T2 and O2 $Li_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ cathode materials

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The layered lithium transition metal oxide T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ was discovered in our lab. It is prepared by ion exchange of the sodium in P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ for lithium. It has a very large reversible capacity of 180mAh/g and a good capacity retention cycling at 30°C and 55°C[1]. In $Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$, the Ni is believed to be in the +2 oxidation state while Mn is believed to be in the +4 oxidation state. When Li is extracted from $Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ during the first charge process, it is believed that that Ni is oxidized, since Mn can not normally be oxidized beyond +4 in these materials. In this case, substitution for Ni should strongly affect the electrochemical behavior of these materials. Co neighbors Ni in the periodic table and can substitute for Ni in $Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$.

We have reported the effects of Co substitution for Ni on the structure and electrochemical behavior of $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ [2][3]. When Co gradually replaces Ni, the super-lattice ordering of the transition metals in transition metal layer is gradually suppressed, as confirmed by neutron diffraction measurements [2]. This gives $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ with a stacking faulted O2 structure[2][4]. In addition, for x ≥1/12, the ion exchange of Li for Na in P2-$Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ is not complete. There are traces of the peaks of P2-$Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ in the x-ray diffraction patterns of $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$. We believe that many of these problems are related to the fact that when Co^{3+} replaces the Ni^{2+} in P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ and T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$, **a portion of Mn will be in the +3 oxidation state instead of the +4 oxidation state.**

In this presentation, we report the structure and electrochemistry of P2-$Na_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ and T2/O2-$Li_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ for x=0, 1/12, 1/8, 1/6, ¼, 1/3, 5/12, 1/2, 7/12 and 2/3. Here, the stoichiometries of the transition metals are adjusted so that **all the Mn is believed to be in the +4 oxidation state.** The results can be summarized as follows:

(1). When the Co content, x=2/3, $Li_{2/3}[Co_{2/3}Ni_{1/3}]O_2$ adopts the T2 structure. Even when the Co content, x=7/12 or ½, (containing a small amount of Ni) $Li_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ is still in the T2 structure. When the Co content, 1/6 ≤ x ≤5/12, $Li_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ adopts an O2-type stacking faulted structure.

(2). The ion exchange of Li for Na in P2-$Na_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ is complete except when x=1/8 or 1/6, where a trace of an intermediate phase can be detected [5].

(3). All the lithium can be extracted from $Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$ during the first charge process. Its behavior is contrasted to $Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$, from which only about 1/2 of the initial lithium can be removed [6]. The first charge curve of $Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$ and $Li_{2/3}$-$[Ni_{1/3}Mn_{2/3}]O_2$ are shown in Fig.1 for comparison.

Studies of the structure and electrochemical behavior of $Li_{2/3}[Co_xNi_{1/3-x/2}Mn_{2/3-x/2}]O_2$ are still in progress but will be presented at the meeting.

References:
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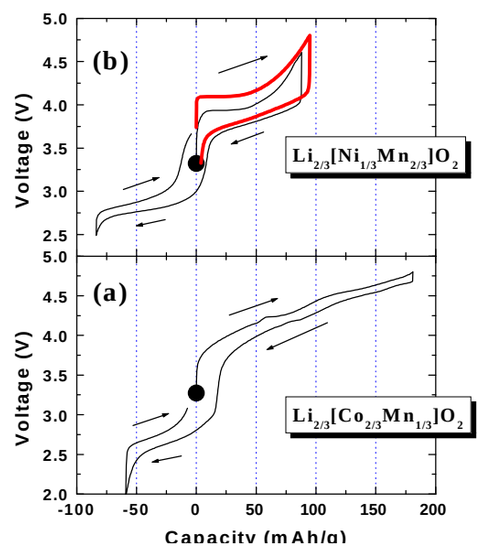

Fig.1 The charge-discharge curve of T2-$Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$ (a) and T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ (b) in 1M $LiPF_6$/EC-DEC(35:65). OCVs on cell assembly are marked with a solid circle. The thick solid line in panel (b) shows the first cycle of T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ in 1M $LiPF_6$/EMS (EMS=Ethyl Methyl Sulfone) between 3.0V and 4.8V vs Li/Li+. EMS was used since it has an electrochemical window up to 5.5V vs. Li/Li+. The theoretical capacity of T2-$Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$ and T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ are about 190 mAh/g assuming that all the lithium could be extracted completely. Fig.1 suggests that all the lithium can be removed from T2-$Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$, but not from T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$