

## Improving the rate capability of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through substitution of Co for Ni element

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**Abstract.** Spinel compound  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  was synthesized by a sol-gel process together with a calcinations process. The as prepared product could be indexed to  $F_{d3m}$  space group. The dopant Co resulted in more oxygen vacancy in crystal structure. The doped compound exhibited better cycle rate capability than pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . At high charge and discharge current rate of 10 C, its main discharge voltage remained above 4.5 V, and the discharge capacity reached  $83 \text{ mAh g}^{-1}$ .

### Introduction

Spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has a high working voltage of about 4.7 V at which Li ion can be inserted into or extracted from its crystal structure. Its theoretical specific energy density can reach about 658 Wh/kg (Specific energy density = specific capacity  $\times$  average operating voltage), exceeding most other cathode materials such as  $\text{LiCoO}_2$  (518 Wh/kg),  $\text{LiMn}_2\text{O}_4$  (440 Wh/kg),  $\text{LiFePO}_4$  (591Wh/kg) and so on [1].

With the advantage of high working voltage, it has been considered as a promising candidate material for more powerful lithium ion batteries to be used in the field of hybrid electrical vehicles (HEVs) and plug-in hybrid electrical vehicles (PHEVs). However, there is a prominent problem for spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , i.e. its poor rate capability. According to the previous reports, oxygen deficiency and  $\text{Mn}^{3+}$  are correlated with each other, and the  $\text{Mn}^{3+}$  can improve the conductivity and increase the lattice parameter which is beneficial for  $\text{Li}^+$  to be transported in the crystal [2].

Element substitution is an effective way to improve the electrochemical properties of spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . For example, the Al, Fe, Cr and Co-doped compounds exhibited improved rate capability. The substitution of  $\text{M}^{3+}$  for  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  helps to keep the  $\text{Mn}^{4+}$  oxidation state unchanged ( $2\text{M}^{3+} = \text{Ni}^{2+} + \text{Mn}^{4+}$ ,  $\text{M}^{3+} = \text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$ )[3-5].

In this study, partial substitution of Ni by Co was carried out to synthesize  $\text{LiNi}_{0.4}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$ . The effect of dopant Co on the structure and properties of material was investigated in the aspect of oxygen deficiency and  $\text{Mn}^{3+}$ . The test results show that doping Co could improve the rate capability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

## Experimental

Preparation of  $\text{LiNi}_{0.4}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$ : At first, stoichiometric amounts of  $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{CH}_3\text{CO}_2)_2\cdot 4\text{H}_2\text{O}$  were dissolved in distilled water and stirred for some time. In order to compensate for the loss of Li at high reaction temperature, additional 3% of Li salt was made up. Then citric acid aqueous solution was also prepared with mole ratio of total metal ions to citric acid being 2: 1. Then the two solutions were mixed, stirred and evaporated at 120 °C to turn into dried gel. The dried gel was calcinated at 900 °C for 12 h in air furnace. Then an annealing process was carried out at 650 °C for 12 h. Finally, the product was obtained when it was cooled down to room temperature. In the same way, spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  was synthesized.

Characterizations: X-ray diffraction pattern was carried out on a Philips X-ray diffractometer equipped with Cu  $K\alpha$  radiation. The morphologies of the products were examined with a Hitachi scanning electron microscope (SEM).

Electrochemical evaluations: Electrochemical performances were measured with coin half-cells composed of the nominal spinel cathode and metallic-lithium anode with 1 mol  $\text{L}^{-1}$   $\text{LiPF}_6$  in 1:1 diethyl carbonate/ethylene carbonate electrolyte and Celgard polypropylene separators. The cathodes were prepared by mixing 88 wt % active material with 6 wt % acetylene black and 6 wt % PVDF binder in NMP; the mixture was coated on aluminum foil, dried in an oven and punched out circular discs of 0.95 cm in diameter. All coin cells were assembled in an argon-filled glovebox. The cells were galvanostatically cycled under different current densities and elevated temperature 55 °C between 3.50 V and 4.90 V. In EIS measurement, the excitation voltage applied to the cells was 5 mV and the frequency range was between 100 kHz and 10 mHz.

## Results and discussion

Fig. 1 shows the X-ray diffraction of the as prepared products. All peaks can be indexed as the cubic spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  phase. There are no apparent impurity peaks at 37.5°, 43.7° and 63.6°, indicating no  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  phase in the samples. Because there are no additional lines located at  $2\theta=15.4^\circ$ , 39.8°, 45.8° and 57.6° which are superlattice peaks indicating Ni/Mn long-range ordering in the octahedral sites, the sample should belong to  $F_{d3m}$  space group [6].

