High-Potential Electrode Performance and Reaction Mechanism of O3-$NaNi_{1/2}Mn_{1/2}O_2$

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Na-ion battery is one of the promising next-generation batteries because sodium is an Earth-abundant element and its resources are evenly distributed in the world. To realize high-energy Na-ion batteries, larger capacity and higher operating voltage are required for positive electrode materials because standard electrode potential of Na is lower than that of Li and average working potential of carbon negative electrode is close to 0 V vs. Na^+/Na. One of the idea to achieve high-energy is to raise upper cut-off potential. Most O3-type layered oxides such as $NaFeO_2$ and $NaCrO_2$ show large irreversible capacity and small reversible capacity in Na cells. $NaNi_{1/2}Mn_{1/2}O_2$ (O3-NiMn) delivers, however, large reversible capacity of ca. 200 mAh g^{-1} in 2.2 – 4.5 V.[1] Despite, the capacity decays rapidly during charge/discharge cycle. Indeed, cycle performance of O3-NiMn is improved by lowering the upper cut-off voltage into below 3.8 V, but reversible capacity also decreases to 125mAh g^{-1}. In this study, we investigate charge/discharge mechanism of O3-NiMn especially in high potential region by *operando* X-ray diffraction (XRD) and X-ray absorption spectroscopy.

O3-NiMn was prepared by a conventional solid-state reaction from starting materials of Na_2CO_3, $Ni(OH)_2$, and Mn_2O_3. The mixture was calcined at 800 °C for 24 h in air, then quenched to room temperature. The electrode was prepared by mixing O3-NiMn, acetylene black, and poly(vinyl difluoride) at a weight ratio of 80:10:10. Electrolyte used was a solution of 1 mol dm^{-3} $NaPF_6$/EC:PC (1:1 in volume). Charge/discharge curves of O3-NiMn at initial and 10th cycle are shown in Fig. 1. O3-NiMn shows initial discharge capacity of 206 mAh g^{-1} even after charging to 4.5 V, but the capacity decreases to 136 mAh g^{-1} after 10 cycles. In addition, flat voltage plateaus above 4.0 V gradually become sloping profiles with larger polarization after 10 cycles and the capacity degradation is attributed to that in the plateau region. *Operando* XRD for O3-NiMn reveals phase transition from the O3-type to an O3-type phase with much narrower interslab space via. P3-type one. Detailed charge/discharge mechanism related to the electrochemical properties of O3-NiMn will be presented.

References:
[1] S. Komaba, *et al.*, *Inorg. Chem.*, **51**, 6211 (2012).

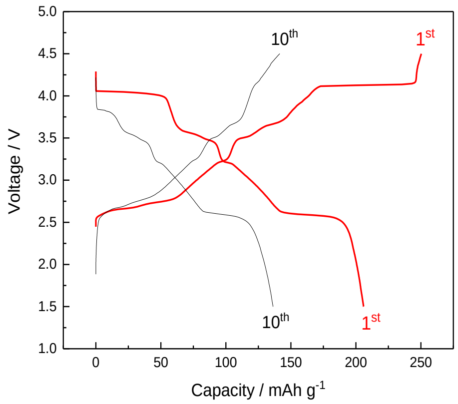

Fig. 1 Charge/discharge curves of O3-NiMn in 1.5 - 4.5 V at 1st and 10th cycle.