

## Synthesis and electrochemical properties of $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite

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**Abstract:**  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite was synthesized by in-situ composite technique using  $\text{LiMn}_2\text{O}_4$ , lithium acetate, tetrabutyl titanate as starting materials and characterized by various electrochemical methods in combination with X-ray diffractometry (XRD), infrared (IR) spectroscopy and scanning electron microscopy (SEM). The results show that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is coated on the surface of crystalline  $\text{LiMn}_2\text{O}_4$  to form  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite. The structure of  $\text{LiMn}_2\text{O}_4$  does not change due to the introduction of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . By being coated with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , the rate capability and high temperature cyclability of  $\text{LiMn}_2\text{O}_4$  is improved greatly. At room temperature, the discharge capacity of  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite is more than 108.4 mA·h/g and the capacity loss per cycle is only 0.053% after 20 cycles at 2.0C. While at 55 °C, the discharge capacity of  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite is more than 109.9 mA·h/g and the capacity loss per cycle is only 0.036% after 60 cycles at 1.0C.

**Key words:**  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ;  $\text{LiMn}_2\text{O}_4$ ; in-situ composite technique; lithium ion batteries

### 1 Introduction

$\text{LiMn}_2\text{O}_4$  is of great interest for the replacement of  $\text{LiCoO}_2$  in Li ion batteries due to its low cost, nontoxicity and environmentally-friendly properties [1–2]. However, there are still some problems in terms of the wider application of  $\text{LiMn}_2\text{O}_4$ . The main problem is the capacity loss upon cycling at elevated temperature above 50 °C [3–6]. Recently, this problem has partially been resolved by metal cation doping [7–8] and surface modification treatment [9–10].

Besides the long cycling life and safety, the high rate performance is also important for commercial batteries. In spite of the success in improving cycle stability, little has been reported on the enhanced rate capability of  $\text{LiMn}_2\text{O}_4$ . In particular, it is necessary to improve the rate capability of  $\text{LiMn}_2\text{O}_4$  in order to be used as a cathode material of Li ion batteries for electric vehicles. The reason for poor rate capability of  $\text{LiMn}_2\text{O}_4$  is not clear but it may be attributed to its low chemical diffusion coefficient ( $10^{-9}$ – $10^{-12}$  cm<sup>2</sup>/s) [11–12]. The low diffusion coefficient of  $\text{LiMn}_2\text{O}_4$  can limit the current flow between particles, which may decrease its rate

capability. Therefore, the increase in diffusion coefficient of  $\text{LiMn}_2\text{O}_4$  probably improves its rate property.

$\text{LiMn}_2\text{O}_4$  was surface modified by nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles to improve the high rate capability, in consideration of the following factors: 1) the chemical diffusion coefficient of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  ( $10^{-6}$  cm<sup>2</sup>/s) [13] being larger than that of  $\text{LiMn}_2\text{O}_4$ ; 2) both  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{LiMn}_2\text{O}_4$  sharing the same spinel structure and space group of  $Fd3m$  [14–15]; 3)  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  showing exceptional rate capacity retention even as high as 10C [16]; 4)  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  being a zero-strain material, which means that there is no structural change during the insertion/extraction of lithium ions [15].

In the present work,  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite was synthesized by in-situ composite technique and its electrochemical properties were investigated in detail.

### 2 Experimental

#### 2.1 Preparation of $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite

A certain quantity of tetrabutyl titanate was solved in ethanol absolute with the volume ratio of tetrabutyl titanate to ethanol absolute of 1:5. The solution of

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tetrabutyl titanate was added to an aqueous ethanol solution of lithium acetate by stirring strongly according to the stoichiometric ratio of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  to get a clear yellow sol. A certain quantity of  $\text{LiMn}_2\text{O}_4$  (the mass ratio of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  to  $\text{LiMn}_2\text{O}_4$  is 1:19) used in lithium ion batteries was dispersed uniformly in this sol with ultrasonic wave and stirrers. After stirring for 2–3 h, a black gel was obtained. The gel was dried at 105 °C for 4 h in vacuum to get a black precursor. The precursor was calcinated at 800 °C in Ar atmosphere for 6 h to obtain  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite.

## 2.2 Characterization of $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite

Phase identification studies of the samples were carried out by an X-ray diffractometer (Rigaku D/MAX-gA) with Cu  $K_\alpha$  radiation. The surface morphology was done by scanning electron microscope (JSM 5600LV). The IR spectra of samples were conducted on a Fourier transform infrared spectrometer (Nicolet).

