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Short Communication

Synthesis and Improvement on the Electrochemical Properties of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ by Fluorine Doping

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The $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ and $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$ cathode materials were synthesized by a sol-gel method. The synthesized materials were characterized with X-ray diffraction (XRD). The electrochemical performances of the materials were tested by constant-current cyclic testing at room temperature for 60 cycles. The XRD results show that the samples of cathode materials synthesized by the method possess well-layered structures. The $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$ powder has a better cyclic performance. A high initial specific discharge of 268 $mAhg^{-1}$ has been obtained at the calcination of 800 ^{o}C for 12 h, with an capacity retention of 90.3% after 60 cycles. It is evident that the doping of F^- can improve the capacity and cycling performance.

Keywords: Lithium-ion battery; Li-rich Cathode materials ; Sol-gel method; Doping

1. INTRODUCTION

The layered lithium transition metal oxide $LiCoO_2$ has been used as the cathode material for Li-ion battery for a long time and still used [1-3]. However , its high cost,toxicity and unsatisfactory thermal stability seriously limit its use [1-3]. Other cathode materials such as spinel $LiMn_2O_4$ [4] and olivine $LiFePO_4$[5] have been successfully applied in lithium ion batteries, but they typically deliver low capacities of 100—160 $mAhg^{-1}$.

In recent years, much research work has done for the Li-rich solid-solution layered cathode materials zLi_2MnO_3-(1-z)$LiMO_2$ (M=Co, Ni, Mn, etc.), which can deliver higher capacity (>250 $mAhg^{-1}$) when charging to 4.8 V[6-14]. Also this kind of cathode material could be subject to long-time cycing, especially at higher temperature. The cathode material $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ [15,16], which can be represented as $0.5Li_2MnO_3$-$0.5LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, could show excellent electrochemical performance. The material shows a high discharge capacity when it is cycled with an upper cutoff voltage of 4.8 V. As Kang and his co-worker[17]reported, they synthesized $Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z$ ($0\leq z\leq 0.1$) by a sol-gel method, when z=0.05 , the charge-discharge tests showed that at room temperature between 2.0~4.6 V, the discharge capacity of $Li[Li_{0.2}Ni_{0.175}Co_{0.10}Mn_{0.525}]O_{1.95}F_{0.05}$ was about 230 $mAhg^{-1.}$

In this work, the materials of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{2-Z}F_Z$(z=0, 0.05), were successfully synthesized by a sol-gel method, then the crystal structure and cyclic stability are characterized with X-ray diffraction (XRD) and charge-discharge tests. Both capacity and cycling performance have been improved by F doping.

2. EXPERIMENTAL

The $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{2-z}F_z$(z=0,0.05) materials were prepared by citric acid sol–gel method in following manner, similar to the work as those in our labarotory[18,19]. Stoichiometric amounts of $Ni(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Mn(CH_3COO)_2\cdot 4H_2O$ and LiF were dissolved in distilled water. Then $LiNO_3$ solution with citric acid as chelating agent was added slowly into the mixed solution prepared above. The solution pH was adjusted about to 7.0 with aqueous ammonium hydroxide. The solution was heated at 75 ^{o}C with continuous stirring until the gel was obtained. The dried precursor was precalcined at 500 ^{o}C for 6 h, then ground and made into pellets. The target compound was finally gained by sintering the pellets at 800 ^{o}C for 12 h in air and then quenching to room temperature.

X-ray diffraction (XRD) data were collected with a Bruker Advanced D8 X-ray diffractometer with Cu Kα radiation between 2θ =10 and 90°.

The charge-discharge tests were carried out using CR2032 coin-type cell. The coin cells have been made as our previous work[18,19].The positive electrode consisted of 80 wt.% active material, 12 wt.% acetylene black , and 8 wt.% polyvinylidene difluoride (PVDF) binder on aluminum foil and dried at 80 ^{o}C for 12 h in a vacuum oven. The cells were assembled with the cathodes as-prepared, metallic lithium foil as counter electrode, Cellgard 2325 porous polypropylene film as separator and 1M $LiPF_6$ dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as electrolyte in Argon-filled glove box (Super, Mikrouna, China). Constant current charge-discharge was made for the cells at the current density 0.2 $mA\cdot cm^{-2}$ (equal to about C/10) between 2.0~4.8V (versus. Li/Li^+) at room temperature. The measuring instrument is Land battery testing instrument made in China.

