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Surface modification and characterization of F-Co doped spinel $LiMn_2O_4$

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Abstract: Spinel $LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ as cathode material was modified with $LiCoO_2$ by the sol-gel method, and the crystal structure, morphology and electrochemical performance were characterized with XRD, SEM, EDS, AAS and charge-discharge test in this paper. The results show that a good clad coated on parent material can be synthesized by the sol-gel method, and the materials with modification have perfect spinel structure. $LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ materials coated by $LiCoO_2$ improve the stability of crystal structure and decrease the dissolution of Mn into electrolyte. With the $LiCoO_2$ content increasing, the specific capacity and cycle performance of samples are improved. The capacity loss is also suppressed distinctly even at 55 ℃.

Key words: lithium ion batteries; spinel $LiMn_2O_4$; ion doping; surface coating

1. Introduction

Since the introduction of lithium ion batteries by SONY, they have been widely applied in many electronic devices such as mobile telephones, portable computers, camcorders and so on[1]. Cathode materials for lithium secondary batteries, such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$, have been studied intensively[2]. Among them, spinel $LiMn_2O_4$ has received much attention due to its low cost, environmental merit, easy preparation and thermal stability at high temperature, therefore, it is considered as one of the most promising candidates of cathode materials for lithium ion batteries. However, spinel $LiMn_2O_4$ shows significant capacity fading and poor cycle performance, especially at elevated temperature (> 55 ℃). It can be mostly attributed to dissolution of Mn, Jahn-Teller distortion and decomposition of electrolyte[3-5].

In order to solve above problems, many researchers used transition cation partly instead of Mn^{3+} or used other anion instead of O^{2-}. The ion doping methods can improve the stability of spinel structure, and suppress the Jahn-Teller distortion[6], but investigations indicate the dissolution of Mn mainly occurs on the interface between spinel $LiMn_2O_4$ and electrolyte, whether during charge or discharge. Hence, reducing the interface is also very important to improve the properties of material except ion doping. Surface modification is considered as the best way to solve the problem[7-9].

In this paper, based on the F-Co doped $LiMn_2O_4$ as parent material synthesized by mechanical activation-solid state reaction[10], $LiCoO_2$ was coated on the material by the sol-gel method, and the coating content (wt.%) is 0%, 3% and 5%. Finally, the crystal structure, apparent morphology and electrochemical performance were characterized with XRD, SEM, EDS, AAS and charge-discharge test.

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2. Experimental

2.1. Materials preparation

$LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ was prepared by the mechanical activation-solid state reaction using lithium carbonate (Li_2CO_3), electrolytic manganese dioxide (EMD), cobalto-cobaltic oxide (Co_3O_4) and lithium fluoride (LiF) as starting materials. These starting materials at a mole ratio Li:Co:Mn:F = 1:0.09:1.91:0.08 were put into an agate mortar with appropriate alcohol and thoroughly mixed for 3 h with agate ball grinder, then activated by ultrasonic cavitation for 1 h. Well ground mixtures were dried at 120 ℃ for 3 h, followed by ball milling for 30 min. Finally, the compounds were heated at 750 ℃ for 24 h, and cooled to room temperature spontaneously.

Synthesized $LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ was used as parent material and $LiCoO_2$ was coated on its surface by the sol-gel method. The detailed operations were shown as follows. Reagent grade Li(CH_3COO)·$2H_2O$ and Co$(CH_3COO)_2$ at certain mole ratio dissolved into ethylene glycol with citric acid, stirred mechanically for 30 min, then adjusted pH to 7.5 by dropping NH_4OH and got sol. The $LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ powder was dispersed into sol with violent stirring at 80 ℃ until forming gel precursor. The precursor was calcined at 750 ℃ for 12 h to obtain $LiCoO_2$-coated $LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ cathode materials.

2.2. Characterization

The crystal structures of samples were identified by the X-ray diffraction (XRD) analysis with Cu Kα radiation at 35 KV and 20 mA. Data were collected in the 2θ range 10°-80° with a step size of 0.02° and a count time of 10 s per step. The surface micrographs were observed through scanning electron microscopy (SEM). The elements contained in the samples were determined by an energy dispersive spectrometer (EDS). The amount of Mn dissolution into electrolyte was measured by atomic absorption spectrophotometer (AAS).

2.3. Electrochemical test

The electrochemical performances of samples were performed using CR2032 coin-type cells. The cell consisted of a cathode and an anode of lithium metal foil separated by a porous polypropylene film as separator (Celgard 2300). The mixture, which consisted of 85% cathode material, 8% acetylene black as conductive material and 7% PVDF (polyvinylidene fluoride) in 1-Methyl-2-Pyrolidinone (NMP), was coated on an aluminum foil as cathode. Cathode disks (Φ13 mm) were punched from the sheet rolled, with an average weight of 3 mg of active material. The electrolyte injected was 1 $mol \cdot L^{-1}$ $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at the volume ratio of 1:1. The cell was assembled in the glove box filled with argon gas. The charge and discharge experiments were carried out using a secondary battery testing instrument. The charge and discharge current density was 0.5 $mA \cdot cm^{-2}$ and voltage was in the 3.0-4.3 V range vs. Li^+/Li. The performance tests at elevated temperature were measured in constant temperature cabinet.

