



Cathode material $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2/\text{LaPO}_4$ with high electrochemical performance for lithium-ion batteries

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ABSTRACT

In order to enhance the electrochemical properties of nickel-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode material, lithium-ion conductor shell was coated on the surface of the material through a facile wet chemical route. The morphologies, structures and chemical compositions of the samples were characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction, energy dispersive spectrometer and X-ray photoelectron spectroscopy. The result shows that the particle surface was uniformly coated by a very thin LaPO_4 layer. Electrochemical measurements proved that the LaPO_4 -coated sample exhibited excellent cycling performance. The capacity retention of LaPO_4 -coated sample was 91.2% at 1 C after 100 cycles, which was higher compared with that of the pristine sample (76.4%). Moreover, the rate performance of the coated sample was greatly enhanced especially at 2, 5 and 10 C rate. The LaPO_4 -coated sample showed smaller charge transfer resistance and higher diffusion coefficient of lithium ions compared with those of the pristine sample.

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1. Introduction

Lithium-ion batteries are being intensively studied in many fields due to energy crisis and environmental pollution problems [1–6]. Layered cathode material $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ ($0 < x, y, z < 1$) is promising to replace LiCoO_2 due to lower cost, higher discharge capacity and better heat stability [7,8]. It has a wide application and may be one of the most promising electrode materials for the batteries of electric vehicles or hybrid electric vehicles [9,10]. However, its poor cycling stability and rate performance still existed in $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ on account of the formation of unstable Ni^{4+} ions in the electrode, which has strong oxidizing property and could react with the electrolyte [11,12].

Surface modification is regarded as a very useful method to enhance the electrochemical properties of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material. Many coating materials, such as Al_2O_3 [13], FePO_4 [14], SiO_2 [15] and CaF_2 [16], are reported to have been used to improve its electrochemical performance, as the side reaction could be suppressed by avoiding the direct contact between electrolyte and

cathode material. However, the lithium-ion and electronic conductivity of the coating materials are poor and may decrease the capacity and lithium ion diffusion coefficient. LaPO_4 is a good ionic conductive material with strong P=O bonds, which inhibit the direct contact between the electrolyte and cathode material, and benefit for the lithium-ion transport through the interfaces [17,18].

In our previous work, we found that the introduction of LaPO_4 to $\beta\text{-LiVOPO}_4$ is an effective way to enhance the electrochemical performance of LiVOPO_4 [17]. Han Gab Song et al. [18] first introduced the solid electrolyte LaPO_4 as a coating material to enhance the electrochemical property of lithium ion battery. However, the influence of LaPO_4 coating on nickel-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ has not been studied. In this work, LaPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material was prepared through a facile wet chemical method for the first time. The influence of LaPO_4 coating on the physical and chemical properties of the cathode material was systematically investigated. The LaPO_4 coated sample exhibited excellent cycling performance and rate stability.

2. Experimental

Pristine $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ sample was synthesized by solid state reaction method. Precursor $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ purchased

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from Hunan Jinchi Environmental Protection Technology Company Limited in China and $\text{LiOH} \cdot \text{H}_2\text{O}$ were mixed with the molar ratio of 1:1.05. The mixed material was sintered in oxygen flow at 450 and 750 °C for 4 and 12 h, respectively. For preparing LaPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ sample, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in the solvent containing distilled water and ethyl alcohol at a mass ratio of 1:9. Then, a certain amount of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ powder was added into the $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution. After that, $\text{NH}_4\text{H}_2\text{PO}_4$ solution was introduced by dripping slowly under strong agitation. The molar ratio of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ was 1:1. When the reaction was done, the obtained solution was evaporated at 70 °C until the dried powder was obtained. Finally, the powder was fired at 500 °C for 6 h to obtain LaPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material, in which the amount of LaPO_4 was 3 wt%.

The crystalline phases of the pristine and LaPO_4 -coated samples were studied by X-ray powder diffraction (XRD, Rint-2000, Rigaku, Japan) using $\text{Cu-K}\alpha$ radiation. The lattice parameters were obtained by using software (Jade). The morphologies of the samples were observed by scanning electron microscopy (SEM, JEOL, JSM-5600LV, Japan) and transmission electron microscopy (TEM, F30 S-Twin, Philips-FEI, Netherlands). The element contents of the synthesized samples were identified by energy dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS, PHI 5600, PerkinElmer) tests were conducted to obtain chemical valence states of the materials.

