



Improving the electrochemical properties of high-voltage lithium nickel manganese oxide by surface coating with vanadium oxides for lithium ion batteries



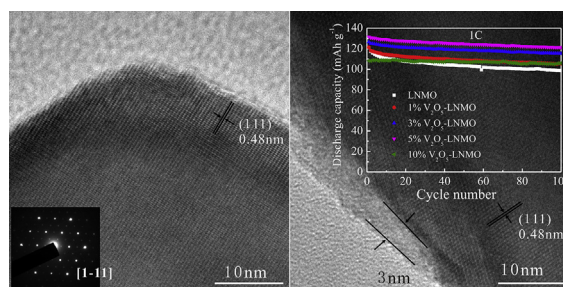
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HIGHLIGHTS

- V_2O_5 can react with $LiOH/Li_2CO_3$ impurities in the bulk layer during calcination process to form a close contact.
- Surfaces coating with V_2O_5 increase ionic conductivities of electrode as well as inhibit the dissolution of transition metal.
- The electrode electrochemical performance and cycling life is enhanced because of structural integrity.

GRAPHICAL ABSTRACT



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ABSTRACT

The V_2O_5 -coated $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode materials are synthesized via a wet-coating method. V_2O_5 is capable of lithium intercalating, so the surface of materials is purified. Furthermore lithium ion conductor V_2O_5 is not only a barrier between electrolyte and LNMO surface to prevent electrolyte decomposition especially at high voltage, but also a HF scavenger thus the spinel structural integrity of LNMO can be preserved for a better cycling reversibility, especially at high temperatures under which conditions the dissolution of Mn^{3+} ions into electrolyte via reacting with HF is severely problematic for pristine LNMO as cathode materials. The amount of V_2O_5 coating affects the electrochemical properties of these samples. We discover that the optimal amount of V_2O_5 on LNMO surface is about 5 wt%. Compared with pristine LNMO, the coating amount with 5 wt% exhibits an excellent rate capability and better reversibility. The discharge capacity is increased by 15.8%, 17.9%, 16.2%, 16.3%, 19.1% and 21.0% in comparison with pure LNMO, presenting a discharge specific capacity of 123.9, 119.1, 120.8, 117.5, 111.9 and 105.3 $mAh\ g^{-1}$ at the rates of 0.2, 0.5, 1, 2, 5 and 10C respectively. In addition, the sample presents a discharge capacity of 131.5 $mAh\ g^{-1}$ at 1C, with a retention of 92.2% after 100 cycles. Even cycling at 5C rate and 55 °C, the cell with 5% V_2O_5 -coated LNMO cathode can have a capacity of 126.3 $mAh\ g^{-1}$, with 92% capacity retention after 100 cycles, implying that V_2O_5 -coating of LNMO is an effective modified method for lithium ion batteries.

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1. Introduction

The dawn of new automobile era of environmental friendly

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electric vehicle (EV), hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) accelerates the development of rechargeable battery technologies [1–7]. The ‘old-type’ rechargeable batteries can hardly meet the demands for high energy and high power; on the other hand lithium ion batteries emerge as one of the most possible power sources for electrical vehicles due to their many advantages such as high voltage, high specific capacity and excellent cycling life and so on [8,9]. The performance of lithium-ion batteries, such as working voltage and power density, is mainly determined by the property of the cathode materials. Therefore, the development of high voltage cathode materials is pivotal for lithium ion battery with high energy density [10].

Because of its low cost, low toxicity, great abundance and good safety especially under extreme conditions, spinel LiMn_2O_4 (LMO) was considered as an ideal cathode material for lithium ion batteries [11,12]. Doping with a certain amount of transition metal elements M (M = Fe, Co, Ni, Cr etc.) to form solid state solution $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ alters the Fermi energies of the materials and their electrode potentials are raised as a result [13]. Of these spinel $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ cathode materials, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits an acceptable performance and stable discharge capacity. Different greatly from LMO, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows one high voltage discharge plateau at ca. 4.7 V and a small plateau around 4 V, the later one similar to LMO [13–15]. The plateau around 4.7 V is assigned to the oxidation–reduction of $\text{Ni}^{2+}/\text{Ni}^{4+}$, while the 4.0 V one is attributed to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ oxidation–reduction process [16,17]. The weight energy density of LNMO is higher than those of the conventional cathode materials, such as LiCoO_2 [18], $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ [19,20] and LiFePO_4 because of its unmatched high voltage [21,22]. The spinel LNMO can be expected to meet the high energy and high power demands for personal consumer electronics and electric equipment for a possible replacement of standard LiCoO_2 cathode material. It is also one of the few cathode materials to pair up with high working voltage anode materials such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to construct batteries with very high power capabilities and without much sacrifice in energy density [23]. Thus it is one of the most attractive cathode electrode materials for the next generation advanced lithium ion batteries.

