Short Communication

Effect of Cl doping on the structural and electrochemical properties of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_2$ as cathode materials for Lithium-ion Batteries

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The layered LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$(x=0.00, 0.03, 0.05, 0.10) samples were prepared by using a sol-gel method. The crystal structure, electrochemical properties are characterized by XRD, charge-discharge tests and CV. The XRD results show that it remains a well-layered structure with single phase of hexagonal after chlorine doping. CV measurements suggest that the reversibility of the cathode materials is enhanced by chlorine doping . Charge-discharge tests show that the best electrochemical performance composition is for x=0.05, which has a higher initial discharge capacity of 169.9 mAh g^{-1} between 2.5 and 4.4 V at 0.2C rate and better cycling performance than that of others.

1. INTRODUCTION

For many years, the layered LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ oxides(NCM) have become attractive as an alternative cathode material for lithium-ion batteries due to its higher capacity, lower cost, and enhanced safety features compared to the conventional LiCoO$_2$ cathode[1-19]. Among these ternary layered oxides, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111) has been studied extensively[4,13,18,19], the LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523) has been paid more attention in recent years[3,6-7,9-10] . However, compared with LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_2$ with less expensive Co content can reduce the material cost and environmental pollution caused by production process. More Ni content could contribute to more for the capacity ,the higher the relative concentration of nickel in the material is, the higher the specific capacity is. Furthermore, the increase of Mn concentration would increase the safety performance.Thus it is a cathode material that deserves more research works. So more research work has been done for many years[11,14-17]. However, this kind of material suffers from such drawbacks as shortage of cycling performance and rate capacity[20-22].

Doping with alien ions is an important method adopted in improving the electrochemical performances of the cathode materials, which has been extensively applied in the modification of $LiNiO_2$[23], $LiMn_2O_4$[24]. Currently, most of the doping ions for cathode materials are metallic ions[25,26]. However, the improvement in structure and performance of cathode materials is also remarkable when doping with anions individually or a combination of anions and cations [19,27,28]. More published papers have been found for the cation doping for NCM materials[6,8,1-11,13,16,18,19], bue few work has been done for NCM442 materials. In comparison with a little more publications about fluorine doping, other anionic doping is rarely reported. In our past research work, it was found that chlorine doping could improve the electrochemical performances of MCM111 cathode material[19] . So we have been encouraged to do research on the effect of chlorine doping on ternary cathode material $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$.

2. EXPERIMENTAL

$LiNi_{0.4}Co_{0.2}Mn_{0.4}O_{2-x}Cl_x$ (x=0.00, 0.03, 0.05, 0.10) powders were prepared via a sol-gel process using citric acid as chelating agent. A stoichiometric amount of $LiCH_3COO \cdot 2H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $Co (CH_3COO)_2 \cdot 4H_2O$ and $LiCl \cdot H_2O$ were dissolved in distilled water, and then added the aqueous solution of citric acid into the mixture metal solution. The molar ratio of citric acid to total metal ions was unity. The pH of the solution was adjusted in the range 7–8 by adding aqueous ammonium hydroxide. The reagent solution was stirred continuously at 80 °C until form homogeneous sol-gel. The resulting gel was dried at 120 °C for 8 h and then heated at 500 °C for 6 h to eliminate the organic residues. The final powders were gained by a thorough grounding step, a final calcining at 850 °C for 20 h in air and followed by quenching to room temperature.

The X-ray diffraction (XRD) with Cu Kα radiation operated at 40kV and 40mA was used to analyze the crystalline structure of samples by using PANAlatical X'PERT Powder Instrument (Made in Holland). The scan data were in the 2θ range from 10° to 90° with a step of 4°/min.

