Ac Impedance Spectroscopic Analysis of $LiMn_2O_4$ Positive-electrodes for Deterioration Diagnosis of Lithium-ion Batteries

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Introduction

In recent years, large-format lithium ion batteries (LIBs) have been intensively developed for use in hybrid vehicles, electric vehicles and large-scale energy storage. Diagnosing systems with low cost and easy operation are required to detect the state of deterioration in LIBs and improve the charge/discharge performances. Electrochemical impedance spectroscopy (EIS) is one of the powerful techniques for the diagnosis because it can separate the impedance into each component of the internal resistances [1]. We are developing an analysis method using Z transformation by which the state of deterioration of LIBs can be evaluated from transient responses without interrupting operation. This analysis method needs information on the frequency range that closely relates to the deterioration of LIBs.

In this study, we investigated electrochemical properties of $LiMn_2O_4$ electrodes by EIS. In addition, surface analysis of the $LiMn_2O_4$ electrode was conducted by X-ray photoelectron spectroscopy (XPS) to elucidate the changes in the impedance in detail [2].

Experimental

Composite electrodes were prepared from a slurry of commercially available $LiMn_2O_4$, acetylene black and poly(vinylidene fluoride) with a weight ratio of 8:1:1 dissolved in 1-methyl-2-pyrrolidinone. The slurry was coated onto Al-foil, and then dried at 80°C under vacuum for 18 h. The counter and reference electrodes were Li foil. The electrolyte solution used was 1 M $LiPF_6$/EC+DEC (1:1 by vol.). Charge-discharge characteristics were evaluated by constant current-constant voltage (CC-CV) charge/ discharge tests with a three-electrode coin-type cell. The durability tests were performed at 30 and 60^{o}C. Ac impedance spectra were obtained at the 50th cycle over a frequency range of 100 kHz to 1 mHz at 30^{o}C at several depths of discharges (DODs) using a galvanostatic intermittent titration technique (GITT).

Results and Discussion

Figure 1 shows the variations of discharge capacity retention for $LiMn_2O_4$ electrodes at 30 and 60^{o}C. The discharge capacity gradually decreased with increasing cycle number at 60ºC, while it remained almost constant at 30^{o}C.

Nyquist plots of the $LiMn_2O_4$ electrodes after 50 cycles at 30 and 60^{o}C are shown in Figure 2. The total resistance significantly increased at 60^{o}C, compared to that at 30^{o}C. Thus, the capacity fading is closely related to an increase in the internal resistance upon cycling. The two semi-circles were observed in the frequency range > f=1 Hz, which are assigned to the resistances of surface films and interfacial charge transfer at $LiMn_2O_4$. Both became larger at 60^{o}C than 30^{o}C. These results suggest that transient responses need to be measured with intervals shorter than 1 s (=1/f) for deterioration diagnosis by the Z transformation method.

Reference

[1] M. Itagaki *et al.*, *Electrochim. Acta*, **51**, 1629 (2006).
[2] T. Maekawa *et al.*, *the 53rd Batteriy Symposim in Japan*, 2A10.

Acknowledgement

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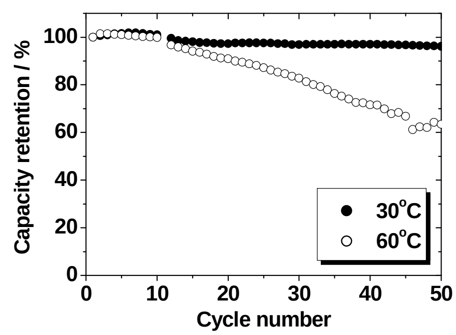

Figure 1 Variations of discharge capacity retention for $LiMn_2O_4$ electrodes with cycle number at C/4 rate between 3.5-4.3 V in 1 M $LiPF_6$/EC+DEC (1:1).

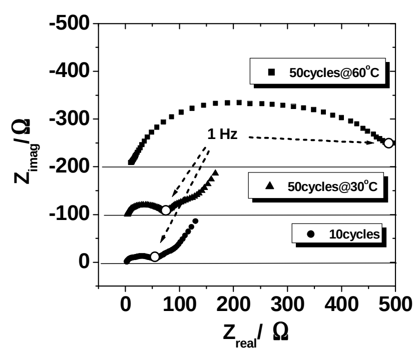

Figure 2 Nyquist plots of the $LiMn_2O_4$ electrodes at around 3.83V during discharging at C/4 rate in 1 M $LiPF_6$/EC+ DEC (1:1).