However, even though LNMO suppresses John-Teller distortion which is accounted for the structural instability of LMO [24], it still shows a fast fading of capacity, which is attributed to the surface reactions between cathode/electrolyte at the high operating voltages of ~5 V [25] and the dissolution transition metal ions by the attack of trace HF in electrolyte solution. A conventional method to prevent reactions between the electrolyte and LNMO is to coat a thin layer of metal oxide or metal phosphate [8] on the LNMO particle surface as a barrier to block direct contact between them. Metal oxides such as ZnO [26], ZrO_2 [27], Bi_2O_3 [25], SiO_2 [28] and Al_2O_3 [29] have been investigated as surface coatings to improve the electrochemical performance and structural stability of the spinel LMNO. These metal oxides, even though some of them are lithium ion conductors, do not react with LNMO to form an intimate contact, thus an interphase with high electrical resistance is very likely present [30]. On the other hand, vanadium oxides [31,32] and $\text{Co}_3(\text{PO}_4)_2$ [33], both capable of lithium intercalating, have been studied to coat LiNiO_2 -based cathode materials. They can react with $\text{LiOH}/\text{Li}_2\text{CO}_3$ impurities and trace Li ions in the bulk layer when annealed at high temperatures to form a close contact. The formation of lithium ion intercalated compounds LiV_3O_8 or LiCoPO_4 not only lowers the pH value of LiNiO_2 -based materials, but also purify LiNiO_2 -based surface from physical adsorption of residue $\text{Li}_2\text{O}/\text{LiOH}$ to enhance the cycle performance at a high voltage. The composite of surface coating of LNMO with V_2O_5 has not been reported. We think that due to ionic conducting property of V_2O_5 , surface coating with V_2O_5 will increase ionic conductivities of

electrode as well as protect LNMO surface from reacting with the electrolyte and HF, thus enhance the electrode electrochemical performance and its cycling life. In this work, LNMO coating with V_2O_5 is executed firstly via a wet-coating method. The V_2O_5 coating effectively improves the Li ion diffusion coefficient, controls the interfacial side reaction between electrolyte and LNMO at high voltages, keep LNMO structural integrity and enhances electrochemical performance such as cycling stability and rate capability, making the LNMO excellent cycling stability.

2. Experimental

2.1. Materials synthesis

The plate-like precursor compound $[\text{Ni}_{0.5}\text{Mn}_{1.5}](\text{OH})_4$ was obtained by a co-precipitation method. An aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ with a total transition metal ion concentration of 2.0 M ($n_{\text{Ni}^{2+}}:n_{\text{Mn}^{2+}} = 1:3$) was pumped into a beaker (1 L) under an N_2 atmosphere under continuous stirring. At the same time, a solution of NaOH (4.0 M) and desired amount of NH_4OH as a chelating agent was pumped into the reactor. The concentration, pH, temperature, and stirring speed of the mixture in the reactor were carefully controlled. The slurry was aged in the beaker under an N_2 atmosphere at 55 °C for 12 h before filtered. The $[\text{Ni}_{0.5}\text{Mn}_{1.5}](\text{OH})_4$ powders were washed with distilled water and alcohol for several times. After air-drying at 100 °C, the powder was mixed with appropriate LiOH and ball-milled at 200 rpm for 2 h (FRITSCH-Pulverisette 14). The ball-milled mixture was first sintered in air atmosphere at 800 °C for 20 h, then cooled down to 600 °C, and kept at this temperature for 20 h to compensate oxygen vacancy before finally cooled to room temperature slowly. To prepare V_2O_5 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, desired amount of NH_4VO_3 was dissolved in 20 mL of water at 80 °C, after adding 2 g $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the suspension was ultrasonic processing for 30 min before the evaporation of water. The obtained solids were calcined at 400 °C for 5 h to obtain V_2O_5 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The LNMO samples coated with 1 wt%, 3 wt%, 5 wt% and 10 wt% V_2O_5 were denoted as 1% V_2O_5 -LNMO, 3% V_2O_5 -LNMO, 5% V_2O_5 -LNMO and 10% V_2O_5 -LNMO, respectively.

2.2. Materials characterization

The XRD data was collected on Rigaku miniflex 600 with Cu $K\alpha$ radiation operated at 40 kV and 15 mA scanned from 10° to 90° at 1° min^{-1} with a step size of 0.02°. Field emission scanning electron microscopy (SEM, HITACHI S-4800) was used to characterize the morphology of samples, and energy dispersive X-ray spectroscopy (EDS, OXFORD 7593-H, an accessory of SEM) was carried out to analyze the surface elemental distribution of particles with 20 kV acceleration voltage. The X-ray photoelectron spectroscopy (XPS) data was collected with a Quantum 2000 Scanning ESCA Microprobe spectrometer with a focused monochromatized Al $K\alpha$ radiation (1486.6 eV). The pass energies were 60 eV for the survey spectra and 20 eV for particular elements, respectively. Transmission electron microscopy (TEM, JEOL-2100) was used to examine the morphologies and identify the structures of the as-prepared samples. Fourier-transformed infrared spectra (FTIR) were carried out on a Nicolet 330 infrared spectrometer in transmittance mode using KBr pellet method over the range of 400–1000 cm^{-1} . Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on Plasma1000 (NSC, China) to identify the metal ion concentration in electrolyte.

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