

Electrochemical properties of gel polymer electrolyte based on poly(acrylonitrile)-poly(ethylene glycol diacrylate) blend

Byung-Won Cho, Da Hye Kim*, Hee-Woo Lee* and Byung-Ki Na***†

Battery Research Center, KIST, Seoul 136-791, Korea

*Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

**School of Chemical Engineering, Chungbuk National University, Chungbuk 361-763, Korea

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Abstract—Gel type electrolyte was formulated by blending of PEDGA and PAN. PEDGA is a UV curable polymer which forms a chemical crosslink by UV or heat. Gel type electrolyte is very stable in ionic conductivity and interfacial resistance for a long storage time. It has the advantage of manufacturing the battery in a continuous process because oligomer crosslinking occurs in few seconds without heating. Discharge capacity and cycle life were increased by using $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ mixed lithium salt and adding inorganic filler such as TiO_2 .

Key words: Gel-type Polymer Electrolyte, Mixed Lithium Salts, Ceramic Fillers, PAN, PEDGA

INTRODUCTION

The market for lithium secondary batteries has expanded rapidly into the area of mobile telecommunication, notebook computers, and camcorders [1-3]. Lithium secondary batteries are divided into lithium ion battery and lithium polymer battery; the lithium ion battery has been commercialized by massive researches since the 1990s. However, the lithium ion battery uses a liquid electrolyte and it is unstable due to the leakage. It has disadvantages of difficulty in scale-up, limitations in size and shape, and environmental pollution due to organic solvents.

Polymer electrolyte can complement the weakness of the liquid electrolyte [4,5]. A complex of poly(ethylene oxide) (PEO) and lithium salt has been introduced as a lithium polymer electrolyte by Armand et al. [6]. PEO based complex was reported as a solvent free electrolyte and many researches have focused on this material. The complex of PEO and lithium salt shows an ionic conductivity over 10^{-4} S/cm at 80-100 °C, but the value decreases below 10^{-6} S/cm at room temperature, which is too low to be used in a lithium secondary battery. Modification of PEO structure can increase the ionic conductivity by easy movement of the polymer backbone chain. Short ethylene oxide chain was connected to backbone chain of polymer and comb shaped PEO was formed [7]. Low molecular weight PEO and lithium salt formed a complex, and the mechanical strength was increased by crosslinking [8]. These methods successfully increased the ionic conductivity to 5×10^{-5} S/cm at room temperature.

In late 1990s third generation polymer electrolyte was developed by adding plasticizer to increase the ionic conductivity at room temperature [9]. Gel type polymer electrolyte showed ionic conductivity over 10^{-3} S/cm below room temperature. Poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVdF), and poly(methyl methacrylate) (PMMA) were first introduced as gel type electrolyte by Feuillade and Perche [10] in 1975. They have dipole moments and lithium salt is

captured in polymer matrix. Recently, Watanabe [11] and Abraham [12] improved PAN polymer electrolyte which had ionic conductivity over 10^{-3} S/cm at room temperature. However, these types of polymer electrolyte using propylene carbonate as a plasticizer have disadvantages of electrochemical instability due to the decomposition reaction of propylene carbonate at graphite anode and mechanical strength decrease due to the addition of plasticizer. It also shows high viscosity at melt condition and has difficulties in continuous process.

In the present work, polymer electrolyte has been manufactured by blending of PAN with poly(ethylene glycol diacrylate) (PEGDA), which is UV curable polymer. Many plasticizers are contained in the matrix of UV curable polymer electrolyte, so the polymer exists in swelled condition. UV cured polymer electrolyte has fewer problems of plasticizer leakage than linear chain polymer electrolyte. It has the advantage of better capability of salt dissociation than crosslink structure without plasticizer because both ethylene oxide repeat unit and plasticizer can dissociate lithium salt.

Gel type polymer electrolyte was manufactured from blending of PAN and PEDGA without propylene carbonate as a plasticizer to test the electrochemical safety window, surface resistance, and ionic conductivity according to the $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ mixed lithium salt and ceramic fillers such as TiO_2 , Al_2O_3 , and CaCO_3 . Lithium ion polymer battery was assembled with the manufactured electrolyte, and charge/discharge reaction, battery capacity, and cyclic lifetime were measured to compare it with the PAN electrolyte.

