

## 겔 고분자 전해질을 적용한 리튬금속폴리머전지의 충방전 특성 연구

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**Cycling Characteristics of Lithium Metal Polymer  
Batteries Prepared with Gel Polymer Electrolyte**

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**Introduction**

Polymer electrolytes are receiving considerable attention as solid electrolyte materials in advanced applications such as rechargeable lithium batteries, because the use of polymer electrolytes makes the fabrication of highly safe batteries possible and permit the development of thin batteries with design flexibility [1-3]. Conventional poly(ethylene oxide)(PEO)-based polymer electrolytes are the most commonly studied, and exhibited conductivities ranging from  $10^{-8}$  to  $10^{-5}$  S/cm at room temperature, which excludes practical application at ambient temperature [4]. In order to enhance the room temperature conductivity, several classes of gel polymer electrolytes have been developed and characterized. Gel polymer electrolytes are prepared by incorporating liquid electrolytes into a matrix polymer such as polyacrylonitrile(PAN), poly(vinylidene fluoride)(PVDF), poly(methyl methacrylate)(PMMA) and poly(vinyl chloride)(PVC) [5-9]. The ionic conductivities of these systems exceed  $10^{-4}$  S/cm, which is necessary for battery applications. These plasticized polymer electrolytes combine the best features of both liquid and solid electrolytes [10].

In this work, we prepared the gel polymer electrolytes(GPE) composed of acrylonitrile-methyl methacrylate copolymer and liquid electrolyte. The composite cathode based on  $\text{LiMn}_2\text{O}_4$  was also prepared.  $\text{LiMn}_2\text{O}_4$  was used as an active cathode material due to the low price and low toxicity of manganese. With these materials, we have assembled the Li/GPE/ $\text{LiMn}_2\text{O}_4$  cells and investigated their electrochemical characteristics and cycling performance. The characteristics and electrochemical performance of Li/GPE/ $\text{LiMn}_2\text{O}_4$  cells will be presented and discussed.

**Experimental**

The copolymer used in this work, constituted by acrylonitrile(AN) and methyl methacrylate(MMA) was synthesized via the emulsion polymerization with distilled water. Potassium persulfate( $\text{K}_2\text{S}_2\text{O}_8$ ) was used as a free-radical water-soluble initiator, and sodium lauryl sulfate was used as an emulsifier. For preparing the gel polymer electrolytes with AM copolymer, polymer was first dissolved in anhydrous tetrahydrofuran(THF). After the polymer has completely dissolved, a predetermined amount of liquid electrolyte solution, 1 M  $\text{LiClO}_4$

in ethylene carbonate(EC)/propylene carbonate(PC)(1:1 by volume) was added and the solution was further stirred. The resulting viscous solution was cast with a doctor blade apparatus onto a release paper, then left to evaporate the solvent slowly at room temperature. After complete evaporation of THF, the film was separated from a release paper. The resulting films were transparent, and the thickness of cast film was in the range of 80~100  $\mu\text{m}$ . All procedures for preparing the GPEs were carried out in a dry box filled argon gas. Gel polymer electrolyte film was cut into 4  $\text{cm}^2$  squares and sandwiched between the two stainless steel(SS) electrodes for conductivity measurements. The sandwich was vacuum-packed in an aluminized polyethylene bag in order to avoid contamination. The a.c. impedance measurement was then performed using Zahner Elektrik IM6 impedance analyzer over a frequency range of 100 Hz<sub>1</sub> 1 MHz with an amplitude of 10 mV. The anodic decomposition voltage was determined by running linear sweep voltammetry on a stainless steel working electrode with lithium electrodes as the counter and reference electrode at a scanning rate of 1 mV/sec. The  $\text{LiMn}_2\text{O}_4$  composite cathode on an aluminium foil consisted of  $\text{LiMn}_2\text{O}_4$  with gel polymer electrolyte and super-P carbon at the proportions of 60 : 31 : 9 by weight percent. The anode consisted of 50  $\mu\text{m}$  thick Li foil(Cyprus Foote Mineral Co.) pressed onto Cu current collector. The Li/GPE/ $\text{LiMn}_2\text{O}_4$  cell was assembled by sandwiching the gel polymer electrolyte between the lithium anode and composite  $\text{LiMn}_2\text{O}_4$  cathode. The cell was then enclosed in a metallized plastic bag and vacuum sealed. All assemblies of the cell were carried out in a dry box filled with argon gas. The cycle test of Li/GPE/ $\text{LiMn}_2\text{O}_4$  cell was conducted in the voltage range of 3.0j- 4.3 V at different current densities with galvanostatically controlled equipment.

## **Results and Discussion**

The copolymer comprising about 56 % by mole AN was used a matrix polymer for preparing the gel polymer electrolytes in terms of ionic conductivity and capacity to retain organic liquid electrolyte, as described in the previous work [11]. Gel polymer electrolyte was prepared by film casting from a homogeneous solution which contained 4 wt % AM copolymer, 16 wt % 1 M  $\text{LiClO}_4$ -EC/PC and 80 wt % THF. After solution was cast, we measured the film weight as a function of drying time until the free-standing gel polymer electrolyte film was obtained. With this result, 3 hr is thought to be an enough time to prepare the gel polymer electrolyte with desirable GPE composition. From the quantitative analysis by  $^1\text{H}$  NMR, the gel polymer electrolyte obtained after 3 hr was confirmed to be free of THF and to have a composition of about 80 wt % of liquid electrolyte. The ionic conductivity was measured to be  $1.9 \times 10^{-3}$  S/cm from the electrolyte resistance found a.c. impedance spectrum. Gel polymer electrolytes may undergo solvent exudation upon long storage. This phenomenon, known as the syneresis effect, has been encountered in many gel polymer electrolyte systems [12,13]. The solvent exudation results in a rise in the electrolyte resistance, and finally leads to a gradual degradation of performance for rechargeable lithium battery. In order to investigate the solvent exudation upon long storage in AM-based gel polymer electrolyte, the ionic conductivity was measured as a function of storage time. Ionic conductivity remains nearly constant over period of measured time, which means an absence of loss for liquid electrolyte encapsulated in matrix polymer. Since the MMA unit in the copolymer has a carbonyl group(-COO-) in the side chain, it can be presumed that the MMA unit is compatible with the carbonate-based electrolyte such as EC and PC. A strong specific

