



Nanoscale TiO₂ membrane coating spinel LiNi_{0.5}Mn_{1.5}O₄ cathode material for advanced lithium-ion batteries



Shi Tao ^a, Fanjun Kong ^a, Chuanqiang Wu ^b, Xiaozhi Su ^b, Ting Xiang ^b,
Shuangming Chen ^b, Haihong Hou ^a, Lei Zhang ^a, Yong Fang ^a, Zhicheng Wang ^a,
Wangsheng Chu ^{b, **}, Bin Qian ^{a, *}, Li Song ^b

^a Jiangsu Laboratory of Advanced Functional Materials, Department of Physics and Electronic Engineering, Changshu Institute of Technology, Changshu 215500, People's Republic of China

^b National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ARTICLE INFO

Article history:

Received 12 December 2016

Received in revised form

12 February 2017

Accepted 13 February 2017

Available online 20 February 2017

Keywords:

LiNi_{0.5}Mn_{1.5}O₄

TiO₂

High voltage

Cathode

Lithium-ion batteries

ABSTRACT

Spinel LiNi_{0.5}Mn_{1.5}O₄ (LNMO) is one of the most promising high voltage cathode materials for future application. Herein, we report a simple method to prepare nanoscale TiO₂-coated LNMO composites (LNMO-T). The thin TiO₂ coating layer was pasted on the surface of host material, which favors Li⁺ ions diffusions. Compared to the bare LNMO, the surface modified composites LNMO-T shows outstanding rate capability and excellent cycling ability. In particular, a discharge capacity of 74.5 mAh/g can be still delivered at 15 C and about 88.5% capacity retention at 2 C after 500 cycles. These results suggest that the TiO₂ coating can not only suppress the dissolution of manganese in the electrolyte but also enhance the conductivity of cathode. This study demonstrates that the potential of developing high energy density cathode materials by surface modification with TiO₂ membrane at nanoscale for future applications.

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1. Introduction

To meet the requirements for energy storage and utilization of green energy, lithium-ion batteries (LIBs) are considered as one of the most potential energy-storage device, owing to their high energy density, long cycle life and safety [1–3]. But the energy density of current LIBs is still low and not enough for electric vehicles (EVs) and hybrid electric vehicles (HEVs). Among the advanced cathode materials, LiNi_{0.5}Mn_{1.5}O₄ (LNMO) has attracted considerable attention due to its high voltage, potential for low cost, and high thermal stability. With a theoretical capacity of 146.7 mAhg⁻¹ and working voltage of about 4.7 V, LNMO has higher energy density (650 Wh/kg) than LiCoO₂ (518 Wh/kg) and LiFePO₄ (495 Wh/kg), respectively [4,5]. However, the high operational potential will cause the decomposition of electrolyte and salt, consequently forming solid electrolyte interphase (SEI) layer, which increase the cell impedance and traps Li⁺ resulting in capacity fade

with cycling. On the other hand, Mn³⁺ is favorite for dissolving in the electrolyte at high potential, which lead to unstable structure of electrode materials [6,7]. Thus, to overcome these problems of LNMO materials with stable long-term cyclability and rate performance are crucial.

In light of the above issues, many efforts have been employed, such as metal ion doping, surface modification and nanostructure fabrication [8–12]. Among these approaches, coating a protective layer on the LNMO surface to establish a more stable interface to minimize undesirable side reactions has demonstrated as an efficient method to improve the electrochemical performance. The most commonly used coating materials are metal oxides, lithium compounds and carbon materials [13–24]. Recently, Wang et al. reported the spherical LNMO cathode material modified by Fe₂O₃ surface coating and improved the electrochemical performance [25]. Zhang et al. synthesized a layered LiTiO₃ embedded into bulk LNMO and further improved the high-rate performance [26]. Hwang et al. prepared surface-modified carbon nanotube coating LNMO cathodes via mechanofusion method and the composites exhibited an enhanced discharge capacity retention (95.5%) after 80 cycles [27]. Especially, TiO₂ is recognized as the optimal coating material due to its low cost, abundance resources and good

* Corresponding author.

** Corresponding author.

E-mail addresses: chuws@ustc.edu.cn (W. Chu), njqb@cslg.cn (B. Qian).

structural stability for improving the electrochemical properties of cathode materials [28,29]. More recently, Zhang et al. reported porous nanosized TiO₂-coated LiMnO₄ by a modified sol-gel process and electrochemical tests revealed that the TiO₂ coating layer remarkably improved capacity retentions at both room temperature and elevated temperature [30]. To our best knowledge, a fairly homogeneous coating layer tends to be more attractive for LNMO.

In this paper, we present a simple wet chemical process to successfully coat LNMO with a controllable and good physical contact layer of TiO₂. The cathode material LNMO-T exhibits excellent electrochemical performance systematically. At high charge-discharge rates of 7 C, 10 and 15 C, a discharge capacity of 97.6, 88.3 and 74.5 mAh/g can be obtained, respectively. No obvious capacity fading at 2 C after 500 cycles. The results indicate that TiO₂-coating LNMO has great potential as cathode material for high energy density LIBs.

