Research Article

In Situ Carbon Coated LiNi_{0.5}Mn_{1.5}O_4 Cathode Material Prepared by Prepolymer of Melamine Formaldehyde Resin Assisted Method

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Carbon coated spinel LiNi_{0.5}Mn_{1.5}O_4 were prepared by spray-drying using prepolymer of melamine formaldehyde resin (PMF) as carbon source of carbon coating layer. The PMF carbon coated LiNi_{0.5}Mn_{1.5}O_4 was characterized by XRD, SEM, and other electrochemical measurements. The as-prepared lithium nickel manganese oxide has the cubic face-centered spinel structure with a space group of Fd3m. It showed good electrochemical performance as a cathode material for lithium ion battery. After 100 discharge and charge cycles at 0.5 C rate, the specific discharge capacity of carbon coated LiNi_{0.5}Mn_{1.5}O_4 was 130 mAh g^{-1}, and the corresponding capacity retention was 98.8%. The 100th cycle specific discharge capacity at 10 C rate of carbon coated LiNi_{0.5}Mn_{1.5}O_4 was 105.4 mAh g^{-1}, and even the corresponding capacity retention was 95.2%.

1. Introduction

Spinel LiNi_{0.5}Mn_{1.5}O_4 is a promising and attractive cathode material because of its good electrochemical properties and high working potential (~5.0 V) [1–3]. But the high rate discharge capacity is far less than the theoretical capacity due to low electronic conductivity and Li^+ ion diffusion coefficient of LiNi_{0.5}Mn_{1.5}O_4 [4]. Therefore, many efforts have been devoted to enhance the electronic conductivity and Li^+ ion diffusion coefficient by different synthesis routes [5–7], doping [8–12], and coating [13–16].

Carbon coating is easy and popular method at present [17]. In our propahase research, we found that the prepolymer of melamine formaldehyde resin would evenly coat on the surface of metal oxide and obtained the carbon coated metal catalysts with abundant pore structure after high temperature sintering [18]. In this study, in order to prepare the LiNi_{0.5}Mn_{1.5}O_4 as well as to improve the high rate discharge performance, polymer-complex-assisted method was applied. Prepolymer of melamine formaldehyde resin (PMF) is used as carbon source to accomplish the carbon coated LiNi_{0.5}Mn_{1.5}O_4.

2. Experimental Sections

2.1. Material Synthesis. The synthesis route was as follows: LiOH, Ni(NO_3)_2·6H_2O and MnSO_4·H_2O were used as starting precursors with molar ratio of Li: Ni: Mn = 1.0: 0.5: 1.5. Ni(NO_3)_2·6H_2O and MnSO_4·H_2O were dispersed in deionized water under continuous stirring and then slowly dripped the (NH_3)_2C_2O_4 aqueous solution. After reaction at 50°C for 12 h, then centrifugal washing to obtain the Ni_{0.5}Mn_{1.5}(C_2O_4)_2 precipitates. Ni_{0.5}Mn_{1.5}(C_2O_4)_2, LiOH, and PMF (10 wt.%) were dispersed in deionized water by ultrasonic dispersion 30 min into suspension. The suspension was dried by spray-drying method (inlet temperature 220°C and feed rate 6 mL-min). The dried products were pre­sintered...
at 500°C in N2 atmosphere for 5 h and then sintered at 800°C in N2 atmosphere for 20 h to obtain the carbon coated LiNi0.5Mn1.5O4. For comparison, LiNi0.5Mn1.5O4 was also synthesized without PMF.

2.2. Characterization. The structure of the LiNi0.5Mn1.5O4 materials was characterized using powder X-ray diffraction (XRD, XD-3, Beijing Purkinje General, China) with Cu Kα radiation at 36 kV and 20 mA. The morphology of LiNi0.5Mn1.5O4 was identified by field emission scanning electron microscopy (FE-SEM, JSM-5600, JEOL, Japan).

For electrochemical characterizations, 2032 type coin cells were used. The coin-type cells (2032) were assembled with Li plate as anode and LiNi0.5Mn1.5O4 electrode as cathode. The LiNi0.5Mn1.5O4 electrodes were prepared by coating the slurry of a mixture composed of LiNi0.5Mn1.5O4 (80 wt.%), conducting agent (Super-p, 10 wt.%), and binder (polyvinylidene difluoride, 10 wt.%) onto an aluminum foil, and then dried at 120°C for 24 h in a vacuum drier. The weight of active material in the LiNi0.5Mn1.5O4 electrode was 3.0 mg cm\(^{-2}\). The electrolyte was 1 mol L\(^{-1}\) LiPF6 in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. A polypropylene (PP) film (Celgard 2300) was used as the separator. Afterwards, the coin-type cells were assembled in argon-filled glove box. NEWARE multichannel battery-testing unit (CT-3008W, China) was employed to test the cycling and rate performances of LiNi0.5Mn1.5O4 over a voltage range between 3.5 and 5.0 V versus Li/Li\(^{+}\) electrode at room temperature. Firstly, the cell should discharge and charge two cycles at 0.5 C and then discharge and charge 100 cycles at different rates. The cyclic voltammetric (CV) tests were carried out on an electrochemical workstation (CHI660A) at a scan rate of 0.1 mV s\(^{-1}\) in the range of 3.5–5.0 V versus Li/Li\(^{+}\). The electrochemical impedance spectroscopy (EIS) data of the electrodes were acquired at room temperature by an electrochemical workstation (CHI660A) before cycling in the frequency range 10 mHz–100 kHz by imposing an alternate current with an amplitude of 10 mV on the electrode.

