Spinell LiMn\textsubscript{2}O\textsubscript{4} active material with high capacity retention

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Abstract

Heating the mixture of LiMn\textsubscript{2}O\textsubscript{4} and NiO at 650 °C was employed to enhance the cyclability of spinell LiMn\textsubscript{2}O\textsubscript{4}. The results of scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy analyses implied that a LiNi\textsubscript{x}Mn\textsubscript{2−x}O\textsubscript{4} solid solution was formed on the surface of LiMn\textsubscript{2}O\textsubscript{4} particles. And charge–discharge tests showed that the enhancement of the capacity retention of modified LiMn\textsubscript{2}O\textsubscript{4} is significant, maintained 97.2% of the maximum capacity after 100 cycles at charge and discharge rate of \textit{C}/2, while the pure one only 75.2%. The modified LiMn\textsubscript{2}O\textsubscript{4} also results in a distinct improvement in rate capability, even at the rate of 12\textit{C}. The improvement of electrochemical cycling stability is greatly attributed to the suppression of Jahn–Teller distortion at the surface of spinell LiMn\textsubscript{2}O\textsubscript{4} particles.

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1. Introduction

These days, Li-ion batteries hold a big share in electronic products, especially as a promising candidate power for electric vehicles. Spinell lithium manganese oxide (LiMn\textsubscript{2}O\textsubscript{4}), for its low cost, easy preparation and nontoxicity, has been extensively investigated as the cathodes of lithium-ion rechargeable batteries. However, a key problem prohibiting LiMn\textsubscript{2}O\textsubscript{4} from commercialization is its severe capacity fading during cycling [1]. There are two main factors which cause capacity fade of spinell LiMn\textsubscript{2}O\textsubscript{4} as it had been reported by many investigators, are Jahn–Teller distortion [2–6] and Mn dissolution into the electrolyte [7–11] on the surface of spinell LiMn\textsubscript{2}O\textsubscript{4} particles.

Our research team has been dedicating ourselves to improving the cycling performance of spinell LiMn\textsubscript{2}O\textsubscript{4} for years. As described previously [12,13], by using heterogeneous nucleation technique, we prepared a spinell LiMn\textsubscript{2}O\textsubscript{4} core surrounded by a spinell LiNi\textsubscript{x}Mn\textsubscript{2−x}O\textsubscript{4} shell, which shows an excellent cycle performance. However, this technique is complex and is unfavorable to mass production.

In this study, after heating the mixture of LiMn\textsubscript{2}O\textsubscript{4} and NiO at high temperature, we obtained spinell LiMn\textsubscript{2}O\textsubscript{4} coated with a LiNi\textsubscript{x}Mn\textsubscript{2−x}O\textsubscript{4} solid solution, i.e. a spinell LiMn\textsubscript{2}O\textsubscript{4} core surrounded by a spinell LiNi\textsubscript{x}Mn\textsubscript{2−x}O\textsubscript{4} shell. Compared with the heterogeneous nucleation technique, this approach is very simple with low cost, and it is a promising approach for increasing the possibility of mass production and commercialization of cathode material of lithium-ion batteries.

2. Experimental

Spinell LiMn\textsubscript{2}O\textsubscript{4} powder was prepared by a solid-state reaction. A mixed fine powder of Li\textsubscript{2}CO\textsubscript{3} and MnCO\textsubscript{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. As-prepared LiMn\textsubscript{2}O\textsubscript{4} and NiO were mixed in the ball mill for 2 h. Then the well-mixed powders were calcined at 650 °C for 2 h in air, followed by slow cooling to room temperature.

After mixing LiMn\textsubscript{2}O\textsubscript{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. And an electrode was formed.
The CR-2016-type coin cells were assembled in Mikrouna Super (1225/750) glove box under a dry argon atmosphere. LiMn$_2$O$_4$ electrode was used as positive electrode and Li sheet as negative electrode. Electrolyte was 1 M LiPF$_6$ dissolved in ethylene carbonate (EC):diethyl carbonate (DEC):ethyl methyl carbonate (EMC) in a 1:1:1 volume ratio.

Scanning electron microscope (SEM) was taken with a JSM-6700F (JEOL). X-ray diffraction (XRD) analysis was performed with a Rigaku D/MAX-7000 diffractometer, using Cu Kα radiation (λ = 0.154056 nm). Fourier transform infrared (FT-IR) spectroscopy of the samples was performed within wavenumber range 1000–400 cm$^{-1}$ by using IRPrestige-21 from Shimadzu. Charge-discharge characteristics were tested galvanostatically between 3.5 and 4.3 V (versus Li/Li$^+$) at room temperature by LAND Battery Test System.

3. Results and discussion

A series of SEM micrographs in Fig. 1 reveal the morphological changes that occurred during the process of modifying spinel LiMn$_2$O$_4$. As it is shown in Fig. 1(a), the pure LiMn$_2$O$_4$ had obvious visible fringes, indicating that the crystals of spinel LiMn$_2$O$_4$ grow very well and have good crystallinity [14]. After mixing LiMn$_2$O$_4$ and NiO in the ball mill, in Fig. 1(b), it clearly exhibits that the fine powders of NiO distributed uniformly on the surfaces of LiMn$_2$O$_4$ particles. After heat-treatment, however, no individual Ni oxide particles are visible. And the surfaces of modified LiMn$_2$O$_4$ particles are smooth with a similar morphology of the pure LiMn$_2$O$_4$ particles. It is indicated that NiO particles had reacted with spinel LiMn$_2$O$_4$ particles and formed a LiNi$_{1-x}$Mn$_2$O$_4$ solid solution on the surface of LiMn$_2$O$_4$ particles. 

