
Polymer Electrolytes and Their Electrochemical Interfaces

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In order to realize all solid high energy density batteries, polymer electrolytes have received much attention. Especially, it is expected that application of the polymer electrolytes to lithium batteries could overcome problems concerned with safety. We have studied to attain highly ionically conducting polymer electrolytes and developed new network polymer electrolytes having many chain ends¹⁾. However, charge transfer resistance (R_{ct}) between a highly conductive polymer electrolyte and lithium electrodes is much higher than the polymer electrolyte bulk resistance, especially at low temperatures.

In this study we will discuss the factors dominating R_{ct} between polymer electrolytes and lithium electrodes, especially the relationship between the density of free chain ends in network polymer electrolytes and R_{ct} .

Polymer electrolytes having different densities of free chain ends were synthesized as the following procedures. The mixtures of mono-acrylated poly(ethylene oxide-co-propylene oxide) (P(EO/PO)) (MA) and tri-acrylated P(EO/PO) (TA) as shown in Fig. 1, LiN(CF₃SO₂)₂ (LiTFSI) or LiClO₄ and or LiBF₄ and a photo-initiator were cast between glass plates and irradiated with UV light for 5 min. Ionic conductivity of the polymer electrolytes and R_{ct} at the polymer electrolyte/lithium were measured by AC impedance analysis with lithium electrodes.

Ionic conductivity for the polymer electrolytes is different, depending on the density of free chain ends in the network polymer electrolytes, namely the polymer electrolytes having the largest number of ether side chains show the highest ionic conductivity although glass transition temperature is approximately the same. Fig. 2 shows the relationship between R_{ct} and the ionic conductivity for the polymer electrolytes at 60 °C studied in this work. It is clearly indicated that R_{ct} decreases with increasing the ionic conductivity. The big difference of R_{ct} between LiBF₄ and the other salts is observed even if the same matrix polymer is used. On the other hand, in terms of the density of ether side chains, the polymer electrolytes having the largest number of ether side chains show much lower R_{ct} . It is suggested that R_{ct} correlates with the density of ether side chains in the polymer electrolytes.

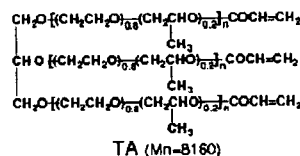
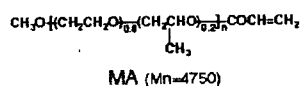


Fig. 1 Structure of P(EO/PO) mono-acrylate (MA) and tri-acrylate (TA) macromonomers.

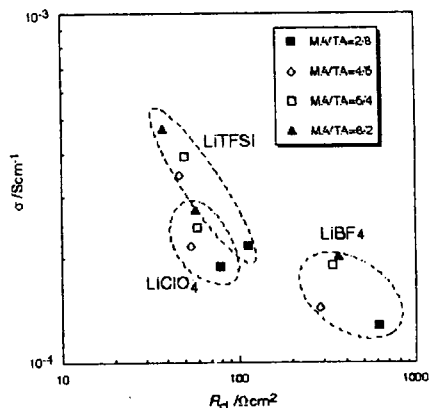


Fig. 2 Ionic conductivity plotted against charge transfer resistance at the interface with lithium electrodes for network polymer electrolytes containing a lithium salt ([Li]/[ether oxygen]=0.04) at 60 °C.

References

1) M. Kono, E. Hayashi and M. Watanabe, *J. Electrochem. Soc.*, **145**, 1521-1527 (1998).