Electrochemical experiments were performed using two-electrode CR2032 type coin cells. The composite cathodes were made by dispersing active material (80 wt.%), acetylene black (12 wt.%), and PVDF (8 wt.%) in N-methylpyrrolidone (NMP) to form a slurry, The slurry was pasted onto Al foil with a Doctor blade technique, then pressed at 10MPa and dried at 120 °C for 10 h in a vacuum oven. The CR2032 coin cells were assembled in an argon-filled glove box (SUPER 1220/750, made in Shanghai, China), using lithium metal as the counter electrode, Celgard 2325 as the separator, and 1 M $LiPF_6$ in 1:1 EC:DMC solution as the electrolyte. Charge-discharge performance of the cells was evaluated within different cut-off voltages and at different discharge rates at room temperature using LAND CT2001A electrochemical test instrument (Wuhan, China).

The cyclic voltammogram (CV) curves were obtained between the cut-off voltage ranges of 2.5-4.8V on an IM6 Electrochemical workstation (IM6, Germany) at a scan rate of 0.1 mV s^{-1}.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_{2-x}Cl_x$ (x=0.00, 0.03, 0.05, 0.10). All of the

peaks can be indexed on the basis of a layered structure of α-NaFeO$_2$ structure (space group: R-3m) and no obvious impurity phase peaks could be observed, indicating that chlorine doping does not change the hexagonal layer structure. The clear split of the (006)/(102) peaks and (018)/(110) peaks for all samples manifests the formation of well hexagonal layered ordering structure[29]. Table 1 shows the lattice parameters of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ cathode materials. Chlorine addition could have caused the expanding effect of the lattice parameters *a* and *c*. The increase of lattice parameter *c* may be due to the difference of radius between Cl$^-$ (1.81Å) and O^{2-} (1.40Å). In addition, the increase of lattice parameter *a* may be partly attributed to the valence balance by the chlorine doping leading Mn^{4+} (0.53Å) to transform to larger Mn^{3+}(0.58Å) [29]. An increase in the intensity ratio of (003)/(104) peak indicates less cation mixing. Moreover, the *R*-factor defined by [I(006) + I(102)]/I(101) is an indicator of the hexagonal ordering; the lower the *R*-factor is, the better the hexagonal ordering[31] is. The *c/a* ratio > 4.96 also reveals the well-defined layered structure, the higher value of *c/a*, the better the well-defined layered structure [32] is. After doping, the values of I(003)/I(104) and *c/a* increase , the values of *R*-factor decrease, suggesting that a small amount of Cl$^-$ substitution for O^{2-} could suppress occupancy of Li$^+$ layers by Ni^{2+}. This means that the cation mixing in Li layer could be decreased by Cl$^-$ substitution. This will be conducive for its electrochemical performances. However, the I(003)/(104) values of Cl-doped samples begin to decrease when the chlorine content is 0.10, which indicates that some cation mixing occurred in the crystal lattice. Compared with the LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_2$, LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{1.95}$Cl$_{0.05}$ has the maximal ratio of I(003)/I(104) and the minimal value of *R*-factor, indicating that it has the best layered structure.
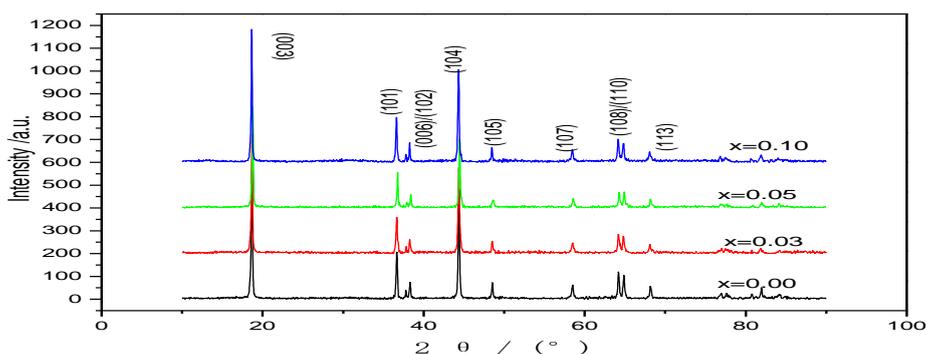

Figure 1. XRD patterns of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ (x=0.00, 0.03, 0.05, 0.10)