3. Results and discussion

Fig. 1 shows the XRD patterns of samples before and after coating. All samples are of single phase and spinel structure with the space group $Fd3m$. There is not diffraction peak of $LiCoO_2$ or other materials in the patterns. With

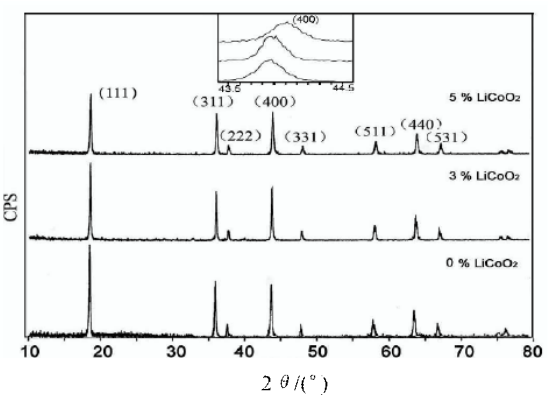

Fig. 1. XRD pattern of samples before and after coating.

the $LiCoO_2$ content increasing, the intensity of diffraction peaks decreases and the peak width at half height increases. Also, it can be seen that the (400) plane peaks shift to high angle from the magnified peak, which indicates the lattice volume of spinel $LiMn_2O_4$ shrinks after coating.

There are three assumptions to explain the above phenomena. First, the Co element is doped into the crystal lattice of spinel $LiMn_2O_4$, and the doped $LiMn_2O_4$ forms, but it is only surface doping which is different from body doping. Second, $LiCoO_2$ coats entirely on the surface of parent material, but the amount of $LiCoO_2$ coated is so small that the XRD analyzer can not measure the $LiCoO_2$ phase. The third possibility is between above mentioned two possibilities, that is, the materials after coating consist of three parts, i. e., exterior clad layer, doping transition layer and interior parent layer. The schematic is shown in Fig.2.

In order to make sure which possibility it belongs, the SEM is firstly performed. The results are shown in Fig.3. It can be seen that the samples have uniform size distribution about 3 μm, but the morphology is different before and after coating . The morphology of crystal is sharp before coating, but it is smooth after coating, especially sample C. However, it is difficult to distinguish that the surface is a coating layer or a solid solution only by SEM photos. Observed the low rate scanning of sample C (Fig.3(d)), the coating by sol-gel method is uniform.

To confirm the components of materials' surface, the energy dispersive spectrometer (EDS) by X-ray was performed as shown in Fig.4. It is evident that there is F element peak before coating, but without it after coating. Moreover, the peak intensity of O and Mn element before coating is higher than that after coating. It can also be seen that the peak intensity of Co element after coating is higher. These indicate that it is not the first possibility (sur -

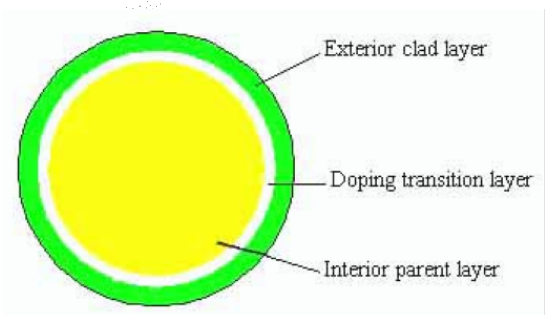

Fig.2. Schematic of surface coating of samples.

