

## New Solid Polymer Electrolyte for Lithium Secondary Batteries

*Jung-Ki Park\*, Yong Min Lee,  
Jun Young Lee, and Myeong Hyeon Ryou*

Department of Chemical and Biomolecular Engineering, KAIST  
373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Korea  
jungpark@kaist.ac.kr

### Introduction

As the world becomes increasingly dependent on portable electronic devices such as cellular phone, PC, PDA and also on electrical vehicles, the use of lithium secondary batteries continuously increases as well. In addition to high performance, it becomes more important to sustain the safety of lithium secondary batteries. In accordance with this, the development of highly conductive electrolytes without any problems associated with volatile and combustible solvents may be required. Solid polymer electrolytes (SPEs) can essentially reduce many chemical side reactions which can lead to explosion in lithium secondary batteries.

Solid polymer electrolytes based on polymer matrix including poly(ethylene oxide) (PEO) have attracted considerable attention since 1970s due to their potential application in solid-state rechargeable lithium batteries. However, they show low ion conductivity and high interfacial resistance at room temperature due to lower mobility of ions in polymer matrix. There have been various efforts to resolve these problems. However, they could not attain the sufficient ion conductivity level ( $\sim 10^{-3}$  S/cm) for practical applications. Although gel polymer electrolytes were developed by adding organic solvents into SPEs to obtain high ionic conductivity on the order of  $10^{-3}$  S/cm, their mechanical strength deteriorates significantly as the content of organic solvent increases. As a result, gel polymer electrolytes reinforced by microporous separator based on typically polyethylene were suggested for practical application. Since they can show high ion conductivity without sacrificing mechanical strength and utilize conventional lithium ion batteries (LIBs) process line, they were easily commercialized as lithium ion polymer batteries (LIPB). However, the usage of organic solvents may inherently cause safety problems.

Therefore, development of pure SPEs without containing volatile organic solvents is still much needed. Unfortunately, it is true that there is a dilemma between ionic conductivity and mechanical strength of SPEs. The ion conductivity of SPE can only be enhanced by making polymer matrix more flexible, but, in that case, its mechanical strength is inevitably deteriorated.

In order to overcome this dilemma, in this work, we consider SPEs consisting of two separate phases: One serves as mechanical supporter, and the other does ion conduction. The main advantage of this system is that the conductivity of ion conduction phase can be highly enhanced by making polymer matrix flexible as much as possible within a range of sustaining dimensional stability.

The salt decomposition causing safety problems is also very significant at rather high voltage and thus the prevention of its decomposition needs to be carefully designed. In this work, we introduce an organic-inorganic hybrid lithium salt to enhance the electrochemical stability window of solid polymer electrolyte.

### Experimental

#### Preparation of polymer electrolyte

Solid polymer electrolyte films were prepared by spreading an UV-curable SPE precursor solution on the PE non-woven matrix and they were irradiated with UV. The SPE precursor solution consists of crosslinking agent, non-volatile plasticizer (PEGDME), anion receptor, hybrid salt, and photoinitiator. The salt was added into SPE precursor solution with a concentration of EO:Li=20:1.

#### Electrical measurements

The ionic conductivities of SPEs were obtained from bulk resistance by a.c. complex impedance analysis over a frequency range

of 100Hz~1MHz. The characteristics of the interface between SPE and lithium electrode were examined by monitoring the time dependence of the impedance of symmetrical Li/SPE/Li cells.

The transference number was determined by DC polarization/AC impedance combination method. A constant polarization of 10mV was applied to the cell. A linear sweep voltammetry experiment was performed at a scanning rate of 1.0 mV/s.

The unit cell was assembled by sandwiching the SPE between Li anode and  $\text{LiCoO}_2$  cathode. The cell ( $2 \times 2 \text{ cm}^2$ ) was then sealed in an aluminized polyethylene bag. The unit cell was cycled between 3.0V and 4.2V at a constant current density at room temperature.

### Results and Discussion

We used non-woven matrix as a mechanical supporter for SPE. It consists of PE fibers with about 20  $\mu\text{m}$  diameter and it has very porous structure. This morphological characteristic is very important to make high conductive SPE, because ion conduction can take place only through the pores filled with electrolytes. In addition, the mechanical strength of bare non-woven matrix is strong enough to maintain the dimensional stability of SPE.

The pores of the PE non-woven matrix are completely filled with ion conduction phase, which consists of crosslinked component, non-volatile plasticizer, anion receptor (PEGB), and lithium salt. The prepared SPE exhibits good mechanical strength. The thickness of the prepared SPE is strongly dependent on that of PE non-woven matrix and the amount of an UV-curable SPE precursor solution to be spread on the matrix. The thicknesses of the prepared SPEs in this work were controlled in the range of 60 ~ 120  $\mu\text{m}$ .

An Arrhenius plot of ionic conductivities for SPEs with and without containing anion receptor is shown in Fig. 2. The measurement was conducted from  $-10^\circ\text{C}$  to  $60^\circ\text{C}$  by every  $10^\circ\text{C}$ . It is found that SPE with anion receptor have higher ionic conductivity of  $5 \times 10^{-4}$  S/cm. It is because that the anion receptor (PEGB) contributes to enhancing the dissociation of lithium salt.

Figure 3 shows the linear sweep voltammetry curves of SPE with hybrid salt. It has high electrochemical stability up to 5.5V.

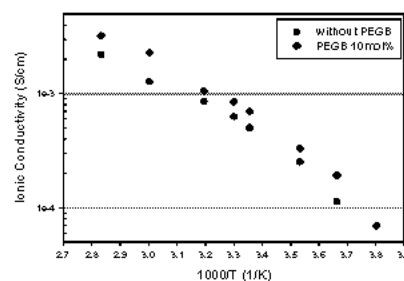


Figure 2. Ion conductivities of SPEs with temperature.

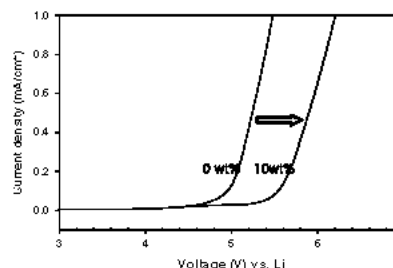


Figure 3. Electrochemical stability window of polymer electrolyte with hybrid salt

### Conclusion

SPEs based on PE non-woven matrix, hybrid salt, and anion receptor were successfully prepared. They could provide high ion conduction phase through the pores of the PE non-woven matrix and also good mechanical strength of the SPE film. They also showed high electrochemical stability and lithium ion transference number. This new type of solid polymer electrolyte is expected to be a good candidate for rechargeable solid state lithium secondary batteries.