Synthesis and Characterization of Layered Lithium Manganese Oxides with Other Transition Metal Ions for High-Capacity Positive-Electrode Materials

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Layered lithium manganese oxides with or without other transition metal ions have been studied for lithium-ion batteries. Of these, $Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2$ shows the highest rechargeable capacity, more than 300 mAh g⁻¹, among the positive-electrode materials examined so far [1]. Then, questions arise as to what is the reaction mechanism being high capacity, why the lithium cells cycle well in voltage ranging from 2 to 5 V in spite of a layer structure, and what is a possible origin of hysteresis in potential profile between charge and discharge. In order to answer these questions, a series of trials has been done. In this paper, we report synthesis and characterization of layered lithium manganese oxides of Li[Li_{3/11}Cr_{2/11}Mn_{6/11}]O₂ (Abbreviated Cr-LMO), $Li[Li_{3/11}Fe_{2/11}Mn_{6/11}]O_2$ (Fe-LMO), $Li[Li_{3/11}Co_{2/11}Mn_{6/11}]O_2$ (Co-LMO), and $Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2$ (Ni-LMO).

According to the X-ray diffraction measurements, all samples show similar XRD patterns to that of Li₂MnO₃ including superlattice lines located near the highest diffraction line of (001) for Li₂MnO₃, suggesting a layered structure together with some cation ordering in the transition metal layer. Figure 1 shows the charge and discharge curves of the Cr-, Co-, and Ni-LMO samples examined in a lithium cell at 25° C. in voltage ranging from 2 to 5 V. The cells are operated All samples show a voltage plateau at 4.6 V on first charge and large voltage hysteresis between charge and discharge. Rechargeable capacities of these materials are more than 200 mAh g⁻¹ During cycling at 25°C, the voltage profiles of Cr- and Co-LMO samples change from sloping curve to two steps at 4 and 3 V, while the Ni-LMO sample is still unchanged.

In order to examine the role of transition metal ions upon the solid-state redox reactions, X-ray absorption spectroscopy using synchrotron radiation at National Synchrotron Light Source (NSLS) were employed. Figure 2 shows the Mn K-egde X-ray absorption spectra of the Cr-, Co-, and Ni-LMO samples measured at pristine, after charging (charged to 5.0 V), and after initial cycle (discharged to 2.0 V). As can be seen in Fig. 2, three curves in the same electrode history are merged in a single curve regardless of transition metal ions contained in LMO. After charging, the peak top shifts toward higher energy for all LMO samples. The spectra of discharged samples are quite similar to those of starting materials.

From these results combined with the X-ray absorption spectra of $LiNi_{1/2}Mn_{1/2}O_2$ and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, we will discuss why these layered lithium manganese oxides show high rechargeable capacities compared with other layer materials, such as $LiCoO_2$, $LiNiO_2$, etc.

References

[1] T. Ohzuku, et al., J. Mater. Chem., 21, 10179 (2011).



Fig. 1 Charge and discharge curves of (a) $Li[Li_{3/11}Cr_{2/11}Mn_{6/11}]O_2$ and (b) $Li[Li_{3/11}Co_{2/11}Mn_{6/11}]O_2$ examined in a cell with LTO at 25°C, and (c) $Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2$ examined in a lithium cell at 25°C.



Fig. 2 Mn K-edge spectra of $Li[Li_{3/11}Cr_{2/11}Mn_{6/11}]O_2$, $Li[Li_{3/11}Co_{2/11}Mn_{6/11}]O_2$, and $Li[Li_{1/5}Ni_{1/5}Mn_{3/5}]O_2$ measured (a) at pristine, (b) after charging (charged to 5.0 V), and (c) after initial cycle (discharged to 2.0 V).