Fig. 2 compares the XRD patterns of pure LiMn$_2$O$_4$ and modified one. The obtained diffraction patterns of both samples are identified as a single-phase spinel LiMn$_2$O$_4$ with a space group Fd3m, indicating that the spinel structure of active material is maintained after LiMn$_2$O$_4$ modification. The lattice parameters of pure LiMn$_2$O$_4$ and modified LiMn$_2$O$_4$ were calculated from the XRD spectrum. The decrease of the lattice parameter of modified LiMn$_2$O$_4$ ($a = 0.824577$ nm) which enhances the structure stability of spinel LiMn$_2$O$_4$ [15–19] is observed compare with that of pure one ($a = 0.823413$ nm), which is in agreement with the report of Matsui et al. [20]. This shrinkage of the lattice parameter indicates that Ni$^{2+}$ enters into the crystal structure of spinel LiMn$_2$O$_4$ during heat-treatment [21], suggesting a LiNi$_{1-x}$Mn$_2$O$_4$ solid solution is formed on the surface of LiMn$_2$O$_4$ particles. This obvious blue shift reveals that the LiNi$_{1-x}$Mn$_2$O$_4$ solid solution on the surface of LiMn$_2$O$_4$ particles enhances the strength of Mn–O bond and strengthens the stability of the spinel structure [23]. This result is in good agreement with the smaller lattice parameter of modified LiMn$_2$O$_4$ calculated from the XRD spectrum.

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. 4. 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 obtained Li$_2$Mn$_2$O$_4$ is due to the Jahn–Teller distortion during the charge–discharge processes [6,24,25].

Fig. 5 shows the cycle performance of pure 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 (versus Li/Li$^+$) at room temperature. The pure LiMn$_2$O$_4$ with initial capacity of 124.4 mAh g$^{-1}$ declined rapidly as cycling, only remained 74.6% of its initial capacity after 100 cycles, which is about 0.306 mAh g$^{-1}$ per cycle, while the loss capacity of modified LiMn$_2$O$_4$ at the 100th cycle, with about 0.031 mAh g$^{-1}$ per cycle, is 2.8% of the maximum capacity that is 111.5 mAh g$^{-1}$. Obviously, the capacity retention of modified LiMn$_2$O$_4$ is remarkably enhanced.

During electrochemical intercalation/deintercalation process, the electronic configuration Mn$^{3+}$, $t^3_{2g}$–$e^1_{g}$ [26], induces Jahn–Teller distortion. As described in Section 1, the cause for capacity fading of spinel LiMn$_2$O$_4$ is considered to be related to Jahn–Teller distortion. In this study, since a LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution is formed on the surface of spinel LiMn$_2$O$_4$ particles, the modified LiMn$_2$O$_4$ effectively suppresses the Jahn–Teller distortion, as confirmed by the results of XRD after 100 charge–discharge cycles. The results of XRD and FT-IR indicate that the modification can strengthen the stability of the spinel structure. Therefore, our modification has greatly improved the cycling performance of spinel LiMn$_2$O$_4$.

Fig. 6 presents the rate capability of pure LiMn$_2$O$_4$ and modified one at charge–discharge rates ranging from $C/2$ to $12C$. Clearly, the modified LiMn$_2$O$_4$ maintained a steady discharge capacity as the charge–discharge rate increases, while the pristine LiMn$_2$O$_4$ showed a rapidly decline at each charge–discharge rate, especially at high rates.

For both pure LiMn$_2$O$_4$ and modified LiMn$_2$O$_4$, the discharge capacity decreased with the increase of charge–discharge rate ($C/2$–$12C$ rate), which is caused by the low diffusion rate of the lithium ions in the LiMn$_2$O$_4$ particles [27,28], however, the decrease of discharge capacity of modified LiMn$_2$O$_4$ was much smaller than that of the pure one. As the charge–discharge rates were reduced from $12C$ to...
C/2, the pure LiMn$_2$O$_4$ only maintained 74.3% of its capacity on the 15th cycle at the same rate, while modified LiMn$_2$O$_4$ showed a very little capacity fading.

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], 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 induce Jahn–Teller distortion. The higher the discharge rates are, the more pronounced Jahn–Teller distortion is. Therefore, the rate of capacity fading of spinel LiMn$_2$O$_4$ is increasing with the increase of charge–discharge rate. From the results of XRD after 100 charge–discharge cycles, the LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution on the surface of LiMn$_2$O$_4$ particles is beneficial to suppress Jahn–Teller distortion, and accordingly, the modified LiMn$_2$O$_4$ effectively enhances the rate capability of active material.

4. Conclusions

By a simple approach, a LiMn$_2$O$_4$ core surrounded by a LiNi$_{x}$Mn$_{2-x}$O$_4$ shell was synthesized. SEM, XRD and FT-IR spectroscopy suggested that a LiNi$_{x}$Mn$_{2-x}$O$_4$ solid solution is formed on the surface of spinel LiMn$_2$O$_4$ particles. The pure LiMn$_2$O$_4$ with an initial specific capacity of 124.7 mAh g$^{-1}$ undergoes a 24.8% capacity loss on the 100th cycle at the rate of C/2 with a cutoff voltage of 3.5–4.3 V. Although the maximum capacity of modified LiMn$_2$O$_4$ is 111.5 mAh g$^{-1}$ at the fourth cycle, the capacity fading at the 100th cycle is only 2.8%. The modified LiMn$_2$O$_4$ also shows a significant improvement of the rate capability performance at rates from C/2 to 12C. After the charge–discharge rate is reduced from 12C to C/2, the pure LiMn$_2$O$_4$ lost 25.7% of its capacity comparing with the 15th cycle at the same rate, while the modified LiMn$_2$O$_4$ hardly shows any capacity fading. Clearly, the electrochemical cycling stability of spinel LiMn$_2$O$_4$ is distinctly improved.

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References