1. Introduction

Due to its low cost, no toxicity and easy preparation, the spinel LiMn$_2$O$_4$ is regarded as a promising candidate for the replacement of current commercialized LiCoO$_2$ for Li-ion secondary batteries. The spinel LiMn$_2$O$_4$ has a cubic structure with a space group of $Fd\text{3}m$ symmetry in which lithium and manganese ions occupy tetrahedral (8a) sites and octahedral (16d) sites, respectively, and a cubic close-packed oxygen array with oxygen ions in 32e sites [1,2].

Although the spinel LiMn$_2$O$_4$ has lots of merits, it suffers severe capacity fading during cycling, which has been a key obstacle to its commercialization [3]. This severe capacity fading is mainly due to the Jahn–Teller distortion on the surface of spinel LiMn$_2$O$_4$ [4–6], the dissolution of manganese in the electrolyte solution [7–9], the spinel LiMn$_2$O$_4$ with oxygen deficiency [10,11] and the decomposition of electrolyte solution on the electrode [12]. In order to overcome capacity fading of spinel LiMn$_2$O$_4$, many strategies have been investigated, which mainly included the partial substitution of mono-, di- or trivalent cations for Mn$^{3+}$ [13–15] and coating the spinel LiMn$_2$O$_4$ particles with organic or inorganic compounds [16–18].

In this study, through combining two methods, coating and doping of spinel LiMn$_2$O$_4$, we proposed a novel approach to synthesize a spinel LiMn$_2$O$_4$ core surrounded by a spinel LiNi$_x$Mn$_{2-x}$O$_4$ shell. Since the shell of LiNi$_x$Mn$_{2-x}$O$_4$ solid solution was formed on the surface of the spinel LiMn$_2$O$_4$ particles, the modified LiMn$_2$O$_4$ can suppress the Jahn–Teller distortion. Therefore, it is expected that the modified LiMn$_2$O$_4$ could show an improved cycle performance.

2. Experimental

The LiMn$_2$O$_4$ powder (marked as sample A) was prepared by a solid-state reaction. A mixed fine powder of Li$_2$CO$_3$ and MnCO$_3$ in 1:4 mole ratio was heated at 600 °C for 6 h, then calcined at 750 °C in air for 72 h with intermittent grinding, and cooled with a rate of 2 °C min$^{-1}$.

The modified LiMn$_2$O$_4$ was synthesized by means of homogenous precipitation. After 4 wt% Ni(NO$_3$)$_2$ was dissolved in the ethanol and distilled water, the pristine LiMn$_2$O$_4$ and CO(NH$_2$)$_2$ were added into the obtained mixed solution, which was reflowed under ultrasonic agitation in water bath at 100 °C for 20 h. The filtered powder (marked as sample B) was first heated at 400 °C for 24 h in flowing air (the image was marked as sample C) and then calcined at 750 °C for 2 h. The resultant powder was marked as sample D, i.e., the modified LiMn$_2$O$_4$.

After mixing LiMn$_2$O$_4$ powder (70 wt%) with acetylene black (20 wt%) and polyvinylidene fluoride (PVdF) binder (10 wt%) in N-methylpyrrolidinone (NMP) solvent, the mixed slurry was attained.
The slurry was coated on an aluminum foil, followed by drying in a vacuum oven at 120 °C for 48 h. The electrochemical test cells were assembled in Mikrouna Super (1225/750) glove box under a dry argon atmosphere. LiMn$_2$O$_4$ electrode is used as positive electrode and Li sheet as negative electrode. Electolyte was 1 M LiPF$_6$ dissolved in ethylene carbonate (EC):diethyl carbonate (DEC):ethyl methyl carbonate (EMC) in a 1:1:1 volume ratio (Dongguan Shanshan Battery Materials Co., Ltd). The LiMn$_2$O$_4$ particles were mounted in the epoxy with a weight ratio of resin:DDSA:NMA:DMP-30 = 30:20:14:1. After cured at 65 °C for 24 h, the epoxy with particles was cut to a trapezoid shape with a thickness of 60 nm by microtome. Transmission electron microscopy (TEM) was taken with a 2000EX (JEOL). Scanning electron microscope (SEM) was taken with a JSM-6700F (JEOL). X-ray photoelectron spectra (XPS) were performed with an Axis ultra spectrometer (Kratos) using Mono Al K$_{α1}$ (1486.71 eV) radiation at a power of 225 W (15 mA, 15 kV). To compensate for surface charge effects, binding energies were calibrated using C$_1$s hydrocarbon peak at 284.8 eV. X-ray diffraction (XRD) analysis was made on a Rigaku D/MAX-2400 diffractometer, with Cu–K$_{α1}$ radiation ($λ = 0.154056$ nm). Cyclic voltammetry tests were performed on Versatile Multichannel Potentiostat 2/Z (VMP2) at a scan rate of 1.0 mV s$^{-1}$ over a potential range of 3.5 V to 4.3 V (vs. Li/Li$^+$). Charge–discharge characteristics were tested galvanostatically between 3.5 V and 4.3 V (vs. Li/Li$^+$) at room temperature by LAND Battery Test System.

