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LiF modification on improving the electrochemical property of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$

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Abstract: LiF was used to modify the Ni-rich ternary cathode materials in this paper through chemical reaction deposit and low temperature sintering. The microstructure of the materials was characterized by XRD and SEM. The electrochemical properties were inspected by Land test system. During the charge/discharge test under different concentrations of LiF modified ternary electrode materials, the electrochemical performance is superior to unmodified one. And the optimum modification ratio is 3%. From charge/discharge test, it can be seen that at 0.2C, Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ has initial discharge capacities of 179mAh/g under the 3% LiF modification ratio.

1. Introduction
Energy crisis and environmental contamination have become increasingly serious in recent years[1,2]. Lithium ion battery is considered as one of the best power sources for hybrid electric vehicles because of its high energy density, long cycle life and friendly environment[3-6]. Ni-rich lithium ion battery cathode material is a kind of very important lithium ion battery cathode material. And high nickel ternary materials Li(Ni, Co, Mn)O$_2$(NCM), have the high irreversible capacity, good thermal stability, which makes it becoming the most promising lithium ion battery cathode material. However, the Ni-rich ternary cathode materials also have problems of low cycle stability and low discharge performance of high current density. To solve these problems, many studies including doping[7,8] and coating[9,10] have been proposed.

In this paper, LiF is used to modify the Ni-rich ternary cathode materials and improve the electrochemical performance. Through LiF surface modification, the electrochemical performance of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ enhanced.

2. Experiment
2.1 Synthesis and characterization
The LiF modified Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode material was synthesized by Low temperature sintering process. Finished product of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ and different contents of LiF(A.R.purity) were mixed by dry mixing and ball milled at the speed of 100r/min for 4 hour. Then the precursor was sintered at 450℃ for 4 hour under oxygen atmosphere, the heating rate was 3℃/min. The Box furnace
(KSL-1200X, HEEF KEJING materials technology co. LTD) was used for the preparation of composite electrode materials.

The phase composition and crystal lattice parameters of all the material samples were detected with Powder X-ray diffraction (XRD, Ultima IV, Rigaku). Particle morphology was observed by scanning electron microscopy (SEM, Inspect S50 FEI).

2.2 Electrochemical measurement
The cathode electrode was prepared by coating the slurry mixture containing 80wt% active materials, 10wt% conductive additive (super-p) and 10wt% polyvinylidene fluoride (PVDF) binder on the aluminum substrate. The aluminum foils coated with cathode materials were cut into wafers with the diameter of 14mm. Then the wafer was dried at 120°C for 10 hours under vacuum, which was done prior to assembling the coin cell. The electrolyte was 1 mol/L LiPF6 in ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC) (1:1:1 in volume ratio). Coin-type half cells (CR2032) were assembled in an argon-filled glove box (Super(1220/750), Mikrouna, Germany) with the water and oxygen content less than 0.1ppm. The cell consisted of the as-prepared working electrode, microporous polypropylene membrane (Celgard 2400, Celgard Inc., USA) as separator and metallic lithium wafer as counter electrode.

The electrochemical performance evaluation of the assembled CR2032 coin cells were carried out on an automatic galvanostatic charge/discharge unit (Land 2001A, Wuhan, China) within the voltages of 2.6~4.3V (vs. Li/Li+) at room temperature.

3. Results and discussion

![Figure 1. XRD patterns of Li_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})O_{2}xF_x](image)

Fig. 1 shows the XRD patterns of Li_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})O_{2}xF_x and different content LiF modified Li_{1-x}(Ni_{0.6}Co_{0.2}Mn_{0.2})O_{2}xF_x. From Fig. 1 it can be seen that, it exhibited a typical layered hexagonal α-NaFeO_2 structure with space group R3m. The clear split of (006)/(102) and (108)/(110) peaks indicate that the samples have an ordered layered structure. Table 1 listed the lattice parameters a, c, c/a, and I_{003}/I_{104}. When the content of LiF is 3%, the c/a and I_{003}/I_{104} is greater than others, which illustrates that this sample has the best stratified structure[11].
Table 1. Cell parameters of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$-xF$_x$

| sample | a/nm | c/nm    | c/a     | I$_{003}$/I$_{104}$ |
|--------|------|---------|---------|-------------------|
| x=0.00 | 0.28627 | 1.42375 | 4.9735 | 1.3962           |
| x=0.01 | 0.28561 | 1.41676 | 4.9605 | 1.6884           |
| x=0.03 | 0.28628 | 1.42725 | 4.9855 | 1.7925           |
| x=0.05 | 0.28656 | 1.42819 | 4.9839 | 1.7685           |

Fig. 2 shows the SEM images of pristine Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ and LiF-modified Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$. Between the pristine and LiF-modified Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ samples, there is no obvious difference in morphology. And all of the samples show irregularly shape with a size of between 250nm to 700nm. When the modification amount of LiF reached 5%, the sample was agglomerated.

Fig. 3 shows the fist charge/discharge capacity of samples at 0.2C in the range of 2.6V to 4.6V. The first discharge capacity of pristine Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ sample is 159mAh/g, and the optimum sample of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ with 3% LiF modification is 179 mAh/g. From Fig. 3 it can be seen that the charging voltage rises rapidly to about 3.7v and then slowly rises to 4.6v. The charging platform in the middle about 3.7V to 3.8V can be attributed to the Ni$^{2+}$/Ni$^{4+}$ oxidation reaction.

Figure 2. SEM patterns of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$-xF$_x$(x=0.0(a), 0.01(b), 0.03(c) 0.05(d))
Figure 3. The first charge and discharge curves of Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$-xF$_x$ ($x=0.0(1), 0.01(2), 0.03(3), 0.05(4)$) at the rate of 0.2C

4. Conclusion
The impact of LiF modified Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$-xF$_x$ on the structure and electrochemical properties have been studied. With the ratio of LiF increasing, the peak separation of two pairs ((006/102) and (108/110)) is becoming more and more obvious. The SEM illustrated that all the samples show the irregularly shape and there is no obvious difference in morphology. Land test shows that, the LiF modified Li$_{1.04}$Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ enhanced the discharge capacity. And the first discharge capacity of 3% modified sample is improved 13% than pristine sample.

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