Enhanced electrochemical performance of F-doped Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ cathode materials for Li-ion batteries

Zhenye Zhu $^{1*}$ Zhuo Sang $^{2}$ Hui Li $^{1}$

1 School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, PR China
2 The Eighth Affiliated Hospital, Sun Yat-Sen University 518033, PR China

Corresponding author: Zhenye Zhu zhuzy@hit.edu.cn

Abstract. F-doped cathode material Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{(2.35-x)}$F$_{x}$ (x=0, 0.05, 0.10, 0.15) were synthesized successfully by two-step co-precipitation method. X-ray diffraction pattern shows that fluorine doping does not bring impurities, but the lattice parameters increase slightly with fluorine content increasing in Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{(2.35-x)}$F$_{x}$. At the current density of 0.5C (125mAhg$^{-1}$), Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.30}$F$_{0.05}$ has the highest capacity retention (94.56%) and discharge capacity (177.4mA•h/g) after 50th cycles, while capacity retention and discharge capacity after 50th cycles of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material are only 86.19% and 164.7 mA•h/g. And Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.30}$F$_{0.05}$ material exhibits a noticeable higher discharge capacity than other Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{(2.35-x)}$F$_{x}$ (x=0, 0.10, 0.15) materials at high current density. The initial discharge specific capacity of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.30}$F$_{0.05}$ material is increased to 121.1 mA•h/g and 82.3 mA•h/g compared to 91.1 mA•h/g and 66.8 mA•h/g of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material at 2C and 5C. It can be concluded that electrochemical performances of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material are improved due to fluorine doping.

1. Introduction

Significant attention has been paid to lithium-ion batteries for their unmatchable combination of high energy and power density[1]. In recent years, lithium-ion batteries have been successfully used in all kinds of portable devices, and even in electric vehicles (EVs)[2-4]. But lithium-ion batteries still have some shortcoming, such as low capacity under high current density, instability, insecurity and so on. Based on these problems, researchers need to find new and effective ways to improve the comprehensive performance of lithium-ion batteries[5].

Li-rich layered oxides, xLi$_2$MnO$_3$·(1−x)LiMO$_2$ (M=Ni, Mn, Co), are the promising alternate cathode material for its much higher capacity (>200mAh$^{-1}$ at lower rate), lower cost, excellent cycling performance[6]. For example, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ has been extensively studied as cathode material for Li-ion battery, since Ohzuku and Makimura reported it[7]. Layer-structured oxides such as Li$_{2}$CoO$_2$...
(1-z)Li[Li_{1/3}Mn_{2/3}]O_{2}·zLi[Mn_{0.5}Ni_{0.5}Co_{3/2}]O_{2} (y=1/6, and 0.25≤z≤0.75) deliver capacities as high as 250 mAhg^{-1} when charged to 4.8 V [8]. Doping modification has been proved an effective method to improve electrochemical performance of electrode materials, such as fluorine substitution [9-16].