3. Results and Discussion

Figure 1 shows the XRD pattern of the as-prepared LiNi0.5Mn1.5O4. Compared with the PDF powder diffraction data file (JCPDS Card No. 80-2162), the diffraction peaks of as-prepared LiNi0.5Mn1.5O4 are in agreement with the standard diffraction peaks. This illustrates that the as-prepared LiNi0.5Mn1.5O4 has the cubic face-centered spinel structure with a space group of Fd\(\bar{3}\)m [19]. There is no change of the station of diffraction peak after carbon coating and no coating. The diffraction peak intensity would be enhanced after PMF carbon coating. The carbon coating would be helpful to improve LiNi0.5Mn1.5O4 crystallinity. Figure 2 shows FE-SEM images of LiNi0.5Mn1.5O4 with no coating and after 10 wt.% PMF carbon coating. The LiNi0.5Mn1.5O4 maintains the micronanostructure after carbon coating, but the surface of samples becomes roughed, and the roughness of samples increases after the PMF carbon coating. The degree of sphericity drops gradually.

Figure 3 shows the 2nd, 50th, and 100th charge and discharge curves of carbon coated LiNi0.5Mn1.5O4 at the rate of 0.5 C. The specific discharge capacity of LiNi0.5Mn1.5O4 increased after PMF carbon coating at around 4.7 V voltage plateau. The 2nd cycle specific discharge capacity raised from 125.1 mAh g\(^{-1}\) (no coating) to 131.7 mAh g\(^{-1}\) (after coating). After 100 discharge and charge cycles, the specific discharge capacity of carbon coated LiNi0.5Mn1.5O4 was 130 mAh g\(^{-1}\), and even the corresponding capacity retention was 98.8%. And yet the specific discharge capacity of no coated LiNi0.5Mn1.5O4 was 88.9 mAh g\(^{-1}\), and the corresponding capacity retention was 71.1%. The discharge and charge curves indicate that the PMF carbon coating reduces the electrode polarization after repeatedly charging and discharging cycle which suggests that PMF carbon coating was in favour of improving the discharge and charge performance of lithium nickel manganese oxide materials. Another reason might be that the PMF carbon coating prevents the Mn\(^{3+}\) dissolving in the process of charging and discharging, thereby reducing the fading rate of discharge capacity [20, 21].

Figure 4 shows the 2nd, 50th, and 100th charge and discharge curves of carbon coated LiNi0.5Mn1.5O4 at the rate of 10 C. The specific discharge capacity of LiNi0.5Mn1.5O4 declines sharply after PMF carbon coating at high rate discharge. The 2nd cycle specific discharge capacity decreased from 117.9 mAh g\(^{-1}\) (before coating) to 110.6 mAh g\(^{-1}\) (after coating). The PMF carbon coating hinders the Li\(^{+}\) conduction at high rate discharge and charge. But the corresponding capacity retention was greatly improved after PMF carbon coating. The 100th cycle specific discharge capacity of carbon coated LiNi0.5Mn1.5O4 was 105.4 mAh g\(^{-1}\), and even the corresponding capacity retention was 95.2%. And yet the specific discharge capacity of no coated LiNi0.5Mn1.5O4 was 85.4 mAh g\(^{-1}\), the corresponding capacity retention was 69.1%.

Figure 5 shows the CV curves of the PMF carbon coated LiNi0.5Mn1.5O4 electrode. In the full range view of CV curves,
one pair of redox peaks around 4 V (Mn$^{3+}$/Mn$^{4+}$) and two pairs of well separated strong redox peaks at 4.6–4.8 V can be observed in CV curve of no carbon coated LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ electrode. The two strong redox peaks indicate a two-stage (Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$) Li$^{+}$ extraction from or insertion into the spinel framework [22]. For PMF carbon coated LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ electrode, the peaks around 4 V should weaken obviously. This indicates that the Mn$^{3+}$ ions dissolution amount of the PMF carbon coated LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ is smaller than no carbon coating [23]. The presence of Mn$^{3+}$ in the LMNO material plays an important role in the capacity retention [9]. And the two redox peaks of LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ with 10 wt.% PMF carbon coating are overlapped to a broad peak. The cyclic voltammetry curves of the PMF carbon coated LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ material exhibit smaller potential intervals that indicated higher electrode reaction reversibility and lower polarization. The PMF carbon coating would effectively restrain the Mn$^{3+}$ stripping and the side reaction between positive electrode active material and electrolyte at high voltage.

Figure 6 depicts the electrochemical impedance spectroscopy of the electrode obtained after the first cycle of charge. The semicircle at high frequency (>100 Hz) in EIS spectra reflects the contact resistances between the active materials and electrolyte or current collector [24]. The significant improvements in electric conductivity for LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ electrode could therefore be attributed to the PMF carbon coating [25].

4. Conclusions

PMF carbon coated LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ was prepared as the 5V cathode materials of lithium ion batteries for the first time. PMF carbon coating increases the crystallinity of
LiNi_{0.5}Mn_{1.5}O_{4}. The as-prepared LiNi_{0.5}Mn_{1.5}O_{4} has the cubic face-centered spinel structure with a space group of Fd3m. The PMF carbon coating greatly promotes electrochemical performance and reduces the LiNi_{0.5}Mn_{1.5}O_{4} electrode polarization in the process of charging and discharging. The cycle life of LiNi_{0.5}Mn_{1.5}O_{4} was significantly improved by PMF carbon coating, especially at high rate discharging and charging.

**Competing Interests**

The authors declare that they have no competing interests.

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