

Structural and Electrochemical Study of Li-rich Mn-based Cathode Material $\text{Li}_2\text{Nb}_{0.15}\text{Mn}_{0.85}\text{O}_3$

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In this research, our structural analysis reveals that by doping the Nb into Li_2MnO_3 , the $\text{Li}_2\text{Nb}_x\text{Mn}_{1-x}\text{O}_3$ compounds adopt NaCl-type cubic structure in a wide compositional range, at least between $x = 5$ at.% and $x = 50$ at.%. One of these cubic materials, $\text{Li}_2\text{Nb}_{0.15}\text{Mn}_{0.85}\text{O}_3$ maintains 100% of its structure even after charge/discharge test up to 50 cycles (2.0 – 4.8 V vs. Li/Li⁺). It implies that Nb plays an important role to stabilize the atomic arrangement of Li and Mn ions in the transition metal layers. And due to its stable structure as well as 5d electron orbits of Nb can stabilize the oxygen redox (which is well known), the cubic $\text{Li}_2\text{Nb}_{0.15}\text{Mn}_{0.85}\text{O}_3$ shows highly reversible capacity from the second cycle, its coulombic efficiency remains stable over 98.5% during the 50 cycles. This indicates Nb doping can substantially modify the structure of pristine monoclinic Li_2MnO_3 and thus improve its electrochemical performance, which gives us a promising pathway to design and optimize the Mn-based lithium rich cathode material.

Keyword: lithium ion battery, lithium rich cathode, rocksalt structure

Background and research objective:

With the rapid development of electric vehicles and large-scale energy storage systems in recent years, Lithium-ion batteries (LIBs) with higher energy density, better cycle stability and higher safety are demanded urgently. To meet these requirements, it is crucial to exploit the electrode materials with high electrochemical performance, especially the cathode materials. LiMO_2 (M: pure transition metal or mixed transition metals) layered compounds have been extensively used as cathode materials in lithium-ion batteries. The specific capacities of these compounds are about 150 mAh/g in practical applications. However, in recent years, the so-called Li-rich layered compounds Li_2MO_3 have been extensively investigated for use as superior cathode materials for lithium-ion batteries because of their higher specific capacities than that of LiMO_2 (more than 200 mAh/g), as can be expected from their Li-rich compositions.

Among the various Li_2MO_3 compounds being explored, Li_2MnO_3 has been examined intensively. In this monoclinic crystal with ABC stacked atomic layers, Li/Mn mixing at the transition metal layers topologically forms long Lithium percolation paths in the atomic configuration. In addition, replacement of Mn^{4+} with other lower-valence transition elements such as Ni^{2+} decreases the potential energy along the paths so that Li^+ can propagate more readily. This is considered a major contributor to the improved charge capacity of $\text{Li}_2(\text{Ni}_x\text{Mn}_{1-x})\text{O}_3$ compounds. $\text{Li}_2(\text{Nb}_x\text{Mn}_{1-x})\text{O}_3$ is another Li_2MO_3 compounds, in which Mn is substituted by Nb; these materials also provide higher charge capacities similar to those of $\text{Li}_2(\text{Ni}_x\text{Mn}_{1-x})\text{O}_3$. And the $\text{Li}_2\text{Nb}_x\text{Mn}_{1-x}\text{O}_3$ compounds adopt NaCl-type cubic structure in a wide compositional range, at least between $x = 5$ at.% and $x = 50$ at.%. One of these cubic materials, $\text{Li}_2\text{Nb}_{0.15}\text{Mn}_{0.85}\text{O}_3$ maintains 100% of its structure even after charge/discharge test up to 50 cycles (2.0 – 4.8 V vs. Li/Li⁺). It implies that Nb plays an important role to stabilize the atomic arrangement of Li and Mn ions in the transition metal layers, but the detailed mechanism of such improvements is not clear yet. In this research, we use various characterization methods to analyze the structural and electrochemical mechanism about this material's performance.

Experimental:

The cubic $\text{Li}_2\text{Nb}_{0.15}\text{Mn}_{0.85}\text{O}_3$ was prepared by the facile solid state reaction. The raw material Mn_2O_3 , Nb_2O_5 , Li_2CO_3 were well mixed in acetone then dried, followed by sintering at 950°C for 24 hours in Ar atmosphere. The $\text{Li}_2\text{Nb}_{0.15}\text{Mn}_{0.85}\text{O}_3$ cathode electrodes were prepared by slurring the active material, acetylene black and PVDF with a weight ratio of 8:1:1, then coating on Al foil. The 2032-type coin cells were assembled for the

electrochemical test. The counter electrode was lithium metal and electrolyte was 1 M LiPF₆ in EC and EMC solvent (3:7 by volume). The charge-discharge test was operated in SD-8 between 2.0 and 4.8 V at 25°C. The cells at various state of charge and discharge were prepared for the ex-situ hard X-ray diffraction measurements, which were conducted at BL19B2 beamlines (SPring-8, Hyogo, Japan).

