

Analysis of Voltage Depression Mechanism after Charge-discharge Cycling tests for Li and Mn-rich Cathode Materials

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1. Introduction

Recently, over lithiated layer oxide (OLO) materials, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M=\text{Mn, Co, Ni}$), are the most attractive material as high capacity cathodes of large-sized Li-ion rechargeable batteries for next-generation electric vehicle. The OLO materials show higher reversible capacities more than 200 mAh g^{-1} after a long charge plateau at the first cycle when cycled over 4.5 V vs. Li/Li^+ . However, there are some drawbacks in the OLO materials which are high irreversible capacity especially at first cycle in high voltage window. The first charge processes of the OLO materials are important to activate their electrochemical characteristics. Many researchers reported that the voltage plateau region at first charge was caused by loss by oxygen from the lattice. We have ever investigated the relationship between the first lithium extraction process and the electrochemical properties of $\text{Li}[\text{Li}_{0.27}\text{Co}_{0.20}\text{Mn}_{0.53}]\text{O}_2$ and concluded that the higher amount of Li^+ extraction from the structure can induce the more electrochemical activation of $\text{Li}[\text{Li}_{0.27}\text{Co}_{0.20}\text{Mn}_{0.53}]\text{O}_2$ [1]. In addition, we have reported that the OLO materials were dramatically improved by applying the newly-developed electrolyte system with fluorinated ether and fluorinated carbonate solvent [2]. On the other hand, the charge-discharge voltage profiles of the OLO materials gradually dropped with the prolonged cycling tests. This phenomenon (we called “ ΔV problem”) led to not only the reduction of charge-discharge capacity (mAh g^{-1}) but also causes the large reduction of battery energy density (mWh g^{-1}) with the cycle; therefore we focused on the ΔV problem of the OLO materials. In order to understand the reaction mechanism of the ΔV problem, we have investigated the local and electronic structural changes of the OLO material electrodes during the prolonged charge-discharge cycling tests.

2. Experimental

The electrochemical measurements were carried out using an R2032 coin-type cell. When assembling the graphite/OLO material full-cells, the graphite as the negative electrode and the OLO material as the positive electrode were used. The assembly of the cells was performed in an argon-filled glove box. The cells were charged and discharged by galvanostatic and potentiostatic method with several voltage windows at 25°C. Crystalline phase identifications of the OLO materials and electrodes were carried out by XRD and *ex-situ* XRD. The morphology of the OLO materials and the electrode surfaces were observed with FE-SEM and TEM.

3. Results and discussion

The OLO material electrodes show typical charge-discharge profiles (Fig. 1). The first charge profile showed a long voltage plateau region, suggesting that the lithium extraction occurred through the OLO material surface. The charge-discharge profiles after 1st charge process showed S-shape curves, like a single phase reaction. Figure 2 shows the comparison of charge-discharge profiles at 3rd, 103rd, and 203rd cycle. Although the reduction of charge-discharge capacity was not so large, the discharge profiles at 103rd and 203rd cycle showed the large charge-discharge voltage depression compared with that of 3rd cycle. It was suggested that prolonged cycling test causes not only the deterioration of the OLO material electrode surface but also the changes of the local and electronic structure of the OLO material electrodes.

This presentation will describe the local and electronic structural changes of the OLO material electrodes during the prolonged cycling tests.

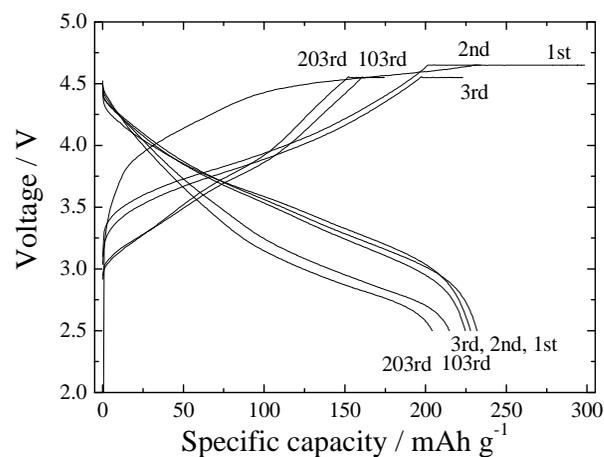


Fig. 1 Typical charge-discharge profiles of the OLO material at 25°C. Cutoff voltage: 2.5 - 4.65 V for 1st and 2nd cycle, 2.5 - 4.55 V after 3rd cycle; current density: 0.5C (CC-CV mode at charge) and 0.2C (CC mode at discharge) for 1st, 2nd, 3rd, 103rd, and 203rd cycle, 1.0C (CC-CV mode at charge and CC mode at discharge) for other cycle.

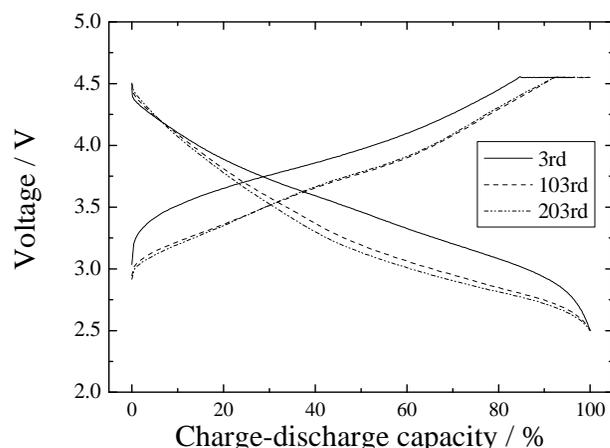


Fig. 2 Comparison of charge-discharge profiles at 3rd, 103rd, and 203rd cycle. Cutoff voltage: 2.5 - 4.55 V; current density: 0.5C (CC-CV mode at charge) and 0.2C (CC mode at discharge); temperature: 25°C.

References

- [1] N. Kumagai, J.-M. Kim, S. Tsuruta, Y. Kadoma, and K. Ui, *Electrochim. Acta*, **53**, 5287 (2008).
- [2] H. Takase, M. Nakano, and T. Endo, *AABC 2012*, LLIBTA Session1 Presentation 3 (2012).