It is reported that fluorine substitution catalyzes the growth of the primary particles of Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_{2}·xF (x=0, 0.025, 0.05, 0.075, 0.1) cathode materials [17]. Although the initial discharge capacity decreases as the fluorine content increasing, the fluorine substituted materials present significant improvement in the cycling performance. Yue and his colleagues found that Fluorine substituted LiNi_{0.5}Co_{0.1}Mn_{0.4}O_{2} material maintained stable layered structure after 100 cycles and still presented smooth surface without any structure transformation [18-20]. And They attributed the phenomenon to fluorine substitution in protecting the electrode from HF attack and maintaining the structural stability. Codoped (Li^{+} and F^{-}) Li_{1+x}Ni_{0.5}Mn_{1.5}O_{4}·xF spinel powders were synthesized by Li, et al [21], the codoped particles formed a smooth and uniform surface film, which mitigated the interaction of active materials and electrolyte solution as well as improved stability of cycling. Kim and his colleagues reported that Fluorine was substituted to facilitate the movement of lithium ions in 0.3Li_{2}MnO_{3}·0.7Li[Mn_{0.6}Ni_{0.25}Co_{0.15}]O_{1.975}F_{0.025} cathode materials [22]. The introduction of fluorine forms a more compact SEI layer and reduces the dissolution of transition metals. The fluorine gradient-doped LiNi_{0.5}Mn_{1.5}O_{4} spinels were synthesized by Luo, et al [23], the fluorine gradient-doped LiNi_{0.5}Mn_{1.5}O_{4} sample exhibited an improved long-term cycling stability and high rate performance, due to the suppression of the reaction between electrolyte and cathode, resulting in a decrease in the total resistance and the formation of a thin, uniform and smooth film on the surface. Li[Li_{1/2}Mn_{0.5}Ni_{0.13}Co_{0.13}]O_{2}·xF (x = 0, 0.05 and 0.10) were synthesized by Zheng and his colleagues [24]. and they found that fluorine incorporation stabilized the electrode/electrolyte interface by suppressing the formation of poorly conducting LiF in the SEI layer and thus maintained stable interfacial resistances. As a result, cycling stability of Li[Li_{1/2}Mn_{0.5}Ni_{0.13}Co_{0.13}]O_{2}·xF was significantly improved. It was reported by Li that the discharge voltage plateau of Li_{1.3}Mn_{0.54}Ni_{0.13}Co_{0.13}O_{2}·xF (x = 0, 0.02, 0.05, 0.08) materials were stabilized by F doping due to the retarded layered-to-spinel phase transition [25], thus a high energy density output of the cell could be maintained. Li[Li_{1/6}Ni_{1/6}Co_{1/6}Mn_{1/2}]O_{2}·xF (x = 0.00 to 0.07) materials were synthesized by Song, et al [26]. Due to the addition of fluorine, the reversible capacity significantly increased as the irreversibility was suppressed during the first cycle. It is also found that the presence of fluorine facilitated the reduction of cobalt and manganese ions in Li-rich layered oxide, and that the reduced transition metal ions suppressed structural changes.

In this study, F-doped material Li_{1.3}Mn_{0.68}Ni_{1/6}Co_{1/6}O_{2}·3.5xF (x=0, 0.05, 0.10, 0.15) was synthesized by two-step co-precipitation method. Phase analysis was implemented on high-resolution X-ray diffractometer (Rigaku,Japan) with Kα radiation. Scanning electron microscopic(SEM) images were operated with a S4700 Field emission scanning electron microscope(Hitachi,Japan). The electrochemical measurements were carried out by using LAND batteries testing system.

2. Experimental

2.1. Synthesis: two-step temperature co-precipitation method
A \([\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}]\text{CO}_3\) precursor reagent was synthesized by two-step co-precipitation method. \(\text{NiSO}_4\cdot 7\text{H}_2\text{O}\) (Shanghai Aladdin, 99.9%), \(\text{CoSO}_4\cdot 7\text{H}_2\text{O}\) (Shanghai Aladdin, 99.999%) and \(\text{MnSO}_4\cdot \text{H}_2\text{O}\) (Shanghai Aladdin, 99%) were used as raw materials. Figure 1. shows the preparation procedure of the precursor \([\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}]\text{CO}_3\) and the cathode material \(\text{Li}_{1.2}\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{O}_{2.35\times\text{F}_x}\). Firstly, the appropriate amount of \(\text{NiSO}_4\cdot 7\text{H}_2\text{O}\) and \(\text{CoSO}_4\cdot 7\text{H}_2\text{O}\) is dissolved in distilled water at a molar ratio of 3:1 and put into the reaction tank together. Then, add the aqueous solution of sodium carbonate slowly at 40 °C. Raise the reaction temperature to 80℃ after the dropwise-addition is completed, and then the mixed solution (\(\text{NiSO}_4\cdot 7\text{H}_2\text{O}\), \(\text{CoSO}_4\cdot 7\text{H}_2\text{O}\) and \(\text{MnSO}_4\cdot \text{H}_2\text{O}\) molar ratio is 0.5:1.5:8) is added into the continuous stirred (900r/min) solution in the reaction tank, while the required \(\text{Na}_2\text{CO}_3\) is also dropped into the reactor. After the completion of the precipitation reaction, the resultant slurry solution is stirred for 3h then aged at 80°C for 12h. After that, the \([\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}]\text{CO}_3\) precipitate is separated by the vacuum filtration procedure and then washed several times with the distilled water and dried in vacuum at 110°C for 12h. Then, in order to prepare cathode material \(\text{Li}_{1.2}\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{O}_{2.35\times\text{F}_x}\), 5% excess \(\text{LiCO}_3\) and 3% excess \(\text{LiF}\) are mixed thoroughly with the obtained \([\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}]\text{CO}_3\). The mixture is first calcined at 500°C for 5h and then 850°C for 15h in air with a heating rate of 5°Cmin\(^{-1}\).