EXPERIMENTAL

1. Preparation of Gel Polymer Electrolyte

PAN (Polyscience, $d=1.21$ g/cm³, MW=150,000) was an amorphous phase and PEGDA (Aldrich, $d=1.120$ g/cm³, MW=742) was a liquid at room temperature. LiPF_6 and LiCF_3SO_3 were used without pretreatment because they were ultra high purity reagents. Liquid electrolyte was prepared by dissolving 1 M $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ into the organic solvent mixture of ethylene carbonate (EC, Aldrich)

†To whom correspondence should be addressed.
E-mail: nabk@chungbuk.ac.kr

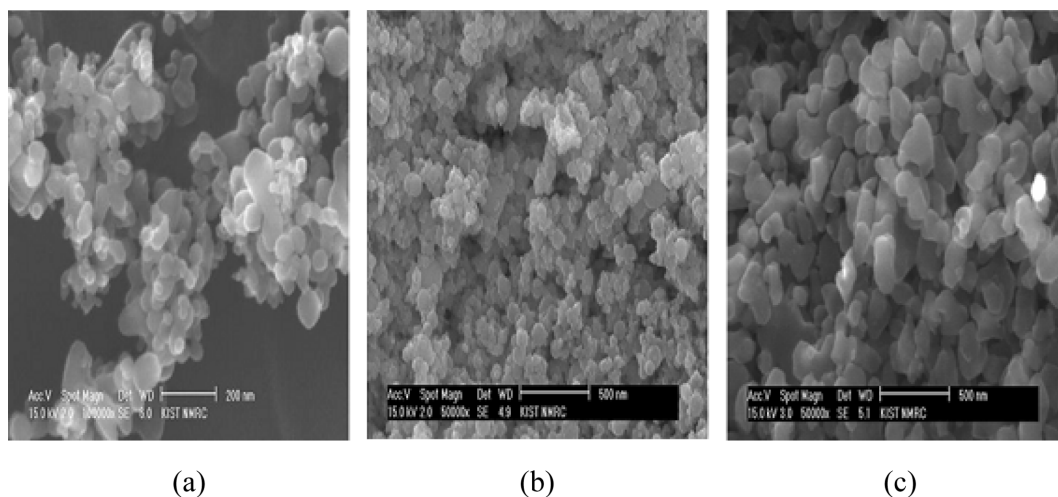


Fig. 1. SEM images of ceramic fillers, (a) TiO_2 , (b) Al_2O_3 , and (c) CaCO_3 .

and dimethyl carbonate (DMC, Aldrich) (EC : DMC=1 : 1). The mixture of liquid electrolyte and PAN/PEGDA polymer (electrolyte : PAN/PEGDA=6 : 1) was agitated at 400 rpm for 7 hrs at room temperature, and nano size inorganic fillers of TiO_2 , Al_2O_3 , and CaCO_3 were added. The amount of inorganic fillers was 1 wt% of the polymer. The mixture was heated slowly and melted up to 160°C . It was poured on a preheated glass plate at 50°C and was cast to 150–170 μm thickness with a doctor blade. PEDGA was cured with 100 W UV lamp (Sanyo Denki GL20, $\lambda=325\text{ nm}$) for 1 hr and gel type PAN/PEGDA polymer electrolyte was manufactured. All processes were carried out in a dry room of moisture content below 10 ppm.