Results and Discussion:

The Fig. 1a shows the electrochemical performance of Li₂Nb_{0.15}Mn_{0.85}O₃ at the rate of 22 mAh/g, the first charge capacity is about 265 mAh/g, all of which is supposed to be contributed by the oxygen redox, for the Mn⁴⁺ is inactive during the charge process. Although it suffers from distinct capacity decay at the first cycle which is probably caused by the initial SEI formation, it shows highly reversible capacity from the second cycles. During the cycles, the average discharge voltage platform has decreased from 3.35 V to 2.85 V, which implies the redox ratio of oxygen and manganese has continuously changed. But as shown in the inset of Fig. 1a, the capacity of Li₂Nb_{0.15}Mn_{0.85}O₃ is gradually increasing till 27 cycles, and its coulombic efficiency remains stable over 98.5% during the 50 cycles. Such stable electrochemical performance could be attributed by its specific NaCl-type cubic structure

To clarify whether Li₂Nb_{0.15}Mn_{0.85}O₃ cathode material remains its structure during the cycle, the hard X-ray diffraction measurements are applied by using SPring-8 synchrotron radiation. The diffraction patterns of Li₂Nb_{0.15}Mn_{0.85}O₃ at various state are demonstrated in Fig. 1b, the pristine material is single phase NaCl-type cubic, while during the 1st and 2nd cycle, there are some non-react parts of active material, which cause double peaks in the patterns. The position of each peaks shows small but regular shift, it can be explained by the lattice constant change during the charge and discharge process. And it is noticeable that Li₂Nb_{0.15}Mn_{0.85}O₃ cathode material remains stable of its cubic structure during the cycle, which could be the critical factor of its highly reversible capacity.

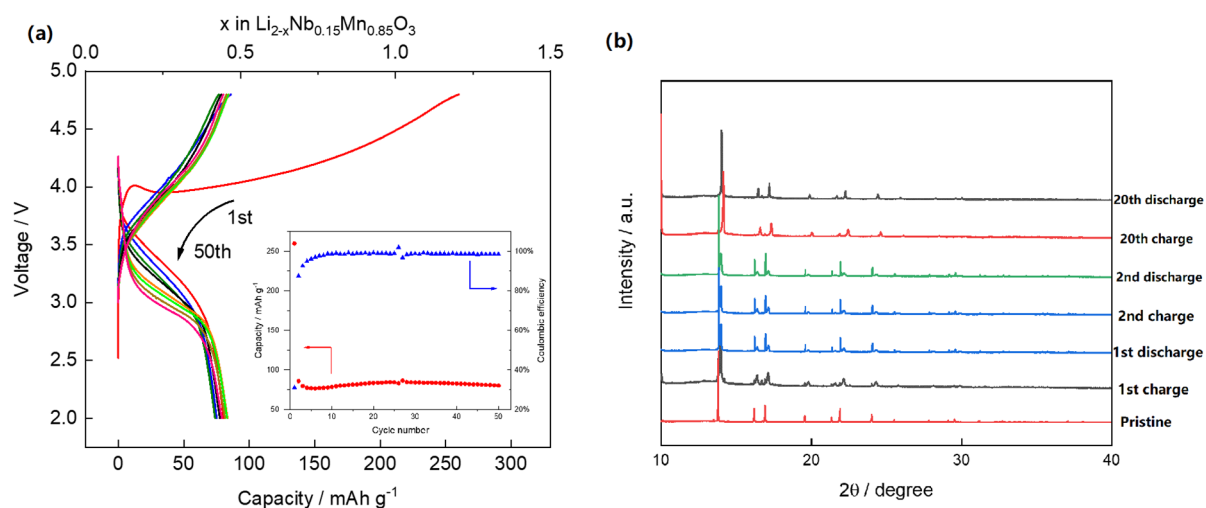


Fig. 1 (a) 50 cycles charge/discharge curves of Li₂Nb_{0.15}Mn_{0.85}O₃ cathode at 22 mAh/g, the inset is cyclic performance. (b) Hard X-ray Diffraction patterns of pristine Li₂Nb_{0.15}Mn_{0.85}O₃ and its various charged and discharged state at different cycles.

Future Subject:

The first coulombic efficiency of Li₂Nb_{0.15}Mn_{0.85}O₃ cathode material still needs improvement by restraining the initial irreversible SEI formation, and the distinct voltage decay which is common in all Mn-based lithium rich cathode material also needs to be further investigated.

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