

Analysis of Deterioration Mechanism of Li-rich Layered Oxide Positive Active Materials after Long Charge/Discharge Cycles

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1. Introduction

Li-rich layered oxide positive active material ($x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMeO}_2$ (Me = 3d transition metal)) draws much attention because of its higher capacity ($> 240 \text{ mAh g}^{-1}$) and lower cost of Mn than that of Co and Ni. However, this active material suffers from capacity and voltage fading^[1] through charge and discharge cycling test. In this research, the deterioration mechanism has been investigated focusing on valence change of transition metal on long charge and discharge cycles by using synchrotron radiation.

2. Experimental

Li-rich layered oxide active material was supplied by BASF TODA Battery Materials LLC. A Li-rich/Gr test cell was charged and discharged for 500 times between 2.0 and 4.6 V at 45°C. The Li-rich positive electrodes were picked up and rinsed with DMC in Ar-filled glove box, followed by reassembling a half-cell combined with a metallic Li counter electrode. For comparison, a pristine Li-rich/Li half-cell was assembled. Each cell was charged and discharged for twice between 2.0 and 4.7 V at 25°C before XAFS measurements to obtain electrochemical characteristic. *In-situ* XAFS measurements were carried out, starting from discharged state to charged one to confirm redox species and their valence change, in the transmission mode at the Ni K-edge in BL01B1, SPring-8.

3. Results and Discussion

Figure 1 shows charge/discharge profiles of the Li-rich/Li half cells. The cycled Li-rich positive electrode indicates almost the same discharge capacity as that of pristine one. Figure 2 shows the Ni K-edge absorption energies of Li-rich electrodes as a function of cell voltage. Ni K-edge absorption energies at charged state (4.7 V) of cycled is lower than that of pristine ones, even though the energies at discharged state were almost the same. Because Ni K-edge shift reflects oxidation state change^[2], the change in average Ni oxidation state of cycled electrode is lower than that of pristine one. These results imply that redox potential and valence range of each species contributes to the redox were changed by the charge/discharge cycles, judging from the fact that the both pristine and cycled show almost the same capacity.

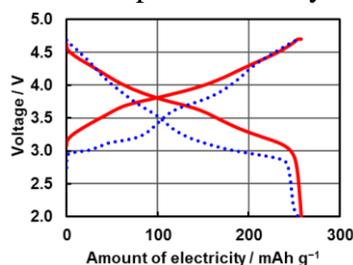


Figure 1 Charge/discharge profiles of pristine (—) and cycled (···) Li-rich/Li half-cells at 30 mA g^{-1} between 2.0 and 4.7 V.

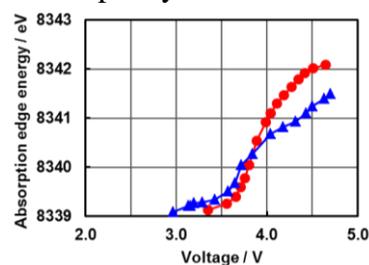


Figure 2 Ni K-edge absorption energies ($\mu\text{t} = 0.5$) of pristine (●) and cycled (▲) as a function of cell voltage.

References:

- [1] E. M. Erickson et al., J. Electrochem. Soc. 164 (2017) A6341–A6348.
- [2] T. Sasaki et al., J. Electrochem. Soc. 156 (2009) A289–A293.