

# Zirconium phosphate wrapped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ used in lithium ion batteries as high voltage cathode material



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## ABSTRACT

To solve the major problem of interfacial side reactions between  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (LMNO) and liquid electrolyte at high voltages, zirconium phosphate (ZrP) wrapped cathode material LMNO@ZrP, with different aspect of ZrP in 2 wt% and 4 wt%, have been prepared by a hydrothermal method. In particular, we focus on the distribution of ZrP on the LMNO surface to find out the optimal coating material and amount. The effects of ZrP coating layer have been investigated by comparison of the properties of the ZrP coated LMNO (LMNO@ZrP) and pristine LMNO electrodes by several electrochemical characterizations. The electrochemical impedance spectroscopy results show that LMNO@ZrP-3M-2 electrode exhibits an improved electrochemical property of suppressing the impedance increase. In the cell life test, LMNO@ZrP-3M-2 electrode shows a high capacity retention of 94.6% after 200 cycles at 55 °C.

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## 1. Introduction

Today the world faces challenges on energy supply and environmental impact. Lithium-ion battery (LIB) technology has become very important in recent years as these batteries show great promise as power sources because of the virtue of their high energy density, long lifetime and low pollution [1,2]. However, it seems that LIB technology is not mature enough. The cathode material is one of the obstacles [3–5]. Lithium-ion batteries in the rapid expanded application fields such as mobile devices, electric vehicles, and energy storage systems ask for improving energy and power densities of batteries. Up to now, it is generally accepted that charging cells at a voltage higher than the conventional cutoff at 4.2 V would be a reliable approach to enhance energy density. Among the many available kinds of cathode materials, spinel-structured  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LMNO) is one of the most preferable candidates from the standpoint of high theoretical capacity of 147 mA g<sup>-1</sup>, high operating voltage (~4.7 V) and good rate capability for various applications ranging from portable electric devices to pure electric vehicles (EV) [6–9].

In the ideal LMNO, the only redox species, participating in the redox reaction during cycling between 4.0 and 5.0 V is  $\text{Ni}^{2+}$ , which oxidizes to  $\text{Ni}^{4+}$ . The  $\text{Mn}^{4+}$  ions do not have electrochemical activity, which lead to stable cycling performance of the LMNO at room

temperature. Unfortunately, when lithium ion batteries cycle at elevated temperature, the cathode material undergoes dramatic capacity fade resulting from the interfacial side reaction between the high-voltage charged LMNO and the conventional carbonate-based liquid electrolyte [10,11].

Thus, until now, lots of methods were introduced to improve the whole performance of this kind of high-voltage cathode materials. Surface modification [12–17] and doping noble metal to form composites [18–20] have been suggested as efficient approaches to controlling interfacial side reaction between LMNO and liquid electrolyte at high voltages, and thus improving the long-term cyclability. Via the surface modification approach, oxides (such as  $\text{Al}_2\text{O}_3$  [8],  $\text{ZnO}$  [8],  $\text{SiO}_2$  [13],  $\text{AlPO}_4$  [8,15]) and conductive materials (such as graphene [16], carbon nanotube [11]) have been applied on the LMNO surface. The modified cathode materials consist of active cores and inert shells. The introduction of an inert skin onto conventional cathode material can potentially improve its overall performance by reducing the interfacial side reaction between the cathode material and the electrolyte at high voltage, meanwhile increasing the thermal stability.

Recently,  $\text{ZrO}_2$  and  $\text{ZrP}_2\text{O}_7$  were reported as novel coating materials and exhibited advantages than their corresponding pristine cathode materials [21–26]. However, it was also reported that the oxides and phosphates tend to be discontinuously deposited onto the cathode materials, which leads to the nonuniform coverage on their surface [25,27].

We investigated a new coating method for applying zirconium phosphate (ZrP) onto the LMNO surface for the purpose of reducing

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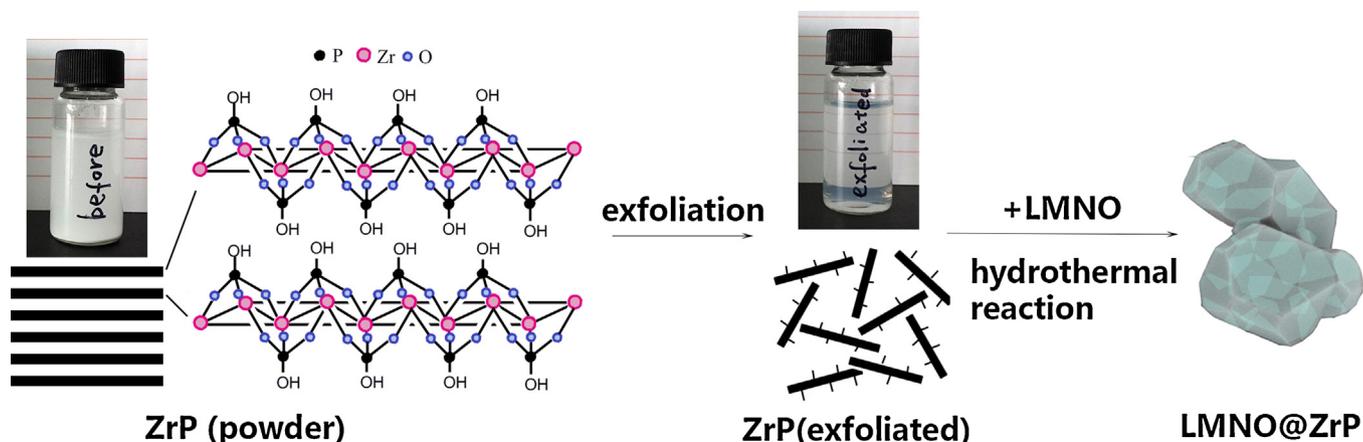


Fig. 1. Preparation of LMNO@ZrP.

the interfacial side reaction between the cathode material and the electrolyte at high voltage and high temperature. In this study,  $\alpha$ -layered ZrP ( $\alpha$ -ZrP) was exfoliated into single or a few layer sheets, which can be deposited onto LMNO surface by a hydrothermal approach. The effect of  $\alpha$ -ZrP aspect on the lithium ion diffusion, electrochemical impedance and long-term cyclability of the lithium-ion battery was studied.

