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

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Abstract. Spinel compound LiNi$_{0.40}$Co$_{0.1}$Mn$_{1.5}$O$_4$ was synthesized by a sol-gel process together with a calcinations process. The as prepared product could be indexed to Fd$_{3m}$ space group. The dopant Co resulted in more oxygen vacancy in crystal structure. The doped compound exhibited better cycle rate capability than pristine LiNi$_{0.5}$Mn$_{1.5}$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 mAh g$^{-1}$.

Introduction

Spinel LiNi$_{0.5}$Mn$_{1.5}$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 × average operating voltage), exceeding most other cathode materials such as LiCoO$_2$ (518 Wh/kg), LiMn$_2$O$_4$ (440 Wh/kg), 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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$, i.e. its poor rate capability. According to the previous reports, oxygen deficiency and Mn$^{3+}$ are correlated with each other, and the Mn$^{3+}$ can improve the conductivity and increase the lattice parameter which is beneficial for Li$^+$ to be transported in the crystal [2].

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

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

Preparation of LiNi$_{0.4}$Co$_{0.1}$Mn$_{1.5}$O$_4$: At first, stoichiometric amounts of LiCH$_3$COO·2H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O and Co(CH$_3$CO$_2$)$_2$·4H$_2$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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was synthesized.

Characterizations: X-ray diffraction pattern was carried out on a Philips X-ray diffractometer equipped with Cu Kα 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 L$^{-1}$ 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 LiNi$_{0.5}$Mn$_{1.5}$O$_4$ phase. There are no apparent impurity peaks at 37.5°, 43.7° and 63.6°, indicating no Li$_x$Ni$_{1-x}$O phase in the samples. Because there are no additional lines located at 2θ=15.4°, 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 Fd$_{3m}$ space group [6].
Fig. 1 XRD pattern of the as-prepared samples

The morphological features of the as-prepared sample LiNi$_{0.40}$Co$_{0.1}$Mn$_{1.5}$O$_{4}$ and LiNi$_{0.5}$Mn$_{1.5}$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 µm in size.

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 mAh g$^{-1}$ and 121 mAh g$^{-1}$ for LiNi$_{0.40}$Co$_{0.1}$Mn$_{1.5}$O$_{4}$ and LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$, respectively. At 5C/5C rate, the capacities are 103 mAh g$^{-1}$ and 77 mAh g$^{-1}$ for LiNi$_{0.40}$Co$_{0.1}$Mn$_{1.5}$O$_{4}$ and LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$, respectively. At 10C/10C rate, their capacities are 83 mAh g$^{-1}$ and 50 mAh g$^{-1}$, respectively. Therefore, the Co-doped LiNi$_{0.40}$Co$_{0.1}$Mn$_{1.5}$O$_{4}$ exhibits better rate performance than the pristine LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$.
Fig. 3 Charge-discharge curves of the as prepared samples

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

Fig. 5 shows the impedance of the as prepared samples LiNi\(_{0.40}\)Co\(_{0.1}\)Mn\(_{1.5}\)O\(_4\) and LiNi\(_{0.5}\)Mn\(_{1.5}\)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 LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), the second semicircle was about 175 $\Omega$, while for the doped compound LiNi\(_{0.40}\)Co\(_{0.1}\)Mn\(_{1.5}\)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.
For the pristine LiNi₀.₅Mn₁.₅O₄, annealed at below 700 °C for sufficient time, the oxygen deficiency will be eliminated. While for the doped compounds LiNi₀.₄₀Co₀.₁Mn₁.₅O₄, even annealed at below 700 °C for the same time as the pristine LiNi₀.₅Mn₁.₅O₄, the oxygen deficiency can not be reduced as the same extent, which can be deduced from the different resided Mn³⁺ in these doped compounds. Based the above experimental results, the Co-doped LiNi₀.₄₀Co₀.₁Mn₁.₅O₄ remains the most amount of oxygen deficiency because it comprises the most amount of Mn³⁺. It has proved that trace Mn³⁺ ions in LiNi₀.₃Mn₁.₅O₄ are beneficial to its rate capability, especially at high rates, by improving the conductivities of Li ions and electrons of the LiNi₀.₃Mn₁.₅O₄ material [7]. Therefore, the Co-doped LiNi₀.₄₀Co₀.₁Mn₁.₅O₄ exhibits excellent rate capability.

Conclusion

This paper studied partially substituting Ni by Co in LiNi₀.₅Mn₁.₅O₄, synthesizing doped compound LiNi₀.₄₀Co₀.₁Mn₁.₅O₄. The dopant Co can create more oxygen deficiency and accordingly form more Mn³⁺ than pristine LiNi₀.₅Mn₁.₅O₄. The product exhibits excellent rate capability. At 10C-charge/10C-discharge rate, its discharge capacity could reach 83 mAh g⁻¹, and especially its main discharge voltage remained above 4.5 V.

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References