**Figure 1.** Schematic diagram of the synthesis of precursor \([\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}]\text{CO}_3\) and cathode material \(\text{Li}_{1.2}\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{O}_{2.35\times\text{F}_x}\).

### 2.2. Structure and morphology analysis

X-ray diffraction (XRD, Rigaku RINT2000 with Cu-Kα radiation) in a 2θ range of 10°-80° with a scan rate of 6°min\(^{-1}\) is employed to analyze the structure and phase composition of synthesized samples. The scanning electron microscopy (SEM, Hitachi) images are taken to get the morphology and size of the samples.
2.3. Electrochemical measurements

The electrochemical properties of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35-x}$F$_x$ composites are examined by using a coin cells (CR2032) assembled in an Ar-filled glove-box. The positive electrode is prepared by spreading the mixture of prepared active material (80wt%), carbon conducting additive (Super-P, 10wt%) and polyvinylidene fluoride (PVDF,10wt%) dissolved in N-methyl-2-pyrrolidone (NMP) onto a smooth aluminum foil. The positive electrode is allowed to dry at 75°C for 3h in the air and then at 120°C for 10h in a vacuum oven. The cathode film is punched into appropriate size to assemble coin cells. Lithium foil is used as negative electrode, Celgard 2400 membrane is used as the separator, and the electrolyte is 1 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with volume ratio 1:1.

3. Results and discussion

3.1. Structure and morphology of F-doped Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35-x}$F$_x$ composites

![XRD patterns](image1)

Figure 2. XRD patterns of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35-x}$F$_x$ (x=0, 0.05, 0.10, 0.15) materials.

![Variation of lattice parameters](image2)

Figure 3. Variation of lattice parameters as a function of F amount in Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35-x}$F$_x$ (x=0, 0.05, 0.10, 0.15) materials.

XRD patterns of synthesized Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35-x}$F$_x$ (x=0, 0.05, 0.10, 0.15) composites are presented in Figure 2. All diffraction peaks of materials can be indexed to cubic structure spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (Space group: Fd-3m), layer structure Li$_2$MnO$_3$ (Space group: C2/m) and layer structure LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ materials. Compared with pristine Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$, there is no new peaks or impurities in the fluorine-doped materials, which demonstrates that fluorine substitution does not alter the crystal structure of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$. By observing the patterns carefully, the S (111) peaks of the F-doped materials shift to small angle obviously, which is caused by the increase of the lattice parameter of the modified material.$^{[27]}$

The variation of lattice parameters as a function of F amounts are shown in Figure 3. The lattice parameter was calculated by JAD 6.0. As indicated in Figure 3, with increasing fluorine content, the lattice parameters gradually increase from a= 8.165(1)Å and v=544.355(9)Å$^3$ to a=8.174(4)Å and v=546.222(1)Å$^3$. The increase of lattice parameters may be induced by two reasons. The first reason is that partial substitution of oxygen by fluorine leads to an unbalance of valence, which requires partial reduction of transition metal ions Mn$^{4+}$(r=0.53Å) to Mn$^{3+}$(r=0.645Å), Ni$^{4+}$(r=4.8Å) to Ni$^{3+}$(r=5.6Å) and Co$^{3+}$ (r=0.545Å) to Co$^{2+}$ (r=0.65Å) for charge compensation, and the second one is that the chemical bond between lithium and fluorine is stronger than that between lithium and oxygen resulting...
from the charge compensation by the fluorine substitution \[^{[28,29]}\].