3. Results and discussion

The surface morphologies of sample A, B, C and D are shown in Fig. 1(a–d) by SEM at a magnification of 50,000, respectively. The particles of sample A have obvious visible fringes, which indicate that the crystals of spinel LiMn$_2$O$_4$ grow very well and have a good crystallinity [19]. And for sample B, the observed obscure fringes are related to the coating of thin inorganic film on the surface of LiMn$_2$O$_4$ particles. Fig. 1 (c) clearly shows that the nanoscale particles, which result from the decomposition of nickel hydroxide, are covered on the surfaces of LiMn$_2$O$_4$ particles. After heat-treatment, however, the surface morphology of sample D became smoother with a similar morphology of sample A. This reveals that the coated nickel oxide particles had reacted with the spinel LiMn$_2$O$_4$ particles and formed a LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution on the surface of LiMn$_2$O$_4$ particles.

The components of active materials were analyzed by X-ray energy dispersive spectrometry (EDS). Clearly, no Ni peaks are observed in the Fig. 2 (a). However, the obvious presence of Ni in Fig. 2 (b) indicated that a LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution is coating on the surface of LiMn$_2$O$_4$ particles.

Fig. 3 shows the TEM image of the cross-sections of the spinel LiMn$_2$O$_4$ without (a) and with (b) modification, respectively. It is observed that a shell of LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution is coated on the surface of LiMn$_2$O$_4$ particles in the case of the modified LiMn$_2$O$_4$, while no shell for pure one. The coated nickel oxides disappear due to their reactions with spinel LiMn$_2$O$_4$, and then formed a shell of LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution on the surface of

![Fig. 1](image_url). Surface morphologies of spinel with and without modification: (a) sample A, (b) sample B, (c) sample C, (d) sample D.
LiMn$_2$O$_4$ particles, which is in good agreement with the result of above SEM. This observation reveals that the shell/core particles were formed after the modification.

Fig. 4 presents the XPS spectra of Mn 2p for pristine LiMn$_2$O$_4$ and modified one, respectively. After spinel LiMn$_2$O$_4$ modification, the XPS emission of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ shift from 642.1 eV and 653.9 eV to 642.5 eV and 654.2 eV, respectively. It means that the average oxidation state of Mn changes and the oxidation state of Mn ions is between +3 and +4. To further understand its surface chemistry change after the modification, XPS Peak software was employed to position the Mn$^{3+}$ 2p and Mn$^{4+}$ 2p doublets using the Shirley-type baseline. According to Mn 2p peak position and the integrated area, the relative concentration of both Mn$^{3+}$ and Mn$^{4+}$ can be estimated. For the relative concentration of both Mn$^{3+}$ and Mn$^{4+}$ for pristine LiMn$_2$O$_4$ are 55.2% and 44.8%, respectively, the average oxidation state of Mn is calculated to be 3.45. However, the average oxidation state of Mn of modified one is 3.55 because of the relative concentration of Mn$^{3+}$ (44.5%) and Mn$^{4+}$ (55.5%). After our modification, the doped Ni$^{2+}$ can occupy the position of Mn$^{3+}$ in the lattices, and then cause the decrease of the Mn$^{3+}$/Mn$^{4+}$ ratio on the surface of LiMn$_2$O$_4$ particle. It is well known that the ionic radius of Mn$^{4+}$ is smaller than that of Mn$^{3+}$. And the lattice parameters of LiMn$_2$O$_4$ are decreased. This helps to stabilize spinel crystal structure during the electrochemical cycling and improve its electrochemical properties [20].