interaction between MMA unit and carbonate-based solvent makes the organic solvent with high boiling point difficult to phase-separate from a matrix polymer. Even though these gel polymer electrolytes contain a large amount of organic liquids, it can behave like dry polymer electrolyte at ambient temperature.

For a Li/LiMn<sub>2</sub>O<sub>4</sub> cell, the potential can approach as high as 4.3 V vs. Li/Li<sup>+</sup>, implying that the gel polymer electrolyte should be electrochemically stable up to at least 4.3 V. The electrochemical stability was evaluated by linear sweep voltammetric measurement. As a result, the decomposition voltage was found to be higher than 4.5 V, which suggests that AM-based gel polymer electrolyte is acceptable for LiMn<sub>2</sub>O<sub>4</sub> cathode. With these gel polymer electrolytes, we fabricated Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cells. Fig. 1 shows the charge-discharge curves of Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell at a constant current density of 0.1 mA/cm<sup>2</sup>, which corresponds to charging(or discharging) time of 5 hr(0.2C). This figure shows that the charge-discharge curves have two distant plateaus, which is characteristics of the manganese oxide spinel structure [14,15]. It has been reported that each plateau delivered half of the total capacity, which confirmed the hypothesis that there were two binary equilibrium states during Li<sup>+</sup> intercalation [14]. The coulombic efficiency of this cell was 99.5 %. The Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell delivered 132 mAh/g based on LiMn<sub>2</sub>O<sub>4</sub> active material. Fig. 2 shows the discharge capacities as a function of cycle number in the Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell. The discharge capacity remained about 117 mAh/g at 90 th cycle, which was 89 % of initial capacity. The coulombic efficiency of the cell was more than 99 % through cycling. In the previous work, the passivation of lithium metal in these gel polymer electrolytes was proven to be stable with time [11]. Thus, the capacity decline of Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell may be mainly related to the deterioration of interfacial contacts of composite cathode, as a result of lattice change of the cathode active material during the charge-discharge cycling. A considerable strain on the interface of composite cathode is believed to deteriorate the electrical contact between the surfaces of the insertion particles, and hence to decrease the capacity of the cathode during repeated charge-discharge cycling.

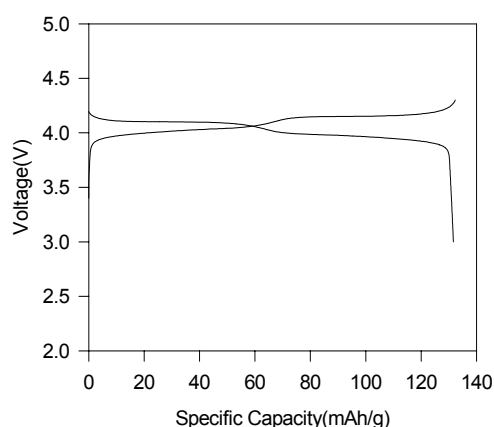


Fig. 1. Charge-discharge curve of Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell at 0.2C rate.

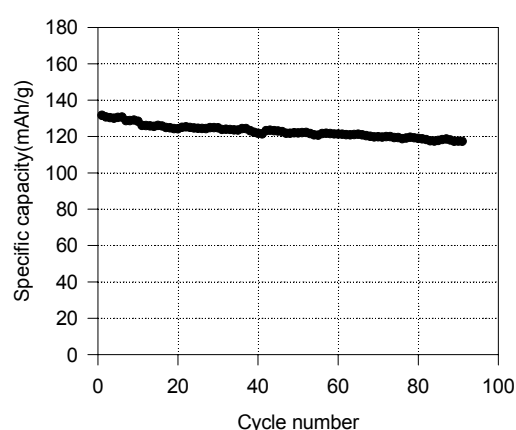


Fig. 2. Discharge capacities of Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell as a function of cycle number.

With these gel polymer electrolytes, we tried to obtain the rate capability of Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cells. It is observed that the polarization was increased as the current rate increased, which results in the decrease of capacity. The discharge capacity is found to drop to 58 mAh/g at a current density of 1.0 mA/cm<sup>2</sup>. The reduced capacity at high current rate is due to the high value of resistance of gel polymer electrolyte. The larger resistance of gel polymer electrolyte due to the thick film (~100 μm) as compared to that of separator with liquid electrolyte (~25 μm) may limit the cycling rates for the Li/LiMn<sub>2</sub>O<sub>4</sub> cell.

### **Conclusions**

Gel polymer electrolyte composed of AM copolymer and LiClO<sub>4</sub>-EC/PC showed high ionic conductivity and sufficient electrochemical stability to allow safe operation in Li/LiMn<sub>2</sub>O<sub>4</sub> cells. A strong specific interaction between MMA unit and carbonate-based solvent makes the organic solvent difficult to exude from a matrix polymer. The Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> cell showed a stable discharge capacity of about 130 mAh/g.

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