The particle morphologies of Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.35}\), \(x\)F composites observed by SEM are shown in Figure 4. Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.35}\) samples have good spherical secondary particles with an average diameter about 5\(\mu m\), and the spherical secondary particles is comprised of a great number of small primary particles with a diameter in range of 200-800nm. The morphology of Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.30}\)F\(_{0.05}\) and Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.25}\)F\(_{0.10}\) in Figure 4 (d) shows that its spherical boundary is not smooth, some particles are broken and particle size is not uniform, which may be attribute to the excess of fluorine damaging the structure of the material. In Figure 4 (b), all the primary particles for Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.30}\)F\(_{0.05}\) have smooth surfaces.

\[\text{Figure 4. SEM images of Li}_{1.2}\text{Mn}_{4/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{O}_{2.35, x}\text{F}_x: (a)x=0, (b)x=0.05, (c)x=0.10, (d)x=0.15.}\]

3.2. Electrochemical performance

The electrochemical measurements were carried out by using LAND batteries testing system. The measurement temperature was 25 °C, the current density for 1 C rate was 250mAh·g\(^{-1}\).

Figure 5 indicates that the discharge capacities of Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.35}\) composites for 50 cycles at the current density of 0.5C (125mAh\(^{-1}\)) at a voltage range of 2.0-4.8V. As shown in Figure 5 (a), though the F-free Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.35}\) has the highest initial discharge of 191.1mAh\(^{-1}\), its capacity decreases gradually in 10-50 cycles, leading to a capacity retention of only 86.19% after 50 cycles. Meanwhile, the capacity retention of Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.35}\)F\(_{0.05}\), was 94.56% for x=0.05, 82.94% for x=0.10 and 78.58% for x=0.15, respectively. It is shown, after 11 cycles the discharge capacity of Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.31}\)F\(_{0.05}\) is at its largest value. But Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.25}\)F\(_{0.10}\) and Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.20}\)F\(_{0.15}\) materials did not show better cycle performance than Li\(_{1.2}\)Mn\(_{4/6}\)Ni\(_{1/6}\)Co\(_{1/6}\)O\(_{2.35}\) material, which may be the excess F damaging the structure of the phases and lead to the decrease of the discharge capacity. Figure5 (b) shows the corresponding initial discharge capacity and capacity retention values. With the content of F increasing, initial discharge capacity of
Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$xF$_x$ cathode material decreases gradually, and capacity retention after 50 cycles first rises and then declines. When $x=0.05$, Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$xF$_x$ cathode material delivers the largest capacity retention (94.56%) and discharge capacity after 50th cycles (177.4mA·h/g).

It can be concluded from the above analysis that fluorine doping positively impact on the structure stability and cycling performance of the cathode materials. The improved cycling performance of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.25}$F$_{0.10}$ composite should be due to the existence of the bonding of Li-F (stronger than the bonding of Li-O) which stabilizes the surface structure and enhances the stability of the electrode materials, and thus avoid the abrupt change of the lattice distortion$^{[30,31]}$.

![Figure 6](image6.png)  
**Figure 6.** Rate capability of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$xF$_x$ ($x=0$, 0.05, 0.10, 0.15) in the voltage range of 2.0-4.8V.

![Figure 7](image7.png)  
**Figure 7.** Initial charge/discharge curves and differential capacity vs. Voltage (dQ/dV) curves of (a) Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ and (b) Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.3}$F$_{0.05}$ electrodes.

| F$^-$ doping amount | First discharge specific capacity at different rates (mA·h/g) |
|---------------------|------------------------------------------------------------|
| ($x$)               | 0.1C | 0.2C | 0.5C | 1C | 2C | 5C |
|---------------------|------|------|------|----|----|----|
| 0                  | 242  | 218.8| 184.1| 137.9| 91.1| 66.8|
| 0.05                | 237.3| 228.2| 198.2| 163.3| 121.1| 82.3|
| 0.10                | 235.7| 220.7| 167.7| 142.5| 104.8| 75.7|
| 0.15                | 238.9| 209.1| 170.5| 155.6| 95.1 | 55.4|