## 2. Experimental

### 2.1. Materials

Manganese acetate tetrahydrate, nickel acetate tetrahydrate, lithium acetate and zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , 98%) were purchased from Aldrich. Reagent-grade oxalic acid dehydrate, aqueous ammonia (24%), phosphoric acid (85%) and tetra-*n*-butylammonium hydroxide ( $\text{TBA}^+\text{OH}^-$ , 1.0 M in methanol) were obtained from Aladdin Industrial Inc. All reagents and solvents were used as received.

### 2.2. Synthesis of spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO)

The spinel  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  powders were synthesized according to the following procedure. In briefly, 5.0426 g of oxalic acid dehydrate was dissolved in 50 ml of de-ionized water to obtain solution A. Stoichiometric amounts of nickel acetate tetrahydrate, manganese acetate tetrahydrate and lithium acetate (with 5% excess lithium), corresponding to 0.02 mol of  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ , were dissolved in 100 ml of de-ionized water (solution B). Solution B was added in a drop-wise manner to solution A in 10 min, followed by the addition of aqueous ammonia to keep pH value at 7. The mixture was heated at 90 °C for 5 h with strong mechanical stirring. The slurry was dried under vacuum at 90 °C for 20 h and then was placed in a furnace at 550 °C for 4 h to get the product of the composition  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ . The compound was slightly ground, heated to 900 °C at a heating rate of 10 °C  $\text{min}^{-1}$  and then directly cooled down to 600 °C, followed by being kept at 600 °C for 8 h to improve the crystallinity of spinel  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ .

### 2.3. Preparation of zirconium phosphate (ZrP) skinned LMNO

In a typical synthetic process of  $\alpha$ -ZrP micro-crystals with different lateral dimensions [28], a sample of 10.0 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was refluxed with 100.0 ml of 3.0 M  $\text{H}_3\text{PO}_4$  at 100 °C for 24 h to synthesize  $\alpha$ -ZrP (noted as ZrP-3 M). A sample of 6.0 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was mixed with 60.0 ml of 6.0 M  $\text{H}_3\text{PO}_4$  in a sealed teflon-lined pressure vessel and reacted at 200 °C for 24 h to prepare  $\alpha$ -ZrP (noted as

ZrP-6M).  $\alpha$ -ZrP (ZrP-3M) and  $\alpha$ -ZrP (ZrP-6M) were used as coatings for composite cathode materials in this research.

The as prepared  $\alpha$ -ZrP micro-crystals were exfoliated by tetra-*n*-butylammonium hydroxide ( $\text{TBA}^+\text{OH}^-$ ) in an aqueous dispersion [29]. In a typical experiment, 0.5 g of ZrP was suspended in 20 ml of water, followed by ultrasonication treatment of 1 h. Then 16.7 ml of TBA (0.1  $\text{mol l}^{-1}$ ) was added in the mixture as the intercalation agent. The dispersion was stirred for 1 h at 0 °C and sonicated for 1 h to give a transparent ZrP dispersion. The concentration of  $\alpha$ -ZrP aqueous dispersion was controlled at a low value (1.5 wt%) to ensure that the dispersed  $\alpha$ -ZrP particles were completely reacted with  $\text{TBA}^+\text{OH}^-$ .

The LMNO@ZrP nanocomposites with different coating amounts of ZrP were made by a hydrothermal method. First, LMNO and ZrP dispersion were mixed to form a slurry, which was diluted with a few de-ionized water and ultrasonicated for 1 h. Then the mixture was transferred to a sealed teflon-lined pressure vessel and reacted at 160 °C for 15 h to deposit ZrP nanosheets onto LMNO particles. After filtration, the resulting powder was dried at 120 °C for 12 h in air. Various amounts of two ZrP were used as coating materials. For example, LMNO@ZrP-3M-2 refers to a sample coated with 2 wt% of ZrP-3M. Fig. 1 shows the preparation of ZrP wrapped  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ .

### 2.4. Physical characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer, using a graphite monochromator with Cu- $K\alpha$  radiation (60 kV and 80 mA) between 10° and 90° with a step length of 0.02°. TEM (JEOL, JEM-2100HR, operating at 200 kV) and SEM (Carl Zeiss, ZEISS Ultra 55, operating at 5 kV) were used to investigate the morphology and size of the LMNO powder and the LMNO@ZrP composites. X-ray photoelectron spectroscopy analysis was carried out with an ESCALAB 250 (Thermo Fisher Scientific). The radiation was a Al monochromatised source (1486.6 eV) under normal pressure below  $1.5 \times 10^{-12}$  bar. The survey measurement with five sweeping cycles was performed in the electron binding energy ranges of 0–1100 eV.

### 2.5. Electrochemical test

The electrochemical properties of the LMNO@ZrP electrodes were determined in tests with CR2025 coin-type cells. To prepare the positive electrode, 0.8 g of cathode material, 0.1 g of carbon black, 0.1 g of PVDF and 4 ml of NMP were mixed in a ball-miller, then the slurry was casted on aluminum foil and dried. Both pristine and ZrP skinned LMNO were tested as cathodes.

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