Table 1. Lattice parameter of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ (x=0.00, 0.03, 0.05, 0.10)

x	a(Å)	c(Å)	c/a	R	I$_{003}$/I$_{104}$
0.00	2.8751	14.268	4.9626	0.563	1.24
0.03	2.8752	14.271	4.9634	0.537	1.38
0.05	2.8755	14.283	4.9671	0.528	1.47
0.10	2.8761	14.285	4.9668	0.591	1.44

Fig. 2(a) shows the initial charge/discharge curves of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ (x=0.00, 0.03,

0.05, 0.10) powders at 0.2C between 2.5 and 4.4 V at room temperature. The first discharge capacity of pristine sample is 160.6 mAh g^{-1}. Compared with the un-doped sample, doped samples with x= 0.03, 0.05 and 0.10 have enhanced discharge capacities of 167.8, 169.9 and 162.6 mAh g^{-1}, respectively. Chlorine substituted samples exhibit higher initial discharge capacity than pristine one. Besides, the discharge capacity of pristine sample gradually decreases, leading to the capacity retention of 93.4% after 40 cycles. On the contrary, chlorine substituted materials show enhanced capacity retentions during the same cycling period, having 98.4% for x = 0.03, 99.8% for x = 0.05, and 95.6% for x = 0.10, respectively. This is because that Cl$^-$ addition may bring about the expanding pathway for Li$^+$ to intercalate and deintercalate because the parameter c has been increased. Besides, it is reasonable to assume that Cl$^-$ doped materials have lower electrostatic repulsions between O-M-O interlayers in the process of Li$^+$ insertion/deinsertion for Cl$^-$ has one electron less than O^{2--}, which is beneficial for the removal of Li$^+$ insertion/deinsertion[33]. Among the Cl$^-$ doped samples, LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{1.95}$Cl$_{0.05}$ displays the the highest discharge capacity and shows the best capacity retention. When the chlorine content is higher than 0.05, the electrochemical performance begins to deteriorate .This means that over doping may cause poor stability because the main structure of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_2$ could be destroyed by too many doped atoms.
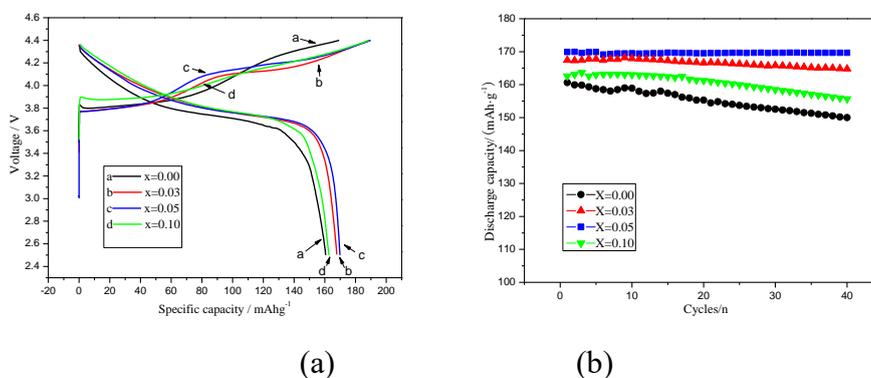

(a)   (b)

Figure 2. (a) Initial charge/discharge curves of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ (x=0.00, 0.03, 0.05, 0.10) at 0.2C at room temperature; (b) cycling performance of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ (x=0.00, 0.03, 0.05, 0.10) at 0.2C at room temperature.

In order to investigate the structural stability and reversibility, cyclic voltammograms of the LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ (x=0.00, 0.03, 0.05, 0.10) samples between 2.5 and 4.8 V for the first two cycles were shown in Figure 3. Evidently two double redox peaks are shown in the curves of bare sample and Cl-doped sample, which indicates that chlorine doping can not lead to structure change of materials. The major redox peak is attributed to the Ni^{2+}/Ni^{4+} and the minor redox peak corresponded to Co^{3+}/Co^{4+} [34]. The major cathodic peaks for the un-doped one of the first cycle center at 4.159 V and the corresponding anodic peaks center at 3.584. Moreover, the major cathodic peaks of LiNi$_{0.4}$Co$_{0.2}$Mn$_{0.4}$O$_{2-x}$Cl$_x$ center at 4.040 V (x=0.03), 3.978 V(x=0.05), 4.070 V(x=0.10) and the anodic peaks at 3.653 V(x=0.03), 3.657 V(x=0.05) and 3.588 V(x=0.10), respectively. It is obvious that the potential difference of the major