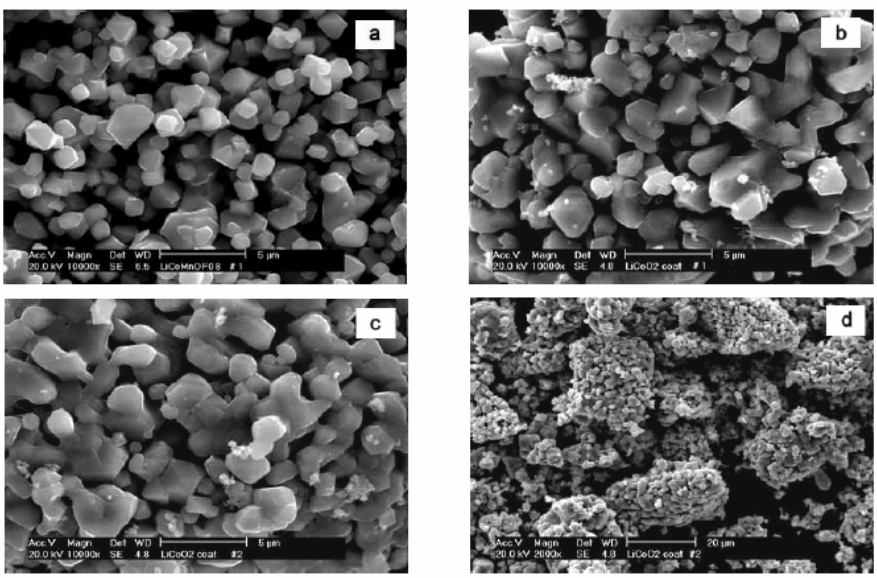

Fig.3. SEM micrographs of samples before and after coating: (a) 0% $LiCoO_2$; (b) 3% $LiCoO_2$; (c) 5% $LiCoO_2$; (d) low rate scanning of sample C.

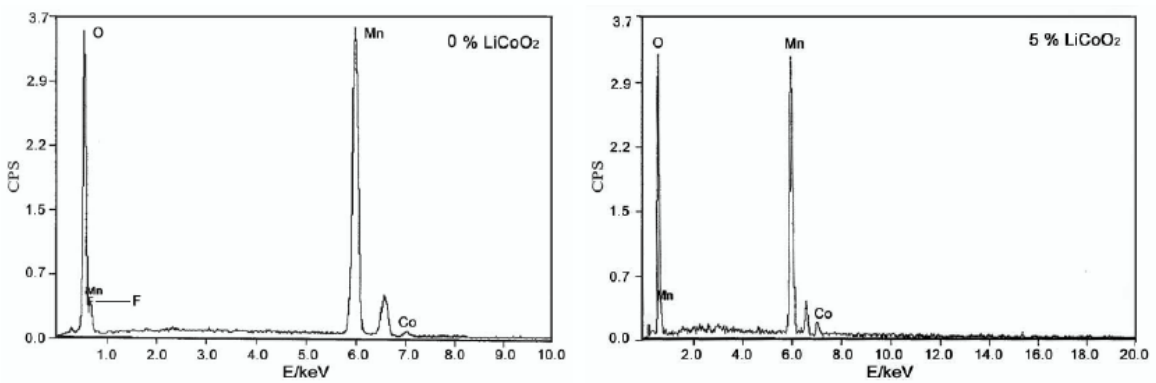

Fig.4. EDS patterns of samples before (a) and after (b) coating.

face doping), but we can not confirm whether it is the second or third assumption. Hence, other tests are necessary to prove it.

3.1. Electrochemical characterization

Fig. 5 shows the first charge-discharge curves of samples at room temperature. Sample without modification shows two distinct voltage plateaus on charge-discharge curve, which is of typical electrochemical characteristics of spinel $LiMn_2O_4$. With $LiCoO_2$ content increasing, the characteristic of voltage plateaus is reducing and the voltage fades slowly at the end of discharge, which are of $LiCoO_2$ characteristic. The specific capacities of first discharge are 119.38, 117.65 and 119.88 $mAh \cdot g^{-1}$. If the second assumption is right, the specific capacity will increase after coating, but the results are not the case. The results can be reasonably explained by the third assumption. The material with 3% $LiCoO_2$ forms more doping transition layer because of small coating content, and the electrochemical active component of Mn^{3+} ions decreases after Mn^{3+} substituted by Co^{3+}, which leads to its capacity drop. The capacity of sample with 5% $LiCoO_2$ only improves a little, which can be attributed to the doping transition layer, or the capacity will increase much. Hence, the doping transition layer lies between exterior clad layer and interior parent material layer.

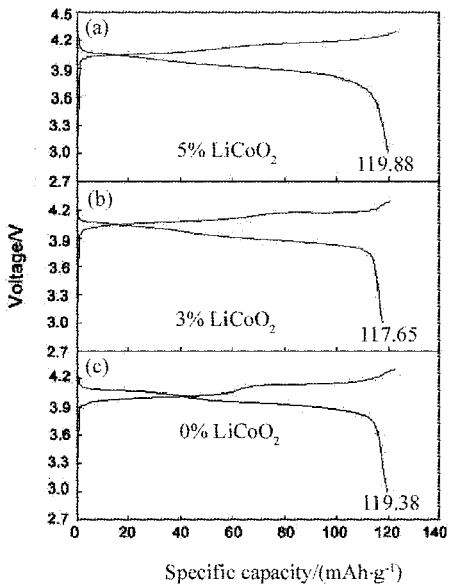

Fig.5. First Charge-discharge curves of samples at room temperature: (a) 5% $LiCoO_2$; (b) 3% $LiCoO_2$; (c) 0% $LiCoO_2$