2. Measurement of Gel Polymer Electrolyte Properties

Surfaces of cathode and anode were observed with SEM (Hitachi, model S-4200). The composition of cathode was 90 wt% LiCoO_2 , 6 wt% conductor (SP) and 4 wt% binder (PVdF). The composition of anode was 96 wt% graphite and 4 wt% binder (PVdF). The samples were dried in a vacuum oven for 24 hrs. Ionic conductivity of polymer electrolyte matrix was measured with AC impedance analyzer (Zahner, IM6). AC frequency was 10 Hz–1 MHz, and perturbation voltage was set to 5 mV. For the ionic conductivity measurement, moisture effect was minimized by storing the UV cured polymer electrolyte film in argon filled glove box for 48 hrs. Interface characteristics of lithium metal electrode and gel type polymer electrolyte were measured with AC impedance method according to temperature. Non-blocking cell of Li/GPE/Li structure was assembled and the impedance was measured in open circuit condition at different temperatures. A unit cell of $4 \times 3\text{ cm}^2$ was assembled with UV cured electrode matrix and charge/discharge behavior was examined with battery cycler (Maccor, model 4300) under 3.0–4.2 V and constant current. Charge/discharge experiment was carried out with constant current at C/5–1C rate.

RESULTS AND DISCUSSION

Ionic conductivity can be increased by lowering the crystallization of the polymer, and addition of plasticizer is the most effective method. Gel type polymer electrolyte contains a large amount of low molecular weight polymer and the movement of the polymer

branch is very active, so the ionic conductivity is very high [13]. Addition of ceramic fillers can increase the ionic conductivity and can decrease the interfacial resistance. Fig. 1 shows the ceramic fillers used in this experiment. All fillers are nano-sized and we can expect an increase of ionic conductivity and decrease of interfacial resistance. The ionic conductivity is increased by increasing the ratio of amorphous phase [14]. Dispersion of nano-sized particles can accelerate the formation of stable polymer electrolyte and the decrease of interfacial resistance.

Fig. 2 shows the ionic conductivity as a function of temperature. LiPF_6 has high ionic conductivity, but the ionic conductivity decreases at low temperature. LiCF_3SO_3 has low ionic conductivity but its temperature dependence is very stable. The mixture of LiPF_6 and LiCF_3SO_3 shows high ionic conductivity at both high and low temperature range. When two materials were mixed together, good properties showed up in this case.

An electrochemical safety window of the polymer electrolytes was tested between 3.0–5.5 V. PAN/PEGDA polymer electrolyte showed no current flow up to 4.5 V and the current increased sharply

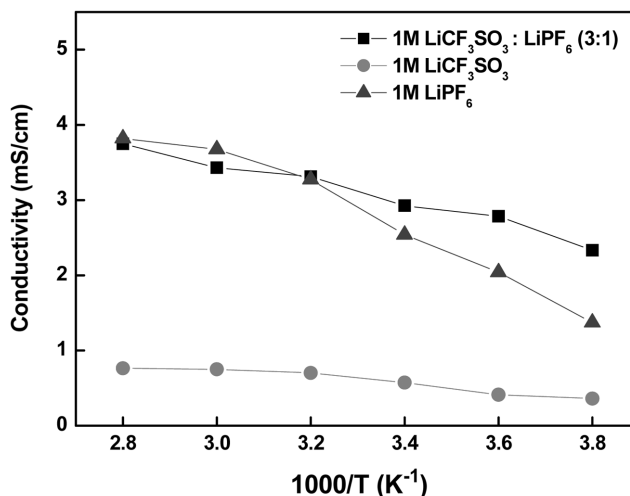


Fig. 2. Ionic conductivity as a function of temperature.

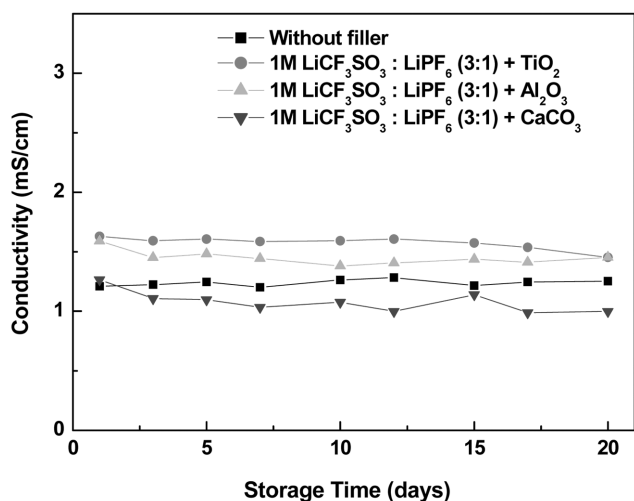


Fig. 3. Ionic conductivity of GPE with various fillers.