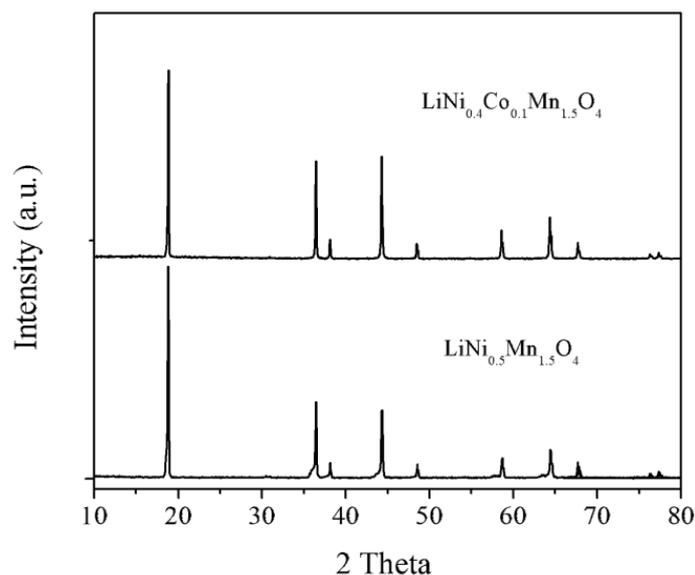
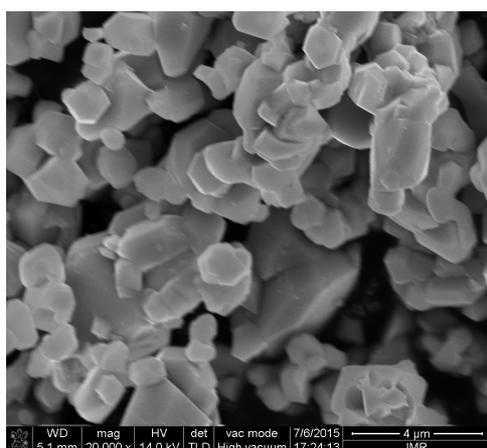
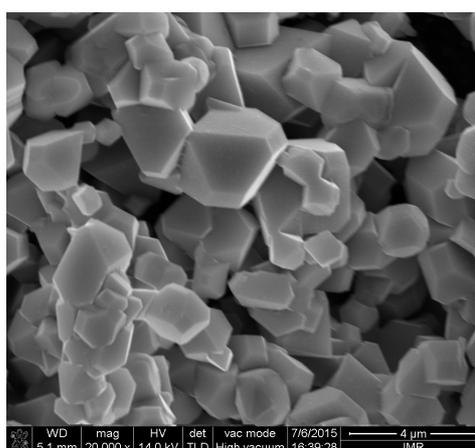


Fig. 1 XRD pattern of the as prepare samples

The morphological features of the as-prepared sample  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  are characterized by scanning electron microscopy, as displayed in Fig. 2. The two samples are polyhedral shape and well crystallized. Most particles range from 1-4  $\mu\text{m}$  in size.



(a)  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$



(b)  $\text{LiNi}_{0.4}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$

Fig. 2 SEM image of the as prepared samples

In order to evaluate the rate capability of the as prepared samples, 0.2C-charge/0.2C-discharge, 5C-charge/5C-discharge, and 10C-charge/10C-discharge rates were investigated, as shown in Fig. 3. The first charge-discharge curves were carried out at 0.2C/0.2C rate, the discharge capacities are about 129  $\text{mAh g}^{-1}$  and 121  $\text{mAh g}^{-1}$  for  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , respectively. At 5C/5C rate, the capacities are 103  $\text{mAh g}^{-1}$  and 77  $\text{mAh g}^{-1}$  for  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , respectively. At 10C/10C rate, their capacities are 83  $\text{mAh g}^{-1}$  and 50  $\text{mAh g}^{-1}$ , respectively. Therefore, the Co-doped  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  exhibits better rate performance than the pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

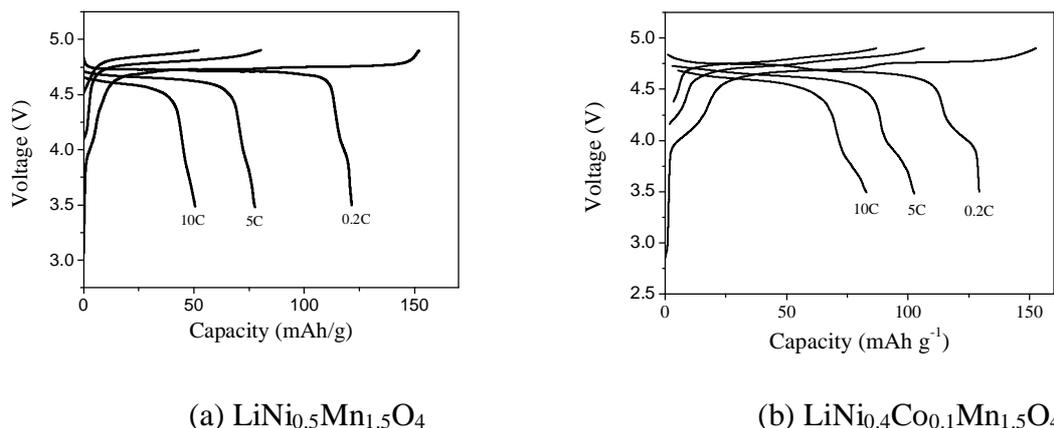


Fig. 3 Charge-discharge curves of the as prepared samples

Fig. 4 shows the cycle performance of the as prepared samples  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  at different current rates. It can be seen that the sample  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  exhibited good cycle performance, while the sample  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  delivered less capacity at high current rates such as 5 C and 10 C.

