All-Solid Polymer Lithium Ion Battery at Higher Temperatures

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The rechargeable lithium ion battery (LIB) has crucial demands of our modern society, such as power source of various devices, EV and HEV. However, conventional LIB suffer from safety problems because they contain volatile and flammable organic solvents in the electrolyte solution. In order to improve the safety, alternative material systems for the electrolyte are urgently desired today. In this respect, there are many studies for developing (1) inorganic solid compound electrolytes, (2) ionic liquid electrolytes, (3) poly(ethylene oxide) (PEO) which has been known to be typically representative of the polymer matrix for all solid polymer electrolytes(SPEs). We thought that the selection of the PEO-based SPEs would be the fastest way for the realization of large-scale LIB with nonflammable property. While PEO-based SPEs containing supporting agent LITFSI have relatively low ionic conductivity (10^{-7} to 10^{-5} S cm^{-1}) at a room temperature. In our group, the addition of aluminate ester (Al-PEG) to monomer (poly(ethylene glycol) mono-methacrylate) (MPG-130MA) containing LITFSI has been tried for anticipating both the increase of the ionic conductivity from the effect of the Lewis acidity of Al in Al-PEG and of the nonflammable property. Al-PEG usually has three EO chains with each methyl end and works as a plasticizer. In other words, we expected the easier diffusion of lithium ion by adding Al-PEG at the first stage[1)]. On the other hand, it is very important to maintain stable and continuous segmental motion of lithium ion in polymer matrix. Accordingly we tried that one of the methyl ends of Al-PEG was replaced by methacrylate ($-CO(CH_3)C=CH_2$) in the present study. It is considered that the C=C double bond in the monomer of both MPG-130MA and Al-PEG might react in each other during polymerization reaction by heating or irradiating UV and form stable polymer chain for keeping up good segmental motion of lithium ion conduction. The Al-PEG in the present study is no longer in the state of a plasticizer but has a roll of part of matrix polymer. In some of the SPEs, 20wt%of triglyme (DMTG) was added to monomer as a prasticizer to increase the ionic conductivity of lithium ion.

The ionic conductivity of obtained SPE containing 5wt% of Al-PEG showed 10^{-4} S cm^{-1} at 60 degree C and the value was a little higher than that of the SPE without Al-PEG ($10^{-4.7}$ S cm^{-1}). Also Cyclic voltammogram of the same SPE showed stable behavior in the voltage range between 2.0 V and 5.0 V at temperatures until 70 degree C.

We constructed laminate-type cell using the SPE containing 5wt% of Al-PEG. $LiFePO_4$ (LFP) and $Li_4Ti_5O_{12}$ (LTO) were selected as the cathode and the anode, respectively. Relatively high charge discharge performance was observed even at a high temperature 100 degree C. In this case, no prasticizer (DMTG) was added, because easier volatility happened at such higher temperatures.

Reference

1) M. Wakihara, Y. Kadoma, N. Kumagai, H. Mita, R. Araki, K. Ozawa and Y. Ozawa, J.

Solid State Electrochem., 16, 847 (2012).