over 5.0 V, so it could be used safely for the lithium polymer battery. When propylene carbonate (PC) was used as a solvent, it was decomposed at the graphite anode because of the side reaction. The stability of the battery was decreased due to the gas forming reaction, and the efficiency of the charge/discharge was also decreased. In this study, EC:DMC base solvent was used because it was very stable at the graphite anode.

When inorganic fillers of TiO_2 and Al_2O_3 are added to $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ mixed lithium salt, the ionic conductivity is increased as shown

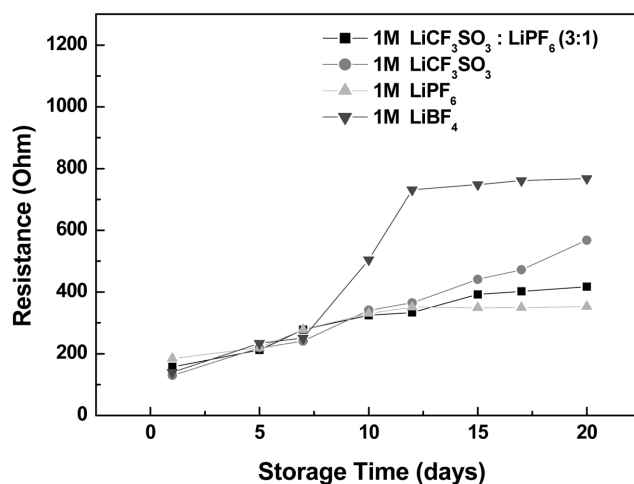


Fig. 5. Interfacial resistance between GPE and lithium metal with various salts.

in Fig. 3. This is because the inorganic fillers are dispersed evenly into the polymer electrolyte and they can provide the passage of ion transfer.

Impedance was measured to test the surface characteristics between Li electrode and PAN/PEGDA polymer electrolyte. The radius of the half cycle increases as time goes on, and it is due to the formation of passivation film on the surface of lithium metal from the reaction of lithium and electrolyte. $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ mixed lithium salt shows very similar impedance as LiPF_6 lithium salt as

