

Electrochemical Impedance Study of Li-Ion Extraction/Insertion at LiMn₂O₄ Single Particle Electrodes

K. Dokko, M. Mohamedi, M. Umeda, I. Uchida

Department of Applied Chemistry, Tohoku University
07 Aramaki Aoba, Aoba-ku, Sendai 980-8579, Japan

Using a microelectrode technique, cyclic voltammetry (CV), potential step chronoamperometry (PSCA) and electrochemical impedance spectroscopy (EIS) were performed to investigate the electrochemical properties of a polycrystalline LiMn₂O₄ single particle (18 μm diameter). The apparent chemical diffusion coefficient (D_{app}) of Li-ion in LiMn₂O₄ particle was determined from both PSCA and EIS, whereas the charge transfer resistance was also evaluated from EIS.

The experimental set up is described in our previous paper [1]. The electrical contact between the LiMn₂O₄ single particle and a Pt filament (10 μm diameter) was done using a micro-manipulator under microscope observation, then electrochemical measurements were carried out. Polycrystalline LiMn₂O₄ was supplied from Nikki Chemical Company, Japan. A lithium foil (1 cm^2) served as a reference electrode and the electrolyte was 1M LiClO₄/propylene carbonate + ethylene carbonate (1:1 in volume). Electrochemical measurements were carried out in a dry box filled with dry air (-50 $^{\circ}\text{C}$ dew point) at room temperature. EIS measurements were carried out using a frequency response analyzer (Solartron 1260) combined with a potentiostat (PAR 283). The applied alternating voltage signal was 5 mV-rms and the frequency range was 110 kHz-11 mHz. Impedance spectra were modeled using a modified Randles-Ershler circuit [2].

Figure 1 shows CV at 0.2 mV/s for a LiMn₂O₄ single particle (18 μm diameter). Two well-defined current peaks characteristics of Li-ion extraction/insertion between LiMn₂O₄ and λ -MnO₂ can be seen at 4.00 V (A/A') and at 4.10 V (B/B'), respectively.

Figure 2 shows a typical EIS of LiMn₂O₄ particle taken at a potential of 4.13 V. The magnitude of the resulting impedance was of M Ω order because of the tininess of electrode. The spectra exhibited a slightly depressed semicircle in the high frequency region due to charge transfer process, and a Warburg-type element at the low frequency region. The size of the semicircle depended on the electrode potential and became smallest at 4.13 V corresponding to the CV peak B/B' (Fig. 1). D_{app} was determined from the Warburg impedance. D_{app} changed depending on the electrode potential in the range of 10^{-10} - 10^{-6} cm^2/s . Recently, we reported chemical diffusion coefficient of Li-ion in LiMn₂O₄ single crystal as 10^{-11} cm^2/s [4], which is smaller than D_{app} evaluated from a polycrystalline particle in this work. This suggests that the Li-ion transfer in polycrystalline particle is faster than in single crystal.

References

1. M. Nishizawa, I. Uchida, *Electrochim. Acta*, **44**, 3629 (1999).
2. K. Dokko, M. Mohamedi, Y. Fujita, T. Itoh, M. Nishizawa, M. Umeda, I. Uchida, *J. Electrochem.*

Soc., **148**, A422 (2001).

3. K. Dokko, Y. Fujita, M. Mohamedi, M. Umeda, I. Uchida, J. R. Selman, *Electrochim. Acta*, **47**, 933 (2001).
4. K. Dokko, M. Nishizawa, M. Mohamedi, M. Umeda, I. Uchida, J. Akimoto, Y. Takahashi, Y. Gotoh, S. Mizuta, *Electrochem. Solid-State Lett.*, **4**, A151 (2001).

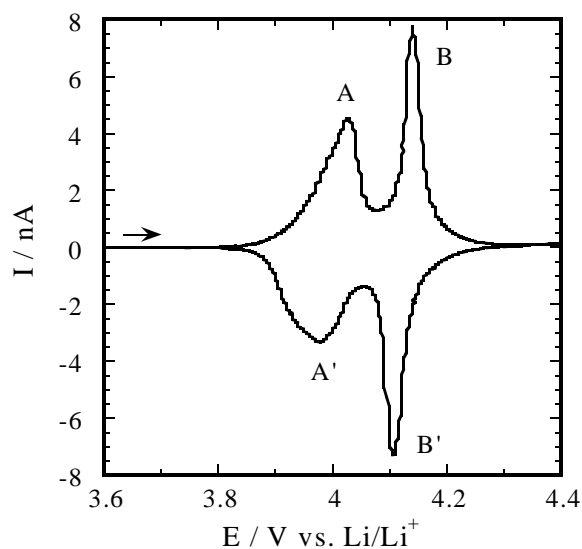


Fig. 1 Cyclic voltammogram of a LiMn₂O₄ single particle (18 μm diameter) taken at 0.2 mV/s in 1M LiClO₄/PC+EC.

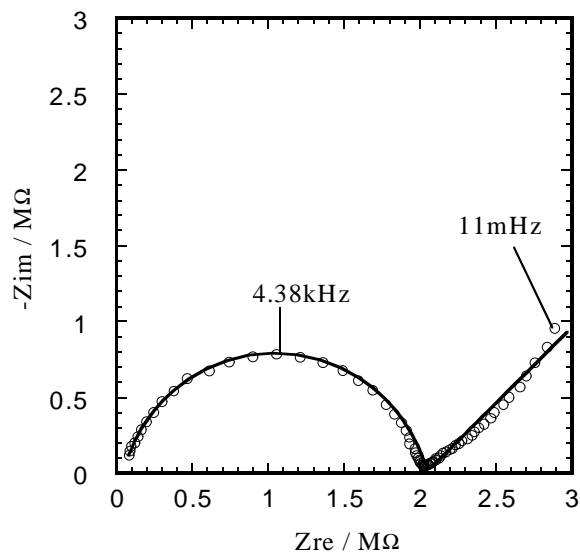


Fig. 2 Typical EIS obtained for a LiMn₂O₄ single particle (18 μm diameter). Electrode potential was 4.13 V.