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Microstructure and electrochemical performances of LiF-coated spinel $LiMn_2O_4$

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Abstract: LiF-coated $LiMn_2O_4$ samples were prepared via a chemical method. X-ray diffraction (XRD) patterns show that the bare $LiMn_2O_4$ and the LiF-coated $LiMn_2O_4$ samples are all spinel structure in $Fd\bar{3}m$ space group. The apparent morphologies, the spectroscopic properties and the LiF distributions of the as-prepared samples were studied by scanning electronic microscopy (SEM), Fourier infrared spectroscopy (FTIR), transmission electronic microscopy (TEM), selected area electron diffractometry (SAED) respectively. The LiF-coated $LiMn_2O_4$ gets a more stable surface than bare $LiMn_2O_4$, and changes the interaction between the cathode material and the electrolyte. Therefore, it can endure overcharge in the secondary lithium batteries, and achieve better electrochemical performances even when charged to 4.7 V and 4.9 V.

Key words: spinel $LiMn_2O_4$; secondary lithium batteries; surface modification; LiF-coating

1 Introduction

Spinel $LiMn_2O_4$ is a widely studied cathode material for secondary lithium batteries. However, there are some barriers on the way to extensive applications of this material, among which Jahn−Teller effect, Mn dissolution and electrolyte decomposition are the major ones. To improve the structural stability and electrochemical performances of spinel $LiMn_2O_4$, many attentions are paid to cation-doping[1−7], or anion-doping[8−11]. Recently, it is found that surface modification can improve the electrochemical performances without change the body phase of spinel $LiMn_2O_4$ heavily. Both chemical modification methods[12−13] and electrochemical modification methods[14] are proved effective.

It is well known that a passivating film will attach on the electrodes in a secondary lithium battery upon cycling. Additionally, the stable inorganic components in the passivating films are LiF, $LiCO_3$, LiOH, etc. Therefore, it is promising to adopt these chemicals to modify $LiMn_2O_4$ surface, and suppress the corrosion from the electrolyte.

In this study, a commercial spinel $LiMn_2O_4$ is selected as the raw material, LiF is coated on $LiMn_2O_4$ surface via a chemical method. The structures and the electrochemical performances of the bare $LiMn_2O_4$ and the LiF-coated $LiMn_2O_4$ are studied and compared in detail.

2 Experimental

2.1 Sample preparation

A commercial spinel $LiMn_2O_4$ (Cellseed M) was selected as the bare $LiMn_2O_4$. To get LiF-coated spinel $LiMn_2O_4$, 200 mL LiOH solution with a concentration of 0.1 mol/L was first placed into a beaker and then 5 g bare $LiMn_2O_4$ was introduced in and stirred thoroughly with the LiOH solution. Subsequently, a 0.1 mol/L KF solution was dropped into the beaker with sustaining stiring. LiF particles were formed and adhered on the $LiMn_2O_4$, and the nominal ratio of LiF to $LiMn_2O_4$ was fixed as 5:95. The precursor of LiF-coated spinel

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$LiMn_2O_4$ was washed with distilled water, and then vacuum-dried at 100 ℃. Finally, the precursor was heated at 600 ℃ for 2 h, and cooled to ambient temperature. Thus, LiF-coated spinel $LiMn_2O_4$ was prepared by this way.

2.2 Structural characterization

XRD patterns of the as-prepared samples were recorded on a Rigaku B/max-2400 X-ray diffraction meter with Cu K_α radiation. The scanning range was from 10° to 100°, and the scanning rate was 8 ℃/min in steps of 0.02°. The apparent morphologies of the as-prepared samples were observed on a JSM-6301 scanning electron microscope (SEM), and the microcosmic structures were observed by a JEOL 200CX transmission electron microscope (TEM). The FTIR spectra are the average of 100 scans obtained on an FTS-60 V spectrometer (BIO-RAD) with a resolution of 4 cm^{-1}.

2.3 Electrochemical tests

The electrochemical performances were tested by adopting Swagelok-type secondary lithium batteries assembled in an argon-filled glove box (MBRAUN), where metal lithium foils served as counter and reference electrodes, and 1 mol/L $LiPF_6$ in a 1:1(volume fraction) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte. A sheet of Celgard® 2300 was used as a separator. The cathodes were prepared by coating slurries of spinel $LiMn_2O_4$ powder, carbon black and cyclopentanone-dissolved polyvinylidene fluoride (PVDF) onto aluminum foils, and the resultant mass ratio of $LiMn_2O_4$, carbon black, and PVDF was 85:10:5. Subsequently, the films were vacuum-dried at 55 ℃ for 24 h, compressed between two stainless steel plates, and then cut into sheets with an area of 0.5 cm^2. Cyclic voltammetry was carried out on a CHI660 electrochemical work station, and the charge-discharge test was performed on a LAND-CT2001A battery tester.

