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## Improvement in capacity retention of cathode material for high power density lithium ion batteries: The route of surface coating

Xi Ke<sup>a</sup>, Zhuozhuo Zhao<sup>a</sup>, Jun Liu<sup>a</sup>, Zhicong Shi<sup>a,\*</sup>, Yunyong Li<sup>a</sup>, Lingyu Zhang<sup>a</sup>, Haiyan Zhang<sup>a</sup>, Ying Chen<sup>a</sup>, Zaiping Guo<sup>a,b,\*</sup>, Qihui Wu<sup>c,\*</sup>, Liying Liu<sup>a</sup>

<sup>a</sup> Guangdong Province Key Laboratory for Functional Soft Materials, School of Materials and Energy, Guangdong University of Technology, Guangzhou, Guangdong 510006, PR China

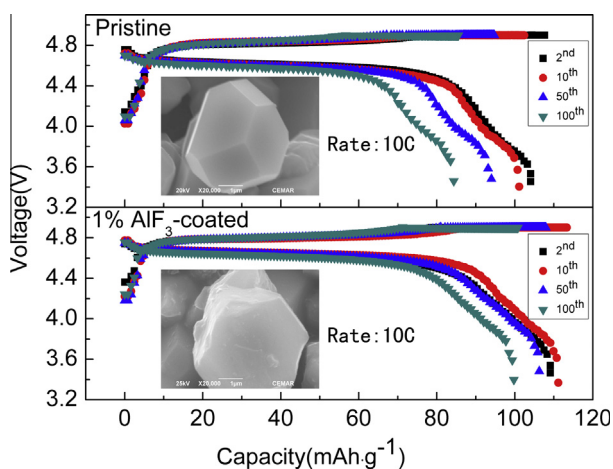
<sup>b</sup> School of Mechanical, Materials, and Mechatronic Engineering, Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, NSW 2522, Australia

<sup>c</sup> Department of Materials Chemistry, College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, Fujian, PR China

### HIGHLIGHTS

- AlF<sub>3</sub> were easily coated on the surface of the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> particles.
- Coating AlF<sub>3</sub> reduces the interfacial reactions and enhances its cycling performance.
- The capacity retention of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> was greatly enhanced after AlF<sub>3</sub> coating.
- AlF<sub>3</sub>-coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> is a promising cathode material for high power LIBs for EVs.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Using electrical vehicles instead of traditional ones is very important for reducing fossil oil consumption and carbon emissions. Spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> is considered as a promising cathode material for advanced lithium ion batteries owing to its high power density. Nevertheless, it suffers badly from the interfacial reactions with the electrolyte at high operation potential, which degrades its electrochemical performance. The strategy of the present study is to prevent direct contact between LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and the electrolyte by using a surface coating in order to reduce solid electrolyte interfacial reactions and consequently enhance its cycling performance. The experimental results indicated that as-prepared LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> sintered at 900 °C possessed the highest initial specific capacity of 132.4 mA h g<sup>-1</sup> at 0.2 C rate, with 81.0% initial capacity retention after 50 cycles. Coating AlF<sub>3</sub> on the particle surfaces of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> using a modified solid-state method can improve its electrochemical properties by enhancing its initial specific capacity from 104.6 to 109.1 mA h g<sup>-1</sup> and increasing its capacity retention from 80.6 to 92.1% at the 10 C rate after 100 cycles.

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\* Corresponding authors at: Guangdong Province Key Laboratory for Functional Soft Materials, School of Materials and Energy, Guangdong University of Technology, Guangzhou, Guangdong 510006, PR China (Z. Guo).

E-mail addresses: [zhicong@gdut.edu.cn](mailto:zhicong@gdut.edu.cn) (Z. Shi), [zguo@uow.edu.au](mailto:zguo@uow.edu.au) (Z. Guo), [qhwwu@qztc.edu.cn](mailto:qhwwu@qztc.edu.cn) (Q. Wu).

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## 1. Introduction

With the energy crisis and environmental pollution concerns, using electric vehicles (EVs) and hybrid electric vehicles (HEVs) instead of traditional ones is very important for reducing fossil oil consumption and carbon emissions in cities. Advanced rechargeable batteries, such as lithium ion batteries (LIBs), redox flow batteries, and sodium nickel chloride batteries, are energy storage devices with high efficiencies [1]. LIBs are the most promising ones for EVs and HEVs because of their high energy and power densities compared to the others [2], which helps drive down the costs and improve bankability for the grid projects. Moreover, LIBs are also ideal energy storage devices for the extra power created by the large scale renewable energy sources such as wind and photovoltaic. In recent years, developing new cathode materials to improve their safety and energy density has become the major research trend for LIBs. At present, LiCoO<sub>2</sub> [3], LiFePO<sub>4</sub> [4], and LiMn<sub>2</sub>O<sub>4</sub> [5] are commercially available cathode materials. Amongst them, spinel LiMn<sub>2</sub>O<sub>4</sub> is exceptionally promising because of its low-cost, simple synthesis process, and environmental friendliness. The serious capacity fading of LiMn<sub>2</sub>O<sub>4</sub>, however, especially at high temperature, due to the dissolution of manganese and the Jahn-Teller effect [6] has aroused strong concern. In order to improve the cycling performance of LiMn<sub>2</sub>O<sub>4</sub>, lattice doping was employed to synthesize LiM<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> (M = Ni, Al, Cr, Zn, etc) with enhanced electrochemical performance [7–10]. In particular, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> could intercalate/deintercalate lithium ions at 4.7 V with a theoretical specific capacity of 146.7 mA h g<sup>-1</sup> and a calculated energy density 20% higher than that of LiCoO<sub>2</sub> [11]. For these reasons, cubic spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> has been intensively studied as a cathode material for high energy density LIBs.