peaks for the doped ones are 0.387 V(x=0.03), 0.321 V(x=0.05) and 0.482 V(x=0.10),respectively, which are obviously decreased when compared to that of the un-doped one (0.575 V). When comparing the second cycle, the polarization of the major peak of the doped one is only 0.326 V(x=0.03), 0.252 V(x=0.05) , and 0.404 V(x=0.10) ,respectively,which are less than that of the un-doped one (0.405 V). This smaller potential difference indicates the weaker electrode polarization is, which ensures reduced capacity fade during cycling . So, the $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_{1.95}Cl_{0.05}$ has the best reversible capacity, which has validated the above conclusion that we've got by charge-discharge test.

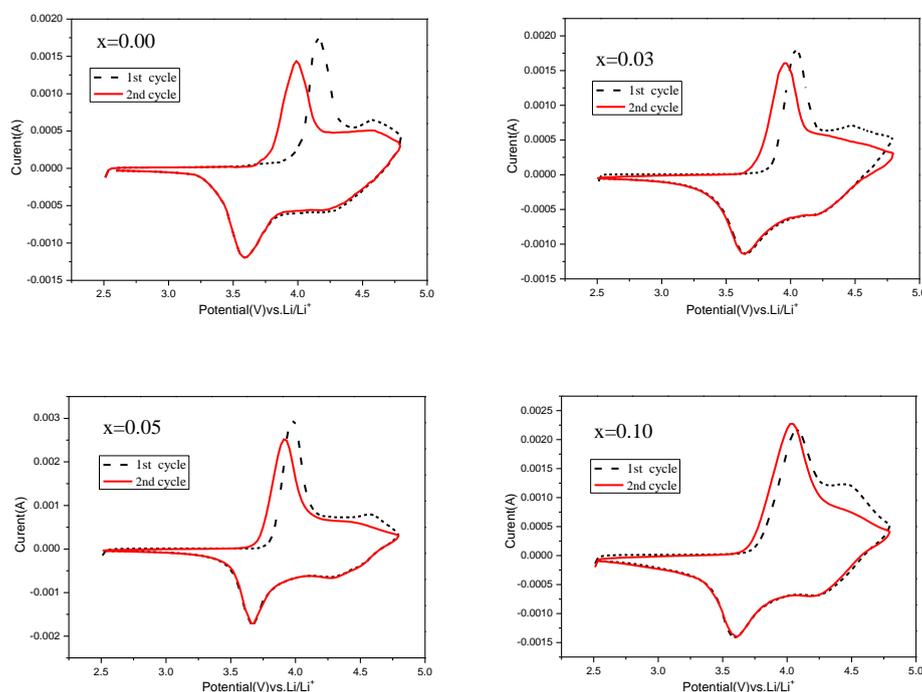**Figure 3.** Cyclic voltammograms of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_{2-x}Cl_x$ (x=0.00, 0.03, 0.05, 0.10)

4. CONCLUSION

In this paper, $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_{2-x}Cl_x$ (x=0.00, 0.03, 0.05, 0.10) cathode materials were synthesized by a sol–gel method. XRD identified that the substitution of chlorine can improve the stability of the materials and the order degree of structure. $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_{1.95}Cl_{0.05}$ cathode material shows higher initial discharge capacity of 169.9 mAh g^{-1} at 0.2C in a voltage rang of 2.5-4.4 V, and the capacity retention is 99.8% after 40 cycles, while for the un-doped material the initial discharge capacity is 160.2 mAh g^{-1} with a capacity retention of 93.4%. CV measurements indicated that the substitution of chlorine can increase reversibility, which is mainly due to expanded pathway for Li^+ to intercalate and deintercalate. So the chlorine doping could improve the electrochemaical performances NCM442 cathode materials with a great deal.

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