## 2.3 Electrochemical tests of $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite

A slurry containing 80%  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite, 10% acetylene black and 10% PVDF (polyvinylidene fluoride) was made using *N*-methylpyrrolidinone (NMP) as the solvent. Electrodes with an area of 1 cm<sup>2</sup> for the measurements of electrochemical characterization were prepared by coating slurries (about 100 μm in thickness) on aluminum foils followed by drying in vacuum at 60 °C for 12 h. Electrochemical tests were conducted using a conventional coin-type cell, employing lithium foil as a counter electrode and utilizing 1.0 mol/L  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (EC/DMC) (with an volume ratio of 1:1 of EC to DMC) as the electrolyte. The assembly was carried out in an Ar-filled glove box. The electrochemical analyses were carried out with an electrochemical analysis system.

## 3 Results and discussion

### 3.1 XRD analysis

Fig.1 shows the X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ . As can be seen, all those materials display nearly the same XRD patterns without any peak shift, which indicates that there is no structural change after the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  surface modification treatment. In the modified samples, no impurity phase is detected, suggesting that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  just exists on the surface of  $\text{LiMn}_2\text{O}_4$  and is not incorporated into the host structure since no changes are detected in the XRD patterns.

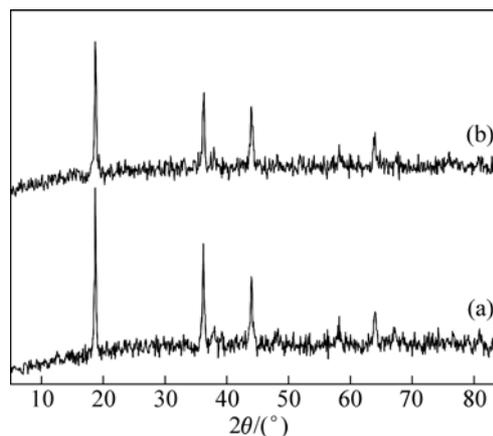


Fig.1 XRD patterns of  $\text{LiMn}_2\text{O}_4$  (a) and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  (b)

### 3.2 IR analysis

Fig.2 shows the IR spectra of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ . It is obvious that the spectra of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  agrees well, suggesting that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  just exists on the surface of  $\text{LiMn}_2\text{O}_4$ . The peaks at 3 200–3 600  $\text{cm}^{-1}$  and 1 600  $\text{cm}^{-1}$  are due to the absorbed water on the surface of samples. The peaks at 2 300–2 500  $\text{cm}^{-1}$  is caused by  $\text{CO}_2$  in air. The peaks between 400 and 1 200  $\text{cm}^{-1}$  are attributed to the metal-oxygen bond in samples.

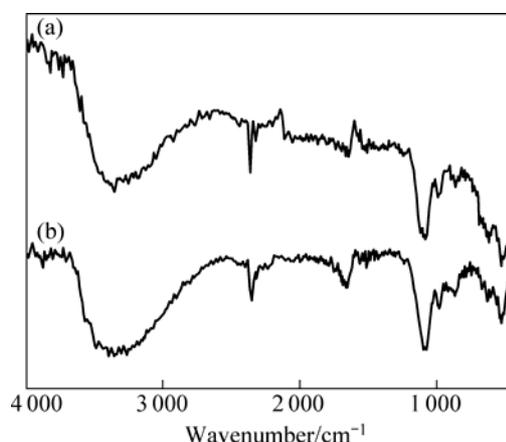


Fig.2 IR spectra of  $\text{LiMn}_2\text{O}_4$  (a) and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  (b)

### 3.3 SEM analysis

The SEM images of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  are shown in Fig.3. It can be seen clearly that the surface of the bare  $\text{LiMn}_2\text{O}_4$  is smooth, but after surface modification treatment, a lot of nanoparticles are observed on the surface of the core materials. Therefore, it is speculated that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles coated on  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  coating would minimize the direct contact area between the cathode and the electrolyte.