Fig. 5 compares the XRD patterns of pristine LiMn$_2$O$_4$ and modified one. No apparent changes are observed in two patterns. In both patterns, only a single phase is observed, and no additional peaks of nickel oxide can be found. The modified LiMn$_2$O$_4$ is a result of the calcinations of whole particle of LiMn$_2$O$_4$ with nickel oxide at 750 °C in a short time (2 h). It implies that the nickel oxide reacted with LiMn$_2$O$_4$ and formed a LiNi$_x$Mn$_{2-x}$O$_4$ solid solution on the surface of LiMn$_2$O$_4$ particles.

The modification does not change the spinel structure of LiMn$_2$O$_4$, but slightly changes the lattice parameters due to atom size effect. The lattice parameters of pristine LiMn$_2$O$_4$ and modified LiMn$_2$O$_4$ were calculated by least square method. Both of them are 0.8246 nm and 0.8228 nm, respectively. The decrease in lattice parameter is due to the smaller ionic radii of Ni$^{2+}$ which replaced the Mn$^{3+}$ at 16d sites. Furthermore, in order to keep the charge balance, Mn$^{4+}$ will replace Ni$^{2+}$ at 16a sites. The EDS analysis of the pristine and modified LiMn$_2$O$_4$ also shows the existence of Ni element.
balance, the substitution of Ni$^{2+}$ for Mn$^{3+}$ increased the content of Mn$^{4+}$ with smaller ionic radii than that of Mn$^{3+}$, as confirmed by above XPS. The lattice shrinkage indicates that the modified LiMn$_2$O$_4$ improves its spinel structural stability[21].

The XRD patterns of pristine LiMn$_2$O$_4$ and modified LiMn$_2$O$_4$ that had been extracted from test cells after 100 charge–discharge cycles at a rate of C/2 are presented in Fig. 6. When comparing XRD pattern of modified LiMn$_2$O$_4$ with that of pristine one, we can find a significant difference. After 100 cycles, the modified LiMn$_2$O$_4$ still keep a single-phase cubic spinel, however, a tetragonal phase of Li$_2$Mn$_2$O$_4$ is observed in the XRD pattern of pristine LiMn$_2$O$_4$. The phase of Li$_2$Mn$_2$O$_4$ is due to the occurrence of Jahn–Teller distortion during the charge–discharge processes [22–24].

The cyclic voltammograms of pristine LiMn$_2$O$_4$ and modified LiMn$_2$O$_4$ in 3.5–4.3 V (vs. Li/Li$^+$) were measured at a scan rate of 207x332.
1.0 mV s\(^{-1}\) (see Fig. 7). For both of the voltammograms, there are two pairs of reversible peaks, i.e., oxidation and reduction peaks corresponding to \(\text{Li}^+\) extraction and insertion, which reflect the typical \(\text{Mn}^{3+}/\text{Mn}^{4+}\) redox processes of the spinel structure in the 4 V domain \([25,26]\).

With increasing cycle number, in Fig. 7(a), the peak current of pristine LiMn\(_2\)O\(_4\) for the 100th cycle is much lower than that for the 20th cycle, which indicates that the pristine LiMn\(_2\)O\(_4\) shows a distinct capacity fading after 100 cycles. By comparison, the peak current of modified LiMn\(_2\)O\(_4\) hardly decrease with cycling, and the curve of the 100th cycle is approximately same as that of the 20th cycle. This clearly demonstrates that the cycling performance of modified LiMn\(_2\)O\(_4\) is improved significantly.