Coin-type cells were assembled to carry out the electrochemical characterizations. For preparing the cathode, the sample material, carbon black (super P) and polyvinylidene fluoride were blended with the mass ratio of 8:1:1. Subsequently, it was spread on an Al foil and dried under vacuum condition. The electrolyte was 1 M LiPF_6 and the counter anode was lithium metal. The CR 2025 coin-type cells were then assembled in a glove box filled with argon. The electrochemical tests were conducted using a galvanostatic charge-discharge unit and a battery test system (BTS-5V5mA, Neware, China), 3.0–4.3 V versus Li/Li^+ electrode. The electrochemical analyzer (CHI660D, CH Instruments, USA) was used for electrochemical impedance spectroscopy (EIS) and the cyclic voltammetry (CV) tests. The frequency range in EIS test was from 0.01 Hz to 100 kHz. The CV test was performed at the scan rate of 0.1 mV s^{-1} , 3.0–4.3 V versus Li/Li^+ electrode.

3. Results and discussion

The illustration of preparation process of LaPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material is shown in Fig. 1. The mixture of lanthanum compound and phosphate compound was obtained by dissolving $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the solvent. As the solvent evaporated, the precursor deposited on the sample particle surface. However, the coating layer was obviously rough and consisted of impurity compounds. After sintering, ammonium compound, nitrate compound and organic compound were removed due to decomposition. Finally, the uniform LaPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ sample was obtained. As LiPF_6 -based electrolyte contains a small amount of water, HF was generated due to the breakdown of the electrolyte. LaPO_4 layer could work as a protect layer to inhibit the corrosion from HF.

Typical SEM images of the samples are displayed in Fig. 2. There was not any obvious difference observed between the pristine and the coated samples in Fig. 2(a) and (c). However, as can be seen from high-magnification SEM images in Fig. 2(b) and (d), the primary particle surface of LaPO_4 -coated sample seems coarser compared with that of the pristine sample, suggesting the sample was uniformly coated by LaPO_4 layer. This can be further confirmed by the TEM images. Fig. 3(a) shows the TEM image of the LaPO_4 -coated sample. It is found that a distinct and thin layer existed on the particle surface, as shown in Fig. 3(b). The thickness of the nano-sized homogeneous layer was about 2 nm. To determine the composition and distribution of chemical elements in the pristine and LaPO_4 -coated samples, EDS analysis was carried out for both samples, which was presented in Fig. 4. The SEM image of the LaPO_4 -coated sample is shown in Fig. 4(a), and the EDS spectrum of the selected region in Fig. 4(a) is shown in Fig. 4(b). The spectrum indicates that the coating layer is composed of La and P elements. The EDS mappings of the coated sample are shown in Fig. 4(c)–(h), corresponding to Ni, Co, Mn, O, La and P elements, respectively. All the elements were distributed uniformly on the sample surface. It is evident that LaPO_4 coating layer was uniformly distributed on the surface of pristine sample. This uniform coating layer, serving as the protection material, could be positive to improve and cycling performance of the cathode material [19].

To understand the influence of LaPO_4 coating on crystal

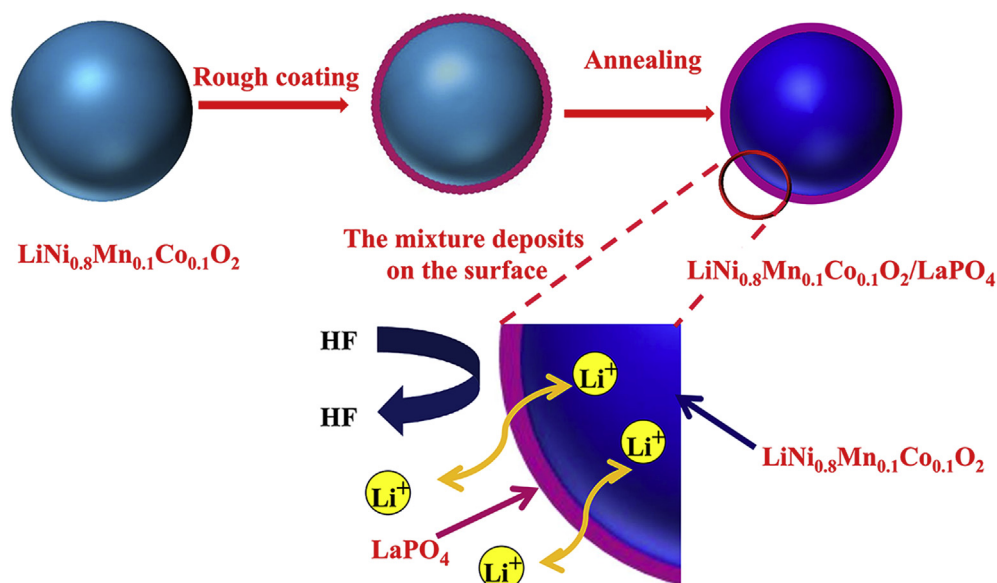


Fig. 1. Schematic illustration of the preparation procedure.

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