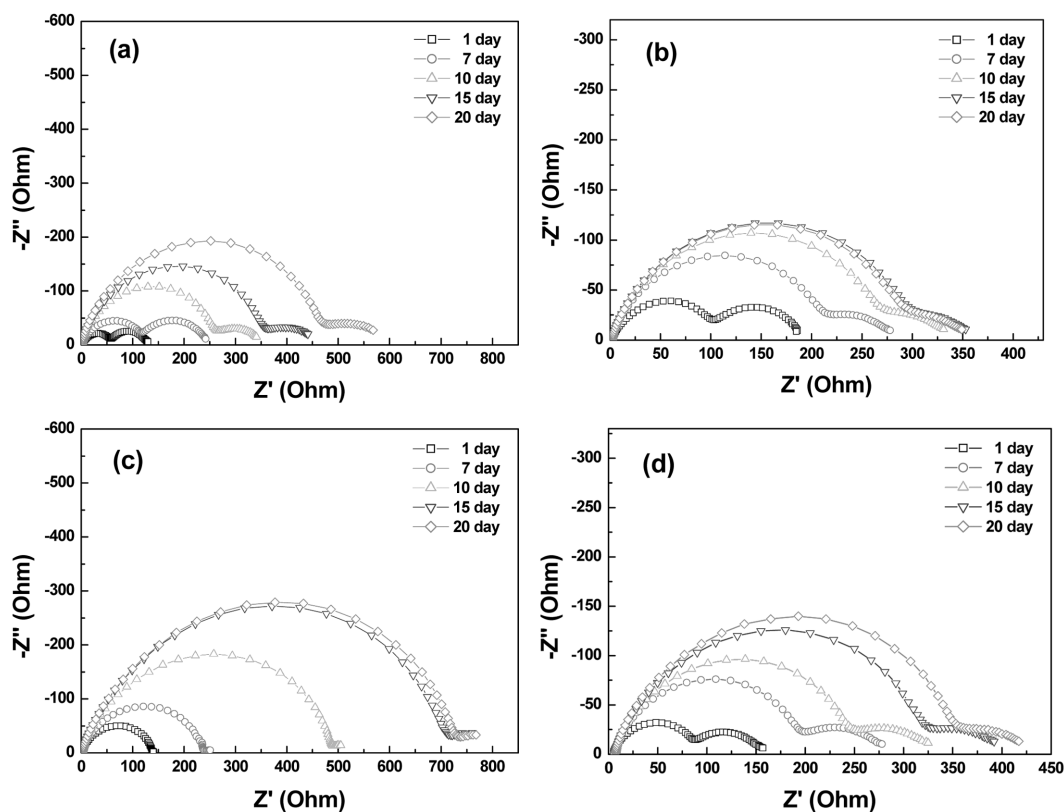


Fig. 4. Electrochemical impedance spectroscopy of GPE with various salts, (a) LiPF_6 , (b) LiCF_3SO_3 , (c) LiBF_4 , and (d) $\text{LiCF}_3\text{SO}_3 : \text{LiPF}_6$ (3 : 1).

shown in Fig. 4.

The resistance of polymer electrolyte is not so high, but the interfacial resistance between the electrode and the polymer is very high. Even if the thickness of the polymer becomes thin, the resistance does not change much because of the interfacial resistance [15]. Fig. 5 shows the changes of interfacial resistance between polymer electrolyte and lithium metal according to time. The difference of interfacial resistance comes from the different reactivity between the electrolyte and the lithium metal, the mixed lithium salt shows the average properties of two salts.

Fig. 6 shows the changes of interfacial resistance between lithium metal and GPE with mixed lithium salt and inorganic fillers of Al_2O_3 , TiO_2 , and CaCO_3 . When TiO_2 was used as filler, the resistance was the lowest after 20 days of storage. Nano-sized inorganic filler can be dispersed uniformly into the polymer matrix, and it can increase the stability of a polymer network. The inorganic filler can preserve the organic solvent into micropores, so the reaction of lithium metal can be reduced to stabilize the interfacial resistance. The polymer electrolyte with $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ mixed lithium salt and

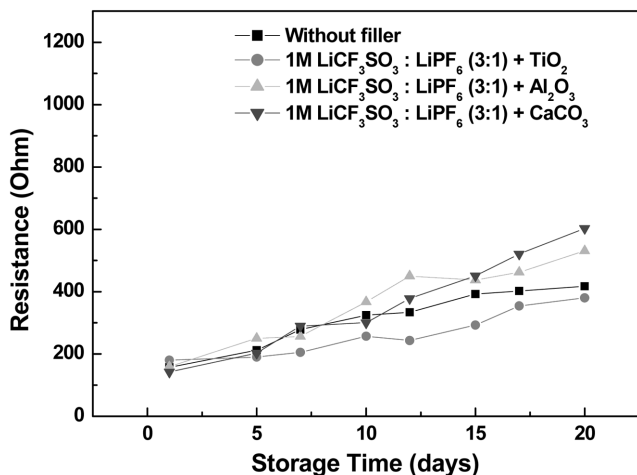


Fig. 6. Changes of interfacial resistance between lithium metal and GPE with mixed lithium salt and inorganic fillers.