3. RESULTS AND DISCUSSION

The XRD patterns of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{2-z}F_z$(z=0,0.05) are shown in Fig. 1. All peaks are sharp and well-defined and could be indexed on the basis of the α-$NaFeO_2$ structure, except for those broadened super lattice peaks around 20-25°. The weak peaks between 20° and 25°, which cannot be indexed to α-$NaFeO_2$ structure, are known to correspond to the ordering of the Li^+,Ni^{2+},and

Mn^{4+} ions in the transition metal layer of the layered lattice, which can be indexed to the monoclinic unit cell C2/m[20,21]. The lattice parameters for a and *c*, the ratios of *c/a* and the intensity ratios of $I_{(003)}/I_{(104)}$ are compared in Table 1.

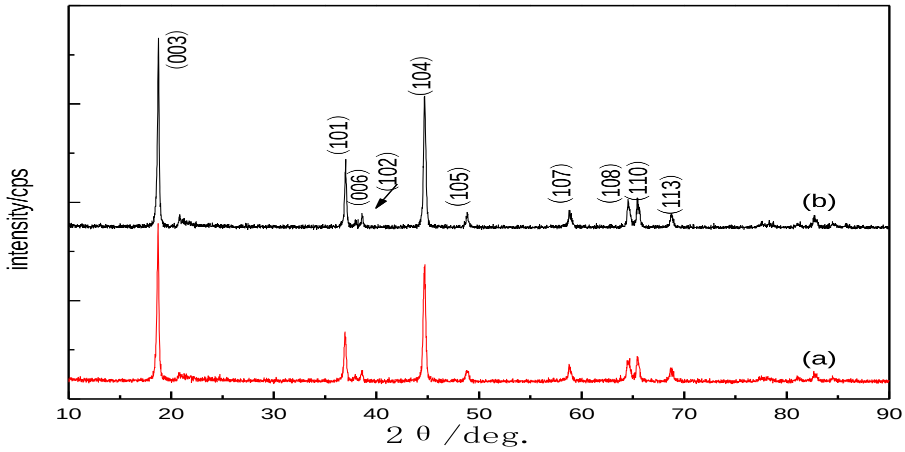

Figure 1. XRD patterns of （a) $Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_2$; (b) $Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$; synthesized for 12h at 800 °C

Table 1. Lattice parameters, *c/a* ratios,I_{003}/I_{004} intensity ratios of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{2-z}F_z$(z=0,0.05) materials

sample	*a(Å)*	*c(Å)*	*c/a*	I_{003}/I_{004}
$Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_2$	2.8508	14.2291	4.9913	1.3569
$Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$	2.8488	14.2165	4.9903	1.4430

It can be found that the materials both show high *c/a* ratios (higher than 4.98) and $I_{(003)}/I_{(104)}$ peak intensity ratios, which indicates that both the materials as prepared form a pure phase with good crystallinity[22]. From the $I_{(003)}/I_{(104)}$ peak intensity ratios, it could be proposed that the crystal orientation of $Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$ is higher than the $Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_2$ material's.

In this work, we investigated the effect of substitution of oxygen with fluorine on the cycling performance. All cells were cycled at a constant current density of $0.2mAcm^{-2}$ ($20mAg^{-1}$) and in the voltage range of 2.0–4.8V at room temperature. The galvanostatic initial, second and 60th cycle voltage profiles for the Li/ $Li[Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$ cell are shown in Fig. 2. The first charge voltage profile is characterized by an initial sloping region up to 4.5 V, followed by a voltage plateau which slowly progresses to the 4.8 V cut-off voltage[23]. In the second cycle, the 4.5 V plateau on the first cycle is not observed, followed a long sloping shape up to 4.8 V just as many similar systems[20-23]. There is no discernible change in the voltage profile of the material in subsequent cycles.