2. Experimental

2.1. Material synthesis

Pristine LNMO was synthesized by solid-state method as described in Ref. [22]. All reagents were all purchased from the Sinopharm Chemical Reagent Co. (Shanghai, China). Nickel acetate (Ni(Ac)₂·4H₂O) and manganese acetate (Mn(Ac)₂·4H₂O) were mixed at a molar ratio of 1:3 and hand milled in a mortar. The mixture was then heated to 500 °C for 5 h. And then lithium acetate (LiAc·2H₂O) was mixed with the mixture at a molar ratio of 2.1:1:3, and the mixture was heated to 500 °C for 5 h again. Then the mixture was hand milled and calcined at 900 °C for 10 h followed by sintered at 700 °C for 10 h.

LNMO-T sample was prepared by a simple wet chemical method. Firstly, a calculated amount of tetrabutyl titanate (the molar ratio of LNMO:Ti = 10:1) was dissolved in ethanol by ultrasonic treatment, and then the solution dropped into acetic acid solution, which a moderate acetic acid in ethanol and water (v/v = 6:4). Secondly, the pristine LNMO powders were added into above solution, stirring 30 min, and then followed by drying at 80 °C. Finally, the mixture was annealed at 750 °C for 3 h.

2.2. Materials characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a D8-Advance power diffractometer with a Cu-Kα radiation source (λ = 1.54178 Å). The morphology of the samples was characterized by a field emission scanning electron microscope ((FE-SEM, SIGMA, ZEISS) and high-resolution transmission electron microscope (TEM, JEOL- 2000CX, 200 kV). The EDX mapping analysis was carried out on Titan G2 80-200 ChemiSTEM with a X-

FEG and four windowless silicon drift EDX detectors. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on ESCALAB 250 (Thermo-VG Scientific) XPS spectrometer. The NEX-AFS (Near-Edge X-ray Absorption Fine Structure) spectroscopy results for Ti and O were collected in total electron yield (TEY) mode at the beamline 4B7B in the Beijing Synchrotron Radiation Facility (BSRF). The storage ring of the BSRF was operated at 2.5 GeV with a maximum current of 300 mA.

2.3. Electrochemical measurements

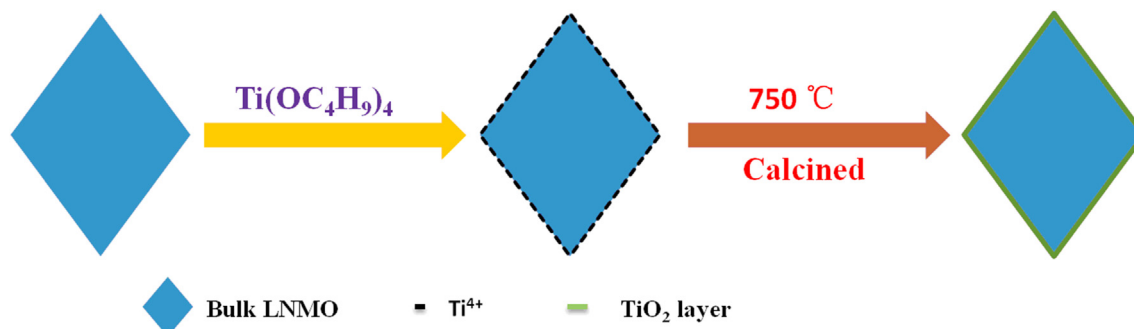
The electrochemical properties of the samples were tested using a CR2032-type coin cells, which were assembled in an argon-filled glove box. The electrodes were fabricated by pasting a mixture of LNMO-T, acetylene black and poly (vinyl difluoride) (PVDF) at a weight ratio of 80:10:10 in the N-methyl-2-pyrrolidone (NMP) solvent on aluminum (Al) foil and dried at 110 °C for 12 h. The loading density of the electrodes is about 2.2 mg cm⁻². The metallic lithium was used as anode and Celgard 2500 was used as the separator. 1 M LiPF₆ (ethylene carbonate, dimethyl carbonate and ethyl-methyl carbonate with a 1:1:1 vol ratio) was used as the electrolyte. The galvanostatically charged-discharged tests were carried out on Land CT 2001 battery tester between 3.0 and 5.0 V vs. Li⁺/Li. Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) measurements of cells were performed on the VSP electrochemical workstation (Bio-logic, France) with a scan rate of 0.5 mVs⁻¹ in the range of 3.0–5.0 V and an amplitude of the signal of 10 mV and frequency in the range 10⁶ Hz–0.01 Hz, respectively.

3. Results and discussion

We prepared TiO₂-coated LNMO composite with Ti:LNMO = 1:10 in molar ratio. The synthetic approach of the LNMO-T consists of two steps that LNMO sample was prepared first, and then the surface modified sample obtained by a wet chemical method followed by final sintering. Scheme 1 shows the synthesis process for the LNMO-T composites. The detailed procedure is described in the experimental section.

The XRD patterns of the synthesized LNMO and LNMO-T samples are shown in Fig. 1. All the diffraction peaks of samples were matched well with the calculated pattern for all samples with the cubic structure of spinel LNMO. This suggests that the crystal structure of LNMO is not affected by the TiO₂ coating and no features of TiO₂ are observed, due to its low loading content and the formation of a thin layer of TiO₂ on the surface of LNMO. All the peaks are sharp and well defined suggesting that the composites are generally well crystallized.

The morphologies of the pristine LNMO and LNMO-T samples



Scheme 1. Illustration of preparation process of LNMO-T composite.

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