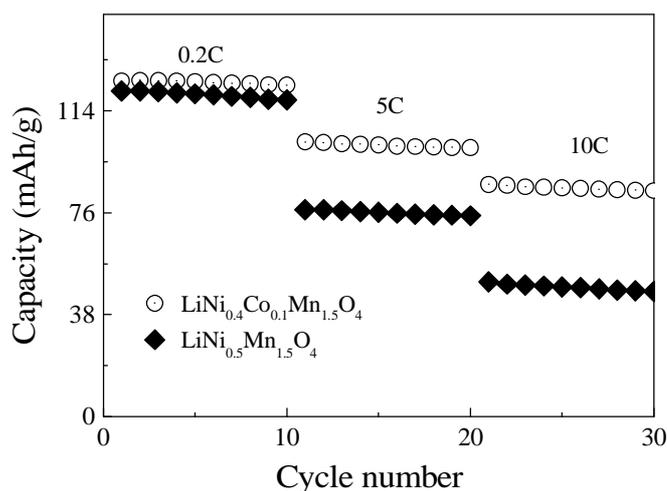


Fig. 4 Cycle performance of the prepared samples

Fig. 5 shows the impedance of the as prepared samples  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . The two samples were conducted 30 charge-discharge cycles. There were two semicircles. According to the previous report, the first semicircle reflected lithium ion migration through the interface between the surface of the particles and the electrolyte, the second semicircle could be regarded as the charge-transfer resistance. For the pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , the second semicircle was about  $175 \Omega$ , while for the doped compound  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$ , the second semicircle was about  $88 \Omega$ . This result indicated that doping Co reduced the charge-transfer resistance, which can improve the rate capability.

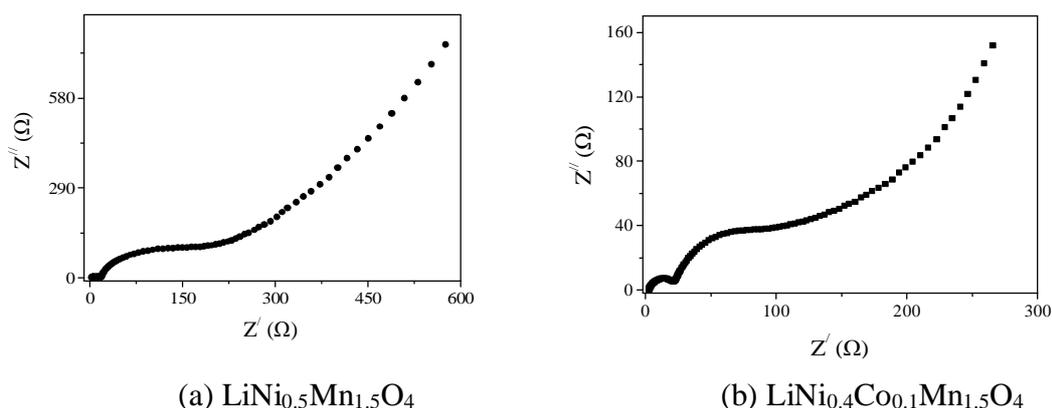


Fig. 5 Nyquist plots of the prepared samples

For the pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , annealed at below  $700\text{ }^\circ\text{C}$  for sufficient time, the oxygen deficiency will be eliminated. While for the doped compounds  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$ , even annealed at below  $700\text{ }^\circ\text{C}$  for the same time as the pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , the oxygen deficiency can not be reduced as the same extent, which can be deduced from the different resided  $\text{Mn}^{3+}$  in these doped compounds. Based the above experimental results, the Co-doped  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  remains the most amount of oxygen deficiency because it comprises the most amount of  $\text{Mn}^{3+}$ . It has proved that trace  $\text{Mn}^{3+}$  ions in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  are beneficial to its rate capability, especially at high rates, by improving the conductivities of Li ions and electrons of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  material [7]. Therefore, the Co-doped  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$  exhibits excellent rate capability.

## Conclusion

This paper studied partially substituting Ni by Co in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , synthesizing doped compound  $\text{LiNi}_{0.40}\text{Co}_{0.1}\text{Mn}_{1.5}\text{O}_4$ . The dopant Co can create more oxygen deficiency and accordingly form more  $\text{Mn}^{3+}$  than pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . The product exhibits excellent rate capability. At 10C-charge/10C-discharge rate, its discharge capacity could reach  $83\text{ mAh g}^{-1}$ , and especially its main discharge voltage remained above  $4.5\text{ V}$ .

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