Fig. 8 compares the cycling performance of pristine LiMn\(_2\)O\(_4\) and modified LiMn\(_2\)O\(_4\) at the rate of C/2 with a cutoff voltage of 3.5–4.3 V (vs. Li/Li\(^+\)) at room temperature. As it is shown in Fig. 8, the pristine LiMn\(_2\)O\(_4\) shows an initial discharge capacity of 117.4 mAh g\(^{-1}\), while the discharge capacity of modified LiMn\(_2\)O\(_4\) reaches the maximum value after 20 cycles, i.e., 107.1 mAh g\(^{-1}\). After 170 cycles, the discharge capacity of pristine LiMn\(_2\)O\(_4\) fades from 117.4 mAh g\(^{-1}\) to 80.2 mAh g\(^{-1}\) with a capacity retention rate of only 68.3%. However, for modified LiMn\(_2\)O\(_4\), the discharge capacity is 104.5 mAh g\(^{-1}\) after the 190 cycles, retained 97.6% of the maximum discharge capacity. As predicted from the results of Fig. 7, the discharge capacity of pristine LiMn\(_2\)O\(_4\) fades very rapidly with cycling, while the modified LiMn\(_2\)O\(_4\) shows higher capacity retention. As expected, the modified LiMn\(_2\)O\(_4\) can meet with the commercial application of cathode material for lithium ion secondary batteries.

According to the results of XPS and XRD, the redox species Mn\(^{3+}\) of modified LiMn\(_2\)O\(_4\) decreased, which results in the decrease of its maximum discharge capacity. However, the LiNi\(_x\)Mn\(_{2-x}\)O\(_4\) solid solution formed on the surface of spinel LiMn\(_2\)O\(_4\) particles stabilizes the spinel structure of active materials. During electrochemical intercalation/deintercalation process, because of the electronic configuration of Mn\(^{3+}\)\(\leftrightarrow\)Mn\(^{4+}\), Mn\(^{3+}\) can induce the Jahn–Teller distortion \([27]\). It is well known that manganese ions in LiMn\(_2\)O\(_4\) are in two oxidation states, consisting of 50% Mn\(^{3+}\) and 50% Mn\(^{4+}\). When the amount of Mn\(^{3+}\) is more than 50%, the spinel LiMn\(_2\)O\(_4\) is apt to exhibit Jahn–Teller distortion \([28]\). During the discharge process, especially at high rates, because the diffusion rate of lithium ions in electrolyte solution is much rapid than that of inside the spinel LiMn\(_2\)O\(_4\) particle \([29]\), in non-equilibrium dynamic condition, lithium ions heap on the surface of spinel LiMn\(_2\)O\(_4\) particles. And a Mn\(^{3+}\)-rich region is formed in this process, which induces Jahn–Teller distortion. As described in introduction, the cause for capacity fading of spinel LiMn\(_2\)O\(_4\) is considered to be related to the Jahn–Teller distortion. From the result of XRD after 100 charge–discharge cycles, the modified LiMn\(_2\)O\(_4\) effectively suppresses the Jahn–Teller distortion. Therefore, our modification has greatly improved the cycling performance of spinel LiMn\(_2\)O\(_4\).

4. Conclusions

In this paper, we presented a novel approach, i.e., combination of coating and doping, to prepare a spinel LiMn\(_2\)O\(_4\) core surrounded by a spinel LiNi\(_x\)Mn\(_{2-x}\)O\(_4\) shell. SEM revealed that a LiNi\(_x\)Mn\(_{2-x}\)O\(_4\) solid solution is formed on the surface of spinel LiMn\(_2\)O\(_4\) particles. The increase of Mn average oxidation state of modified LiMn\(_2\)O\(_4\) causes a decrease of maximum capacity. However, the modified LiMn\(_2\)O\(_4\) remains 97.6% of the maximum discharge capacity after 190 cycles, which shows a significant cycling stability improvement. The result of XRD after 100 charge–discharge cycles demonstrates that this improvement is ascribed to the suppression of Jahn–Teller distortion on the surface of LiMn\(_2\)O\(_4\) particles. The modified LiMn\(_2\)O\(_4\) meets the commercial application for Li-ion batteries. So this novel approach is a very promising approach for increasing the possibility of mass production and commercialization of cathode material of lithium-ion batteries.

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References