

Deterioration Analysis of Li-rich Layered Oxide Positive Active Materials with Different Composition after Charge/Discharge Cycling Test

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1. Introduction

Li-rich layered oxide shows higher specific capacity as a positive active material than conventional layered oxides such as $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and thus is a promising material to achieve next generation Li-ion battery with higher energy density. However, this oxide shows serious capacity and voltage fading through prolonged charge/discharge cycling^[1]. In this research, two kinds of Li-rich layered oxides before and after a cycling test have been investigated in order to obtain the insight to improve their electrochemical properties.

2. Experimental

Two kinds of Li-rich layered oxides, $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMeO}_2$ (Me = 3d transition metal) with different x values were used as analysis samples. These Li-rich layered oxides were supplied by BASF TODA Battery Materials LLC. Charge/discharge cycling tests for 50 times between 2.0 and 4.6 V were conducted using half-cells with a metallic Li counter electrode. Discharge curves before and after the cycling test were measured at 30 mA g^{-1} . The crystal structure analysis of the pristine sample and samples before and after the cycling test was carried out by means of synchrotron X-ray diffraction in BL02B2, SPring-8. Rietveld analysis was conducted using RIETAN-2000 software supposing space group of R-3m.

3. Results and Discussion

Figure 1 shows discharge curves of the half-cells before and after the cycling test. Discharge capacity and average discharge voltage retention are much retained for low x value. Figure 2 shows the change of transition metal occupancy at 3a (Li) site and oxygen occupancy at 6c site before and after the test. Both samples show the increasing of cation disorder and the decreasing of oxygen occupancy through the cycling test, and the degrees of these changes for low x value is suppressed. These results imply that the crystal structure is much retained for low x value. That is, low x value gives both improvement of electrochemical property and stability of the crystal structure. Details will be discussed on the poster presentation.

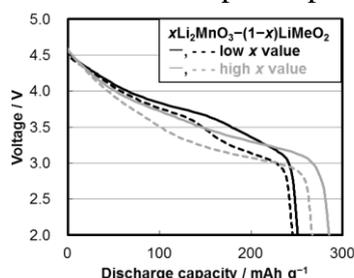


Figure 1 Discharge curves of $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMeO}_2$ (black line; low x value, gray line; high x value); (solid) before and (dotted) after cycling test at 30 mA g^{-1} at 25°C .

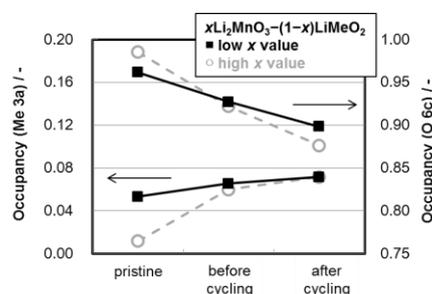


Figure 2 Transition metal (Me) occupancy at 3a (Li) site and oxygen occupancy at 6c site in $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMeO}_2$ refined by Rietveld analysis; (■) low x value and (○) high x value.

References: [1] J. R. Croy et al., J. Phys. Chem. C 117 (2013) 6525–6536.