cell increased from the initial value of 95.4–106.5 mAh g^{-1} after 250 charge/discharge cycles. An increase of discharge capacity may be due to the fact that the interfacial properties are improved with the repeated cycles.

To understand the cycling behavior of lithium-ion polymer cells, we obtained ac impedance spectra of the cells, after 250 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 [14,15]. For a fair comparison, we tried to investigate at fully discharged state of the cell in this work. After charge and discharge cycles, ac impedance spectra showed a poorly separated semicircle. By previous works [14,16], the overlapped semicircle observed from high to low frequency regions corresponds to solid electrolyte interphase (SEI) film impedance and charge transfer process. Since the equivalent circuit for the cell is extremely complex and has to be represented by a large number of series and parallel distribution of RC elements, a rigorous identification of a combination of poorly separated semicircles is beyond the scope of this work. Of particular our interest in the 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 cured by 5 wt.% cross-linking agent has the lowest interfacial resistance. It is plausible that the higher is the degree of cross-linking, the stronger is the interfacial bonding between the electrodes and the membrane, which is essential for efficient charge transport during charge–discharge cycling. However, 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. These results imply that the proper control of cross-linking density in the cell is important to achieve good cycling performances. In our system, the optimum content of cross-linking agent to ensure both acceptable initial discharge capacity and good capacity retention is thought to be about 5 wt.%.

4. Conclusions

The chemically cross-linked gel polymer electrolytes supported by the microporous PE membrane have been prepared with tris(2-(acryloyloxy)ethyl) phosphate. The cross-linking reaction could promote strong interfacial adhesion between the electrodes and the membrane. However, it may block the penetration of liquid electrolyte into the pores of microporous membrane and electrodes, which results in a decrease of reversible capacity. The optimum content of cross-linking agent to ensure both high initial discharge capacity and good capacity retention was about 5 wt.% in this work.

Acknowledgement

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