### 3.4 Electrochemical properties

Fig.4 shows the initial discharge curves of the

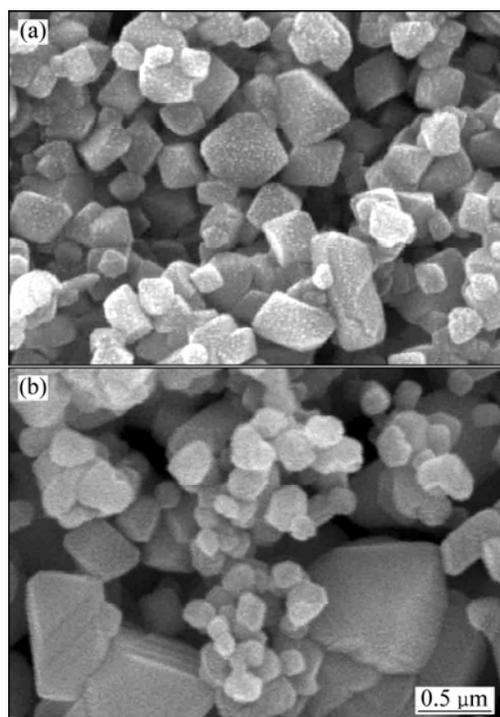


Fig.3 SEM images of  $\text{LiMn}_2\text{O}_4$  (a) and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  (b)

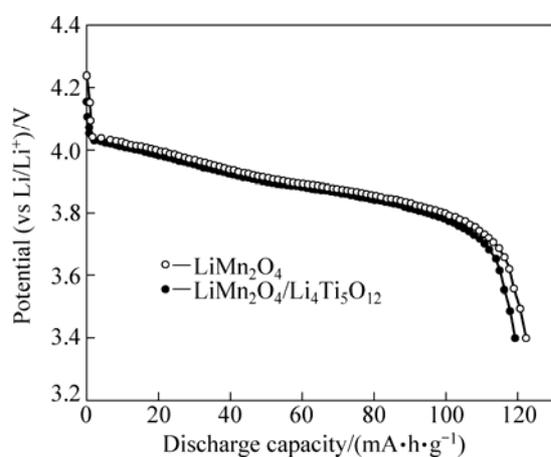


Fig.4 Initial discharge capacities of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 0.1C

uncoated  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode at 1C between 3.4 and 4.3 V. It is evident that all these electrodes display the characteristic two 4 V plateaus, and similar results are also observed under 2C and 5C, which means that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  coating does not change the intrinsic properties of  $\text{LiMn}_2\text{O}_4$ , such as charge/discharge behavior and crystal structure. In addition, the first-cycle discharge capacity of the  $\text{LiMn}_2\text{O}_4$  is 122.2 mA·h/g, while that of the  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  is 119.3 mA·h/g. The capacity decreases with the increase of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  coating amount, which can be attributed to the less active spinel in the electrode.

Fig.5 compares the cycling performance of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 0.1C. After 100 cycles at 0.1C, the discharge capacity of  $\text{LiMn}_2\text{O}_4$  decreases from 122.2 mA·h/g to 118.3 mA·h/g and the capacity loss per cycle is 0.032%. Under the same conditions, the discharge capacity of  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  decreases from 119.3 mA·h/g to 117.1 mA·h/g and the capacity loss per cycle is 0.018%, suggesting that the loading of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  on  $\text{LiMn}_2\text{O}_4$  helps to improve the cycling stability of  $\text{LiMn}_2\text{O}_4$ .

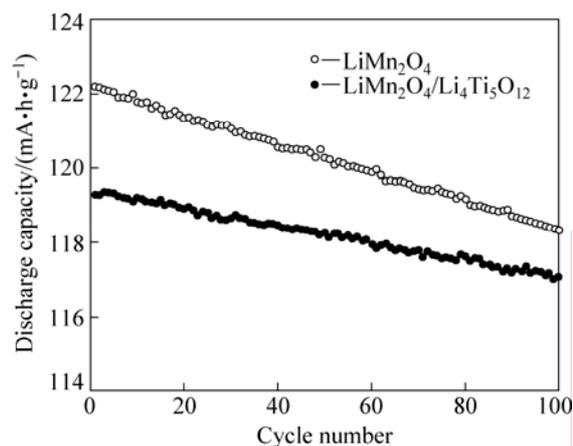


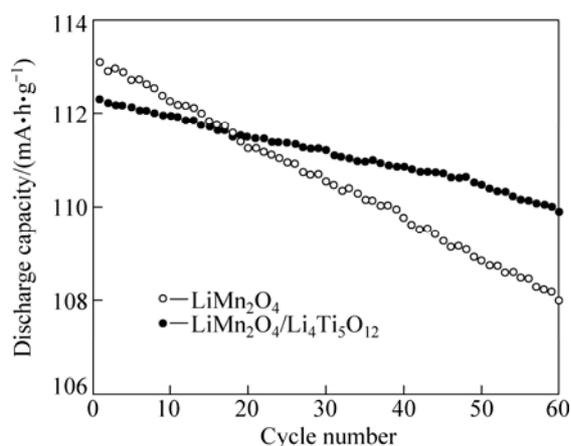
Fig.5 Cycling performance of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 0.1C