The cycling curves of samples at room temperature are shown in Fig.6. The discharge capacity of uncoated material decreases greatly with cycling, capacity fading from 119.38 $mAh \cdot g^{-1}$ in the initial cycle to 110.35 $mAh \cdot g^{-1}$ in the 50th cycle, corresponding to the capacity retention of 92.44%. The capacity fading rate of Co-doped materials decreases steq by step with the increase in $LiCoO_2$ content. The capacity retention rates are 96.24% and 97.69% after the 50th cycle. The improvement of cycle performance may result from the following factors. The $LiCoO_2$ coated on surface avoids the direct contact between $LiMn_2O_4$ and electrolyte, which

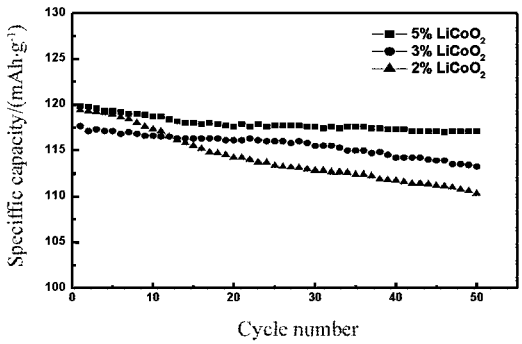

Fig.6. Cycling curves of samples at room temperature.

reduces the Mn dissolution in electrolyte. On the other hand, the doping transition layer improves the stability of spinel structure and effectively suppresses the Jahn-Teller distortion. In addition, the materials after coating possess smooth surface, which reduces the side reactions during charge and discharge and the catalysis of λ-MnO_2 to decomposition of electrolyte.

In order to check the performance of materials at elevated temperature, the Mn dissolution in electrolyte and cycle performance was investigate by using AAS and charge-discharge testing, respectively. The analysis results are listed in Table 1 and shown in Fig. 7. The amount of Mn dissolution into electrolyte reduces with the increase in $LiCoO_2$ cootent, but the Mn dissolution increases with temperature rising. The ability of resistance to dissolution is the best when the coating content is 5%.

Table 1. Amount of Mn dissolution in electrolyte of samples ($\mu g \cdot mg^{-1}$)

Samples	0% $LiCoO_2$	3% $LiCoO_2$	5% $LiCoO_2$
Mn in electrolyte at 20 ℃	22.13	17.28	11.42
Mn in electrolyte at 55 ℃	30.36	19.63	12.96

Fig. 7 shows the cycling charge-discharge curves of samples at 55 ℃. The discharge capacity of uncoated material decreases greatly, the capacity retention is only 89.43% after the 50th cycle, reducing 3.01% compared with that at room temperature. The capacity fading of $LiCoO_2$-coated materials is also higher than that at room temperature, corresponding to the capacity retention of 93.90% and 96.43%. The reducing ranges are 2.34% and 1.26%, which indicates the ability of resistance to dissolution has been improved after surface modification, which is in accordance with the amount of Mn dissolution into electrolyte.

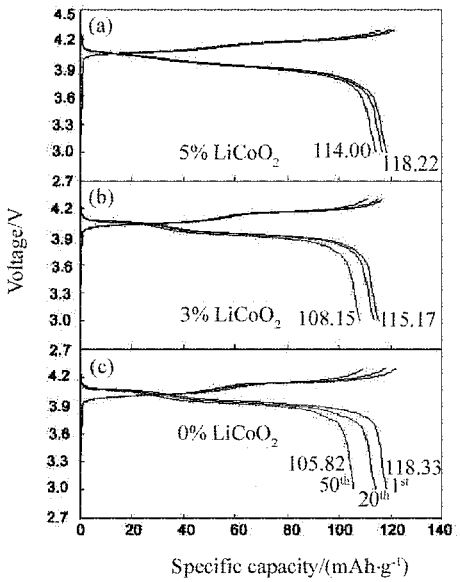

Fig.7. Cycling charge-discharge curves of samples at 55 ℃: (a) 5% $LiCoO_2$; (b) 3% $LiCoO_2$; (c) 0% $LiCoO_2$

4. Conclusions

A good clad coated on parent material can be synthesized by a sol-gel method, and the prepared materials consist of three parts, i.e., exterior clad layer, doping transition layer and interior parent material layer.

The $LiCoO_2$ coated $LiCo_{0.09}Mn_{1.91}O_{3.92}F_{0.08}$ materials show excellent cycle performance, and the capacity retention rates are 96.24% and 97.69% after the 50th cycle, respectively. Even at 55 ℃, the capacity fading rate is only 3.57% after the 50th cycle. It is attributed to the improvement of structural stability and the decrease of Mn dissolution into electrolyte after surface coating.

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