This material still suffers, however, from severe reactions with the electrolyte at high potential and from the dissolution of Mn and Ni ions into the electrolyte at elevated temperatures. The electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> is thus severely suppressed by its structural and chemical instability. Further lattice doping (e.g. Mg [12] and Ru [13]) has been applied to improve the electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, but no obvious impact towards slowing the interfacial reactions was detected. Surface coatings on the particle surface using BiOF [14], ZnO [15], Bi<sub>2</sub>O<sub>3</sub> [16], and AlPO<sub>4</sub> [17] were applied to improve the electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>. This surface modification of the cathode electrode would reduce its direct contact area with the electrolyte, which consequently slows the dissociation of the metal ions into the electrolyte and also possibly reduces the side reactions at the solid electrolyte interphase. The general ways to prepare spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> include the high-temperature solid-state method [18], the sol-gel method [19], the gel-combustion method [20], the emulsion-drying method [21], the spray-drying method [22], and the co-precipitation method [23,24]. Besides at 4.7 V, the cubic spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> typically exhibits a platform at 4.1 V during the discharge progress. The emergence of the 4.1 V platform is usually caused by the loss of oxygen in the spinel oxide prepared during the high temperature annealing process [25], resulting in the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup>. In order to reduce the Mn<sup>3+</sup> ion content and eliminate the 4.1 V plateau, Zhong and co-workers [26] prepared LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> using the traditional solid-state method followed by quenching at a lower temperature after high temperature sintering to oxidize Mn<sup>3+</sup> to Mn<sup>4+</sup>. The traditional solid-state method still suffers from inhomogeneous mixing, however, inducing large variations in the structure and particle sizes [27]. In the present study, high-crystallinity and homogeneous LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> has been synthesized using a modified solid-state method, and then uniform AlF<sub>3</sub> layers were coated onto the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> surface. The electrochemical studies indicated

that the surface coating would enhance the rate performance and cycling stability of the cathode electrode [28].

## 2. Experiment

### 2.1. Synthesis of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

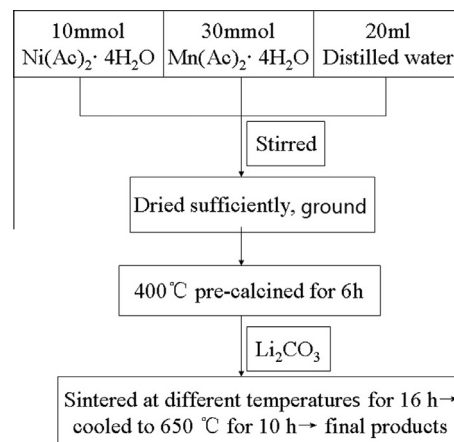
LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> was synthesized using an modified solid-state method, as shown in Scheme 1. 30 mM Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O (≥99.0%, AR) and 10 mM Ni(Ac)<sub>2</sub>·4H<sub>2</sub>O (≥98.5%, AR) were dissolved in 20 ml distilled water and then stirred at 90 °C for 5 h. The solution was dried at 120 °C in air for 10 h to form a solid-state phase mixture. The resulting mixture was ball-milled for 1 h at 500 rpm to obtain a fine powder. The powder was calcined at 400 °C for 6 h to form Precursor A. Then Precursor A was mixed with Li<sub>2</sub>CO<sub>3</sub> (≥99.0%, AR) and sintered at 750, 800, 850, 900, and 950 °C for 16 h in a muffle furnace, followed by a quenching at 650 °C for 10 h during the cooling process in order to obtain the final products. The samples were denoted as A-750, A-800, A-850, A-900, and A-950, based on the sintering temperatures.

### 2.2. Synthesis of AlF<sub>3</sub>-coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

AlF<sub>3</sub>-coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> was produced from sample A-900, as indicated in Scheme 2. Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (≥99.0%, AR) and A-900 were mixed in distilled water by stirring, and then NH<sub>4</sub>F (≥99.0%, AR) solution was dropped into the turbid liquid. The suspended mixture was stirred at 80 °C until the solvent was completely evaporated. The powders were then calcined at 550 °C for 5 h to obtain AlF<sub>3</sub>-coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.

### 2.3. Physical characterization

The structures of the samples were characterized by X-ray diffraction (XRD) using a Bruker D8 AD-VANCE powder diffractometer with Cu Kα radiation at 40 kV and 40 mA in steps of 0.02° from 10° to 80°. The surface morphology was examined using a JEOL 6300F scanning electron microscope (SEM) at 20 kV. The AlF<sub>3</sub> coating was investigated by means of a transmission electric microscope (TEM, JEOL 2010F) using an accelerating voltage of 20 kV and energy dispersive X-ray spectroscopy (EDX, Shimadzu-EP-MA 1600) using an accelerating voltage of 15 kV. Thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) were carried out using a Netzsch STA 409EP thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> from 25 to 550 °C in air.



Scheme 1. The synthesis process for LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.

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