Table 1 presents the comparison of cycling performance of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  at various current rates. With the increase of discharge current rate, the discharge capacities of both samples decrease. This may be due to the increase of the electrode polarization at higher discharge current rate. In the point of capacity loss after 20 cycles, it can be seen obviously that the discharge capacity loss of  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  is lower than that of  $\text{LiMn}_2\text{O}_4$ . After 20 cycles at 2.0C, the discharge capacity of  $\text{LiMn}_2\text{O}_4$  is 108.3 mA·h/g and the capacity loss per cycle is 0.108%. Under the same conditions, the discharge capacity of  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  keeps at 108.4 mA·h/g and the capacity loss per cycle is more than 0.053%, suggesting that the loading of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  on  $\text{LiMn}_2\text{O}_4$  improves the rate stability of  $\text{LiMn}_2\text{O}_4$ . This may be explained that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  coating minimizes the direct contact area between the cathode and the electrolyte[17] and increases the chemical diffusion coefficient of lithium ion, accordingly improves the high rate performance of  $\text{LiMn}_2\text{O}_4$ .

Fig.6 shows the high temperature cycling performance of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 55 and 1.0C. The discharge capacities of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  are 113.1 mA·h/g and 112.3 mA·h/g at 55 , respectively, lower than their discharge capacities at room temperature (as shown in Table 1).

**Table 1** Comparison of cycling performance for  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite at various current rates

Charge-discharge rate	$\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$			$\text{LiMn}_2\text{O}_4$		
	1st cycle discharge capacity/( $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ )	20th cycle discharge capacity/( $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ )	Capacity loss/%	1st cycle discharge capacity/( $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ )	20th cycle discharge capacity/( $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ )	Capacity loss/%
0.1C	119.3	118.9	0.017	122.2	121.3	0.037
0.2C	118.8	118.3	0.019	120.8	119.8	0.043
0.5C	117.1	116.6	0.022	118.9	117.6	0.055
1.0C	114.3	113.6	0.031	115.5	113.9	0.074
2.0C	109.6	108.4	0.053	110.7	108.3	0.108

**Fig.6** High temperature cycling performance of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 1.0C

After 20 cycles at 55 °C, the discharge capacities of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  are 111.3  $\text{mA}\cdot\text{h}/\text{g}$  and 111.5  $\text{mA}\cdot\text{h}/\text{g}$ , and the capacity losses are 0.080% and 0.036% per cycle, respectively. After 60 cycles at 55 °C, the discharge capacities of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  are 108.0  $\text{mA}\cdot\text{h}/\text{g}$  and 109.9  $\text{mA}\cdot\text{h}/\text{g}$ , and the capacity losses are 0.075% and 0.036% per cycle, respectively. The high temperature cycling performance of  $\text{LiMn}_2\text{O}_4$  is improved significantly by coating  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . Surface modification of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  can obstruct the direct contact and suppress the side reactions between the electrode and electrolyte to prevent the spinel  $\text{LiMn}_2\text{O}_4$  from dissolving into the electrolyte, resulting in improved high temperature cycling performance of  $\text{LiMn}_2\text{O}_4$ [8, 18–20].

## 4 Conclusions

1)  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  composite was prepared by in-situ composite technique using  $\text{LiMn}_2\text{O}_4$ , lithium acetate, tetrabutyl titanate as starting materials.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  just exists on the surface of  $\text{LiMn}_2\text{O}_4$  and is not incorporated into the host structure of  $\text{LiMn}_2\text{O}_4$ .

2) By coating  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  on the surface of  $\text{LiMn}_2\text{O}_4$ , the rate capability and high temperature cyclability of

$\text{LiMn}_2\text{O}_4$  are improved greatly. This is because that the surface modification of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  can minimize the direct contact area between the cathode and the electrolyte, increase the chemical diffusion coefficient of lithium ion and suppress the side reactions between the electrode and electrolyte to prevent the spinel  $\text{LiMn}_2\text{O}_4$  from dissolving into the electrolyte.

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