

## Charge-Transfer Reaction Rate at the $\text{LiMn}_2\text{O}_4$ Spinel Oxide Cathode / Electrolyte Interface

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Over the past decades, numerous researches have been carried out on the characteristics of the bulk properties of electrode materials and electrolytes in lithium ion secondary batteries. On the other hand, only a few investigations have been focused on the charge-transfer reaction at the electrode surfaces[1], and the details of the charge-transfer reaction remain to be discussed.

In the present work, the electro-kinetics of the charge-transfer reaction at the interface between thin film of lithium cathode material and polymer electrolyte along with lithium intercalation was investigated using electrochemical impedance spectroscopy(EIS). Spinel compounds were used as thin film materials, and we utilized poly(ethylene glycol) dimethyl ether (PEGDME) based electrolytes. To clarify the key factors which influence the charge-transfer reaction rate at the interface, we measured charge-transfer resistance by EIS in PEGDME based electrolytic solution, whose average molecular weight is 500 (herein after PEGDME500) by adding various amounts of higher molecular weight polyether, PEGDME1000.

Thin film electrode without any co-additives was prepared by the electrostatic spray deposition (ESD) technique. In this technique, a precursor solution is atomized into charged droplets in an electric field. These droplets are electrohydrodynamically carried to a heated substrate, causing film deposition. It has shown many advantages over other conventional deposition techniques, such as relatively simple set-up, an excellent control of stoichiometry and easy control of the morphology of the deposited film[2]. The aspect of morphology control is especially indispensable to analyze surface reaction properties exactly.

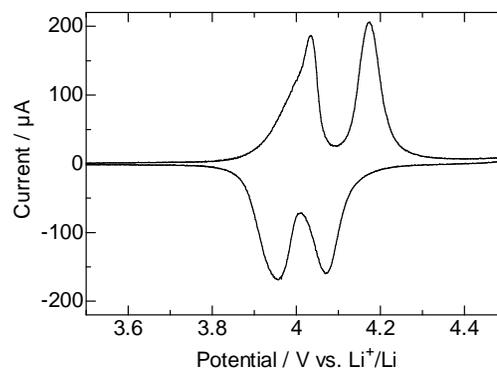
Fig. 1 shows cyclic voltammogram of the  $\text{LiMn}_2\text{O}_4$  thin film electrode in 1M  $\text{LiClO}_4/\text{EC-DEC}$ . Two pairs of sharp peaks which show typical  $\text{LiMn}_2\text{O}_4$  spinel oxide with high crystallinity were observed. These curves reflect oxidation and reduction reactions that correspond to Li ion extraction/insertion occurred properly.

The results of electrochemical impedance spectroscopy showed that the obtained charge-transfer resistances of various PEGDME based electrolytic solutions increased with increasing amount of PEGDME1000. Exchange current density of the charge-transfer reaction is inversely proportional to charge-transfer resistance. Furthermore, exchange current density depends on some factors, such as Gibbs activation energy and viscosity of electrolyte. The charge-transfer resistances were plotted in Arrhenius type in Fig. 2. This result indicates that all arrhenius plots exhibit parallel linear relationships. Accordingly, calculated Gibbs activation energies were almost constant in all PEGDME based electrolytic solutions. In addition, the results of

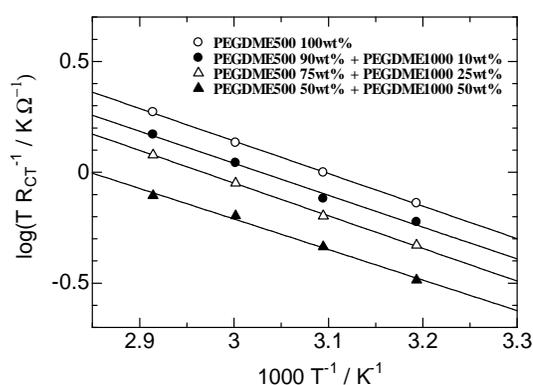
Fig.3 show the relationships between the charge-transfer resistances and the viscosities of the electrolytic solutions. These results indicate that the charge-transfer reaction rate is inversely proportional to viscosities of the electrolytic solutions. Therefore, it is suggested that the viscosity of the electrolyte is one of the most important factors for the charge-transfer rate in lithium intercalation process.

### References

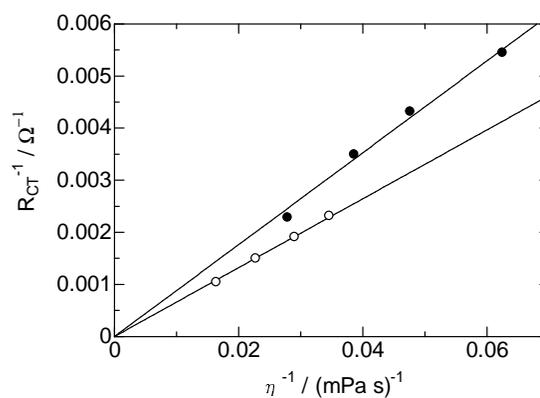
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**Fig. 1**  
Cyclic voltammogram of the  $\text{LiMn}_2\text{O}_4$  thin film electrode in 1M  $\text{LiClO}_4 / \text{EC-DEC}$  at 3mV/s.



**Fig. 2**  
Arrhenius plots for the charge-transfer resistances ( $R_{ct}$ ) at 4.0V in 0.5M  $\text{LiCF}_3\text{SO}_3 / \text{PEGDME500}$  with various amounts of PEGDME1000.



**Fig. 3**  
Inverse of charge-transfer resistances( $R_{ct}$ ) vs inverse of viscosities of 0.5M  $\text{LiCF}_3\text{SO}_3 / \text{PEGDME500}$  with various amounts of PEGDME1000 at various temperatures: ○ at 313K, ● at 343K.