3 Results and discussion

3.1 XRD patterns

It is found that LiF-coating does not change the body structure of spinel, all the samples show spinel phases with the structure of $Fd\bar{3}m$ space group, as shown in Fig.1. Since LiF content is very low in the samples, no distinct LiF diffractions are detected. The lattice constants of bare $LiMn_2O_4$ is 8.220 6 Å, whereas that of the LiF-coated $LiMn_2O_4$ after heat-treatment at 600 ℃ is 8.219 6 Å, which indicates that the diffusion of small amount of LiF into $LiMn_2O_4$ body phase helps the metal-oxygen bonds to shrink.

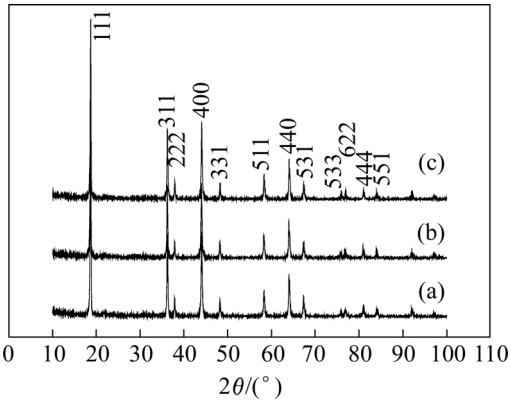

Fig.1 XRD patterns of LiF-coated spinel $LiMn_2O_4$: (a) Bare $LiMn_2O_4$; (b) LiF-coated spinel $LiMn_2O_4$ before heat-treating; (c) LiF-coated spinel $LiMn_2O_4$ after heat-treating for 2 h at 600 ℃

3.2 SEM images

Fig.2(a) shows the SEM image of bare $LiMn_2O_4$, which shows polyhedron particles in the sizes from 100 nm to 300 nm. After LiF deposition on bare $LiMn_2O_4$ particles, the apparent morphologies of the $LiMn_2O_4$ particles show a wider size distribution, see Fig.2(b). After treated at 600 ℃, the particles of LiF-coated $LiMn_2O_4$ distribute uniformly as shown in Fig.2(c).

3.3 FTIR analysis

According to previous study[15], the FTIR absorptions of the samples here are attributed to the asymmetric stretching modes of the Mn—O bands, as shown in Fig.3. For bare $LiMn_2O_4$, the vibrations of the Mn—O bands are located at 615 cm^{-1} and 512 cm^{-1}, respectively. While the vibrations of the Mn—O bands for LiF-coated $LiMn_2O_4$ are located at 620 cm^{-1} and 513 cm^{-1}, respectively.

After treated at 600 ℃, some of the LiF may diffuse into the body phase of $LiMn_2O_4$; the additional fluorine ions will give a diversity of the anions, and disturb the interaction between the Mn—anion bonds, and lead to an obvious shift on the vibration bands. Therefore, it is evident that the Mn—O stretching band at 615 cm^{-1} has a blue shift to 620 cm^{-1}.

3.4 TEM image and SAED spectrum

Fig.4 gives an assured evidence for the existence of LiF on the surface of $LiMn_2O_4$. Fig.4(a) shows the TEM image of LiF-coated $LiMn_2O_4$ heat-treated at 600 ℃, Fig.4(b) shows the SAED spectrum for the selected area marked by the white arrow in the TEM image. The *d* value of the dark ring in the SAED spectrum is the same as LiF (200) diffraction, indicating that there are LiF particles on $LiMn_2O_4$ surface, and has a discrete distribution.