Figure 6. shows the rate capability of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$xF$_x$ composites ($x=0$, 0.05, 0.10, 0.15) between 2.0V and 4.8V at charge-discharge rates from 0.1C to 5C. All composites deliver decreases capacities as the C rate is increased, but it is clearly observed that Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.3}$F$_{0.05}$ exhibits a noticeable higher discharge capacity than Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$, Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.25}$F$_{0.10}$ and Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.2}$F$_{0.15}$ at high rates, and both cycle performance and rate capability of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.3}$F$_{0.05}$ are obviously better than those of other three materials. The corresponding data is given in Table 1, when the current density was 2C, the discharge specific capacity of F-doped Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.3}$F$_{0.05}$ material is increased to 121.1mA·h/g, while that of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material is only 91.1mA·h/g. It is found that Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.3}$F$_{0.05}$ shows the best cycling performance according to our research. In other words, F$^-$ substitution can

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**Table 1.** The first specific discharge capacity of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$xF$_x$ at different rates
improve the cycling performance and rate capability of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ cathode materials.

The differential capacity curves (dQ/dV) of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ and Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ electrodes are depicted in Figure 7. The first potential slope in the initial charge curve between 3.8 and 4.4V of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material is associated with lithium extraction from Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$-like component, accompanied by the oxidation process of Ni$^{2+}$ to Ni$^{4+}$ and Co$^{3+}$ to Co$^{4+}$ in the material$^{[32]}$, and these two processes correspond to peaks near 3.9V and 4.1V in the 1st differential capacity curve. In the two subsequent charging processes, the peaks in the differential capacity curve corresponding to the lithium removal from the Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$-like phase are separated from the peaks of the transition metal oxidation processes. The potential plateau of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material near 4.51V corresponds to that of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ material near 4.65V, corresponding to the loss of O$^{2-}$ and de-intercalation of Li$^+$ (Li$_2$MnO$_3$→2Li$^+$+2e$^-+0.5$O$_2$+MnO$_2$), finally exists in the form of Li$_2$O$^{[33]}$. And the oxidation peaks strength in differential capacity curve decreases and has a small voltage deviation, which is a characteristic of Li-rich oxide electrode. The weakening of oxidation peak is related to the gradual decrease of irreversible phase change of Li$_2$MnO$_3$ during the progress of charging and discharging cycle. In the first charging process of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ material, the voltage of transition metal oxidation and the removal of Li$_2$O are both higher than those of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material, and the corresponding peaks in the differential capacity curve are all shifted to higher voltage, which is due to F doping, while the reason need our further researches. In the discharging process, there are three obvious reduction peaks in the differential capacity curve of both Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material and Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ materials. The peak near 4.4V corresponds to the reduction process of Ni$^{4+}$ to Ni$^{3+}$, and the peak near 3.7V corresponds to the reduction process of Ni$^{3+}$ to Ni$^{2+}$, and the reduction process of Ni is also accompanied by the reduction of Co. The peak around 3.3V corresponds to the reduction process of Mn$^{4+}$ to Mn$^{3+}$. In addition, reduction peaks appeared near 2.6V in the differential capacity curve of both Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material and Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ material, which corresponds to the lithium intercalation process of the spinel phase formed by the surface structure of the material$^{[34]}$.

4. Conclusion

F-doped Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material was successfully prepared by two-step temperature co-precipitation. With the doping of fluorine, the lattice parameter increases slightly but no impurity phase was formed. Electrochemical characterization demonstrated that F doping can improve high-rate capability and cycling performance of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material. Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ composite has the highest capacity retention (94.56%) and discharge capacity after 50th cycles (177.4mA·h/g), compared with only 86.19% and 164.7 mA·h/g of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material. Furthermore, the discharge capacity of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ material was much higher than other Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{x}$ (x=0, 0.10, 0.15) materials at high current density. The initial discharge specific capacity of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{0.05}$ material is increased from 91.1 mA·h/g to 121.1 mA·h/g compared to Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$ material at 2C. A conclusion can be drawn by comparing the properties of all kinds of Li$_{1.2}$Mn$_{4/6}$Ni$_{1/6}$Co$_{1/6}$O$_{2.35}$F$_{x}$ composites (x=0,0.05, 0.10, 0.15) that F doping can indeed improve the electrochemical properties of materials and optimal doping amount was 0.05 (mole ratio).
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