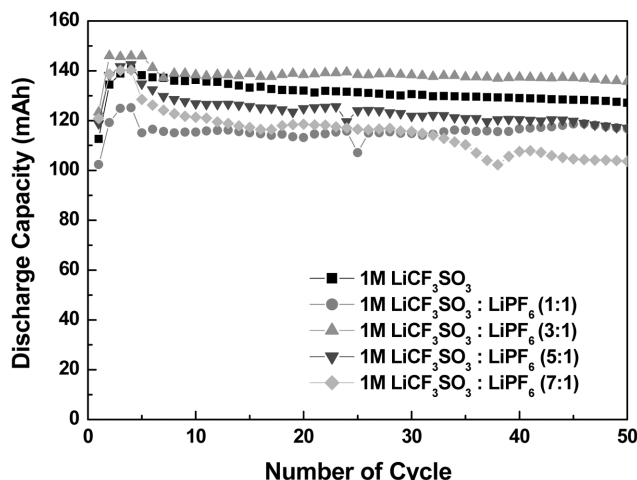


Fig. 7. Effect of lithium salt in GPE on the cycle performance of polymer battery.

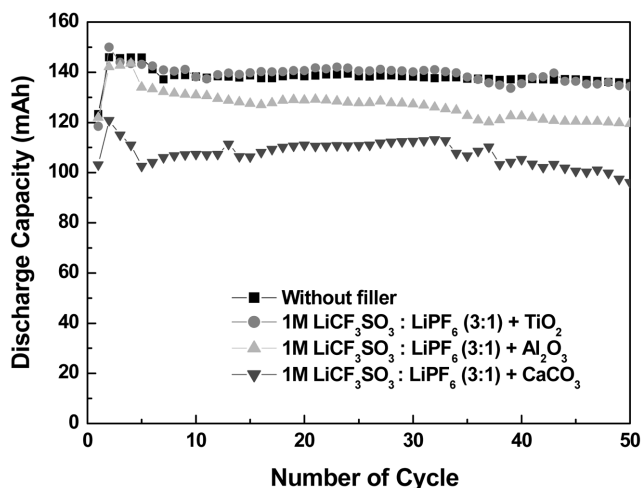


Fig. 8. Effect of filler in GPE on the cycle performance of polymer battery.

inorganic fillers is the optimum material for the anode of the lithium battery [14]. The increase of interfacial resistance increases the internal resistance of the battery, which reduces the capacity and lifetime of the battery.

Changes of discharge capacity according to cycle time are shown in Fig. 7 with various compositions of LiCF_3SO_3 and LiPF_6 . From 1st cycle to 5th cycle the discharge rate was C/5 and after 5th cycle it was changed to C/2. Mixed lithium salt of $\text{LiPF}_6 : \text{LiCF}_3\text{SO}_3$ (3 : 1) shows the smallest changes of discharge capacity when the discharge rate changes from C/5 to C/2. This is due to the formation of stable SEI film [16-18].

Fig. 8 shows the changes of discharge capacity according to cycle time when polymer electrolyte is formulated with mixed lithium salt of $\text{LiPF}_6 : \text{LiCF}_3\text{SO}_3$ (3 : 1) and various inorganic fillers. Addition of inorganic filler can eliminate the possibility of local current flow and the overall battery performance is improved [19,20]. When TiO_2 was used as inorganic filler, the discharge capacity became the highest. Battery performance is affected by the current, especially at large current condition. Uniform interface of the electrolyte is very important to the stability of battery.

CONCLUSIONS

PEDGA is a UV curable oligomer so the crosslinking is initiated by UV or heat. PAN/PEDGA polymer is very stable in ionic conductivity and interfacial resistance for a long storage time. It can be crosslinked in few seconds without heating, so the battery assembly line can be designed as a continuous process and mass production can be possible. Ionic conductivity, electrochemical safety window, and interfacial resistance were measured by using the manufactured polymer electrolyte. Charge/discharge reaction, battery capacity, and cycle lifetime were also measured to conclude the following results.

Weakness of the PAN polymer electrolyte can be complemented by introducing UV curable PEDGA, and discharge capacity, cycle lifetime, and continuous process design can be improved. A mixed lithium salt of LiPF_6 and LiCF_3SO_3 can improve the interfacial resistance because the side reaction between LiPF_6 and fluorine can

be suppressed.

Inorganic fillers with high surface area can affect the crosslinking of polymer electrolyte to improve the chemical stability. Fillers can retain the organic solvent to suppress the side reaction of lithium, so the interfacial resistance and the ionic conductivity can be improved.

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