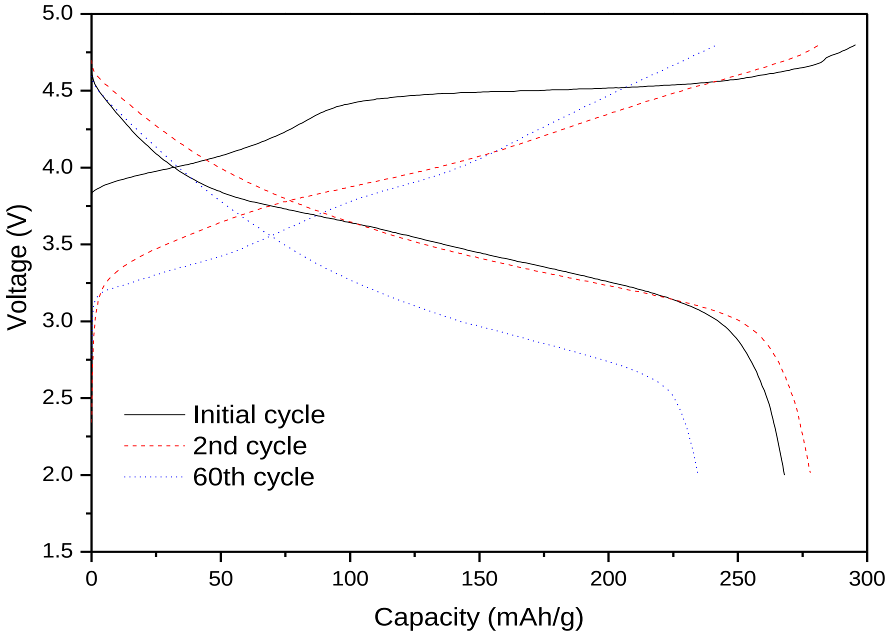

Figure 2. The initial, 2nd and 60th voltage profiles of Li/ Li[$Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}$]$O_{1.95}F_{0.05}$ cell at room temperature between 2.0 V and 4.8 V

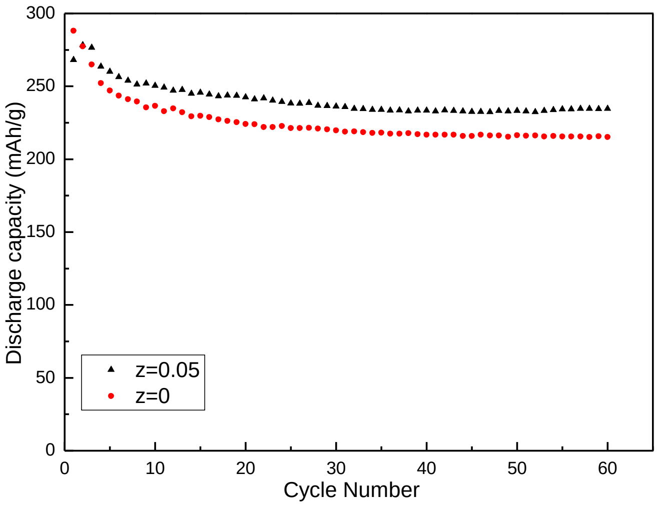

Figure 3. Cycling performance of Li/ Li[$Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}$]$O_{2-z}F_z$(z=0,0.05) cells in the voltage range of 2.0–4.8V at room temperature

Fig. 3 shows the discharge capacity with cycle numbers of Li[$Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}$]$O_{1.95}F_{0.05}$ and Li[$Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}$]$O_2$ materials . Although the first discharge capacity of Li[$Li_{0.2}Mn_{0.45}Ni_{0.13}Co_{0.13}$]$O_{1.95}F_{0.05}$ was slightly reduced, the cycling performance was greatly improved with the fluorine droping. The capacity retention after 60 cycles of the undoped material is

87.1% while the F-doped materials is 90.3%. The lower initial discharge capacity of the fluorine-doped material may be attributed to the stronger Li-F bonds that hinder lithium movement during charge.

4. CONCLUSIONS

Li-rich layered $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{2-z}F_z$(z=0,0.05) materials have been successfully synthesized by a sol–gel method and the effect of the fluorine on the electrochemical properties of the cathode materials was investigated. The initial discharge capacity decreased a little with the fluorine doping, however, capacity and cycling performance have been improved by the fluorine doping. In conclusion, $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_{1.95}F_{0.05}$ is a promising candidate for cathode materials in rechargeable lithium-ion batteries in terms of high capacity and stability.

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