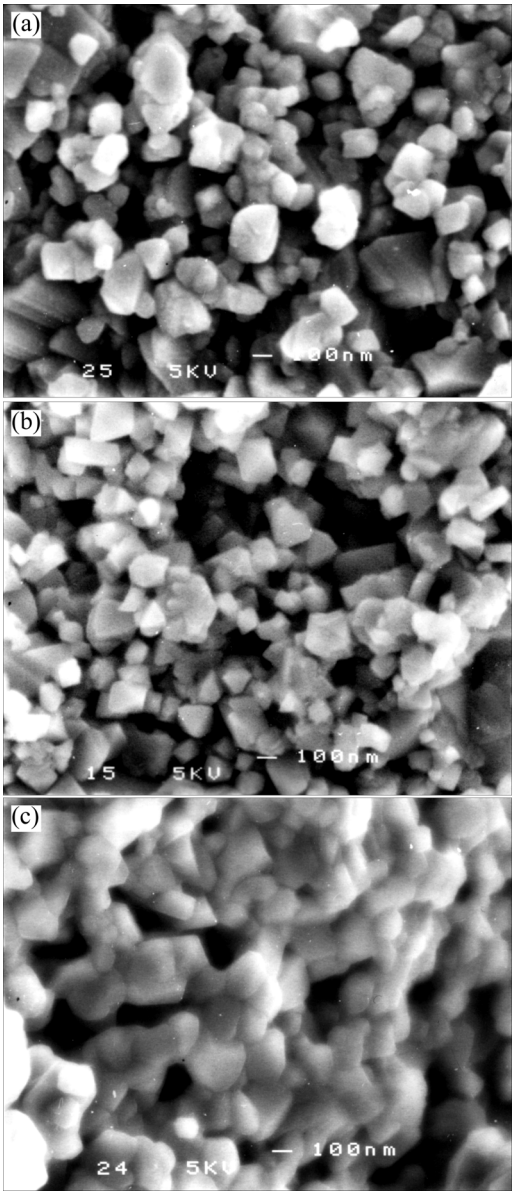

Fig.2 SEM images of LiF-coated spinel $LiMn_2O_4$: (a) Bare $LiMn_2O_4$; (b) LiF-coated spinel $LiMn_2O_4$ before heat-treating; (c) LiF-coated spinel $LiMn_2O_4$ after heat-treating for 2 h at 600 ℃

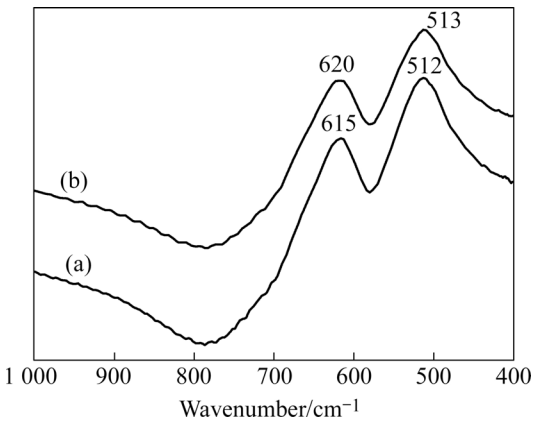

Fig.3 FTIR spectra of LiF-coated spinel $LiMn_2O_4$: (a) Before heat-treating; (b) After heat-treating at 600 ℃ for 2 h

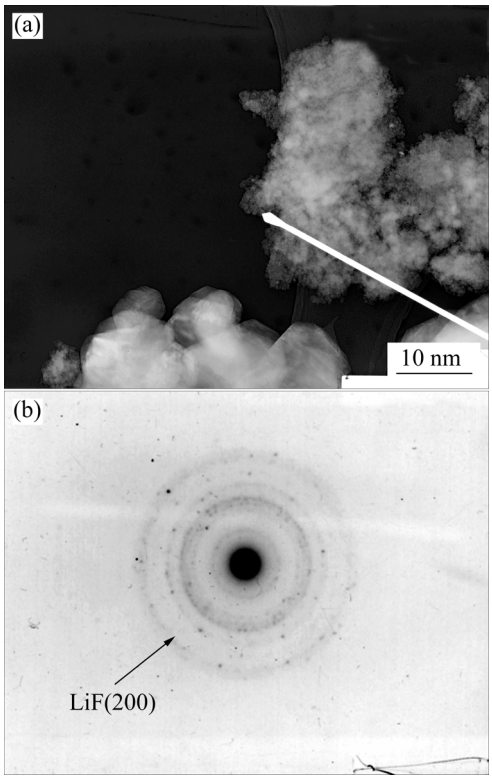

Fig.4 TEM image (a) and SAED spectrum (b) of LiF-coated spinel $LiMn_2O_4$ heat-treated at 600 ℃

4 Electrochemical performances

In previous study[16], cyclic voltammetry result shows that an evident additional peak in the bare $LiMn_2O_4$ emerges at 4.9 V, which indicates the decomposition of electrolyte. In this study, since LiF is a stable component in the passivating films, the LiF particles on $LiMn_2O_4$ help to achieve a good LiF-coating, the 4.9 V peak of the cyclic voltammograms of LiF-coated spinel $LiMn_2O_4$ after heat-treated at 600 ℃ is more flat, as shown in Fig.5, which indicate that

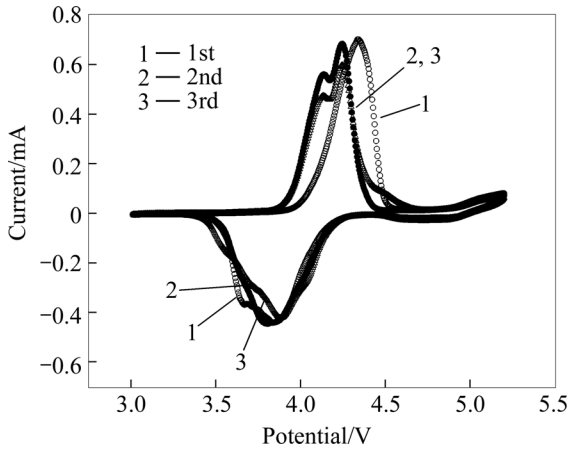

Fig.5 First three cyclic voltammograms of LiF-coated spinel $LiMn_2O_4$ heat-treated at 600 ℃

the decomposition of electrolyte and the corrosions of $LiMn_2O_4$ at high voltage are suppressed. Furthermore, the existence of coating layer on $LiMn_2O_4$ results in a heavy polarization in the initial cycle, as shown in Fig.5.

