Electrolyte Effect on Electrochemical Properties of $LiMn_2O_4$ Evaluated with Impedance Measurements

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Introduction: $LiMn_2O_4$ has been widely used as a cathode material in lithium-ion batteries (LIBs) because of its acceptable cost and high energy density. However, it suffers from severe degradation, leading to shortening the cycle and calendar life of the LIBs. Since the degradation at the surface of $LiMn_2O_4$ has a dominant effect on the durability, it is important to comprehend the surface degradation phenomena. Recently, it has been shown that surface-film formation behavior of $LiMn_2O_4$ thin-film electrodes was largely varied with electrolytes [1-2]. Hence, it is considered that the surface-film formation process in the $LiMn_2O_4$ composite electrode is also influenced by the electrolyte, determining long-term cycleability of the electrodes. In this study, the effect of the electrolyte on the electrochemical properties of the $LiMn_2O_4$ composite electrodes was investigated.

Experimental: $LiMn_2O_4$ powder was prepared by Pechini process using $LiNO_3$, $Mn(NO_3)\cdot 4H_2O$, and citric acid as starting materials. The cathode active materials thus obtained were mixed with 10 wt% acetylene black and 10 wt% polyvinylidene difluoride in N-methyl-2-pyrrolidone solution, and casted on aluminum foil. For electrochemical measurements, lithium metal and 1 mol dm^{-3} $LiPF_6$/ethylene carbonate: dimethyl carbonate (1: 1) were used as a counter electrode and an electrolyte solution. The ac impedance measurements were carried out during charge/discharge tests with frequency range between 3 MHz and 40 mHz.

Results and Discussion: Fig.1 shows scanning electron microscopic image of prepared $LiMn_2O_4$ particles. It showed that sub-micrometer particles, which was much smaller than those of commercially used ones, were prepared. Since the smaller particle has larger specific surface area, it is suitable for focusing on the effect of surface-film formation on the electrochemical properties. Fig. 2 shows Nyquist plots of the cell measured at 4.3 and 3.0 V during the 13th discharge process. Since the semicircle at the medium frequency region showed potential dependence, it was attributed to the charge-transfer resistance. The semicircle at the lowest frequency was observed only at the 4.3 V. Therefore, it was considered to be the resistance derived from the surface film. On the meeting, the electrolyte effect on the electrochemical properties will be discussed.

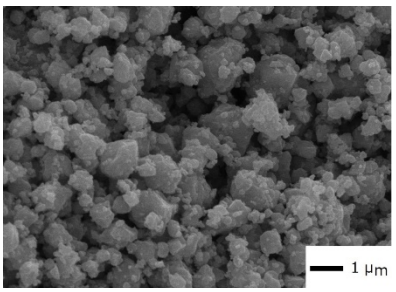

Fig. 1 SEM image of prepared $LiMn_2O_4$ particles.

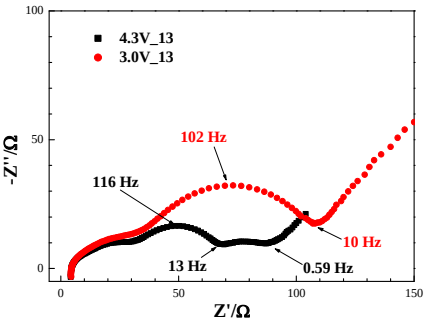

Fig. 2 Nyquist plots of the cell measured at 4.3 and 3.0 V during the 13th discharge process.

References:
[1] J. Inamoto, et al., 230th *ECS Meeting Abstract*, (2016) A01#5.
[2] J. Inamoto, et al., *ChemistrySelect*, **2** (2017) 2895.