Generally, the charge cut-off voltage of spinel $LiMn_2O_4$ does not exceeds 4.3 V. However, since the secondary lithium batteries are often abused in practice, the experimental batteries here are cycled at a constant current density of 0.2 mA/cm^2 in the voltage range of 3.0−4.7 V and 3.0−4.9 V, respectively, as shown in Figs.6(a) and (b). When cycled between 3.0−4.7 V, the LiF-coated $LiMn_2O_4$ has an initial capacity of 119 mA·h/g, which is almost the same as that of the bare $LiMn_2O_4$, 122 mA·h/g. However, the performances of the samples after cycling are quite different. At 25th cycle, the capacity of the bare $LiMn_2O_4$ has a decrease of 12%, and remains at only 107 mA·h/g; whereas the capacity of the LiF-coated $LiMn_2O_4$ only has a decrease of 4%, and remains at 114 mA·h/g.

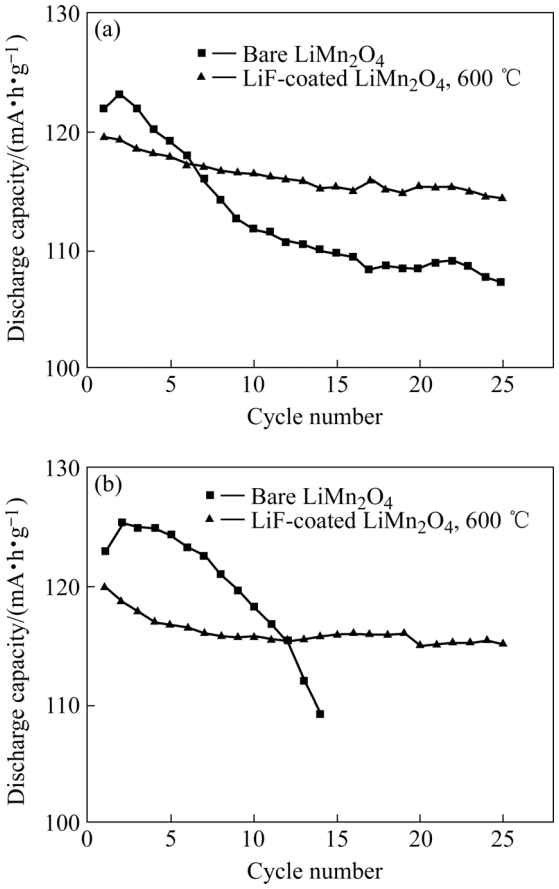

Fig.6 Discharge capacity as function of cycle number for LiF-coated spinel $LiMn_2O_4$ and bare $LiMn_2O_4$: (a) At 3.0−4.7 V; (b) At 3.0−4.9 V

When cycled between 3.0−4. 9V, the LiF-coated $LiMn_2O_4$ has an initial capacity of 120 mA·h/g, which is almost the same as that of the bare $LiMn_2O_4$, 123 mA·h/g. At 25th cycle, the capacity of the bare $LiMn_2O_4$ remains at only 109 mA·h/g, and has a tendency of sharp decrease. Whereas the capacity of the LiF-coated $LiMn_2O_4$ remains at 115 mA·h/g, and the reversible capacity is well kept in the following cycles. It implies that the LiF-coated $LiMn_2O_4$ has excellent endurance for overcharge in secondary lithium batteries.

5 Conclusions

1) The LiF-coated $LiMn_2O_4$ samples were prepared via a chemical method. XRD patterns and SEM images show that small amount of LiF-coating will not change the body structure and the apparent morphologies of $LiMn_2O_4$ evidently. However, FTIR spectra show that Mn—O stretching band has a blue shift after LiF-coating, and TEM tests indicate that LiF has a discrete distribution on $LiMn_2O_4$ surface.

2) The LiF-coated $LiMn_2O_4$ gets a more stable surface than bare $LiMn_2O_4$, and changes the interaction between the cathode material and the electrolyte. Therefore, it can endure overcharge in the secondary lithium batteries, and achieve better electrochemical performances under abused conditions.

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