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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

- V₂O₅ can react with LiOH/Li₂CO₃ impurities in the bulk layer during calcination process to form a close contact.
- \bullet 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.

A R T I C L E I N F O

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ABSTRACT

The V_2O_5 -coated LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cathode materials are synthesized via a wet-coating method. V₂O₅ 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 Mn³⁺ ions into electrolyte via reacting with HF is severely problematic for pristine LNMO as cathode materials. The amount of V₂O₅ 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 has a capacity of 126.3 mAh g⁻¹, with 92% capacity retention after 100 cycles, implying that V₂O₅-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

* Corresponding author. *E-mail address: jbzhao@xmu.edu.cn* (J. Zhao). 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 LiMn₂O₄ (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 LiMn_{2-x}M_xO₄ alters the Fermi energies of the materials and their electrode potentials are raised as a result [13]. Of these spinel LiMn_{2-x}M_xO₄ cathode materials, LiNi_{0.5}Mn_{1.5}O₄ exhibits an acceptable performance and stable discharge capacity. Different greatly from LMO, LiNi_{0.5}Mn_{1.5}O₄ 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 Ni²⁺/Ni⁴⁺, while the 4.0 V one is attributed to the Mn^{3+}/Mn^{4+} oxidation-reduction process [16,17]. The weight energy density of LNMO is higher than those of the conventional cathode materials, such as LiCoO₂ [18], LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ [19,20] and LiFePO₄ 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 LiCoO₂ cathode material. It is also one of the few cathode materials to pair up with high working voltage anode materials such as Li₄Ti₅O₁₂ 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], ZrO₂ [27], Bi₂O₃ [25], SiO₂ [28] and Al₂O₃ [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 Co₃(PO₄)₂ [33], both capable of lithium intercalating, have been studied to coat LiNiO₂-based cathode materials. They can react with LiOH/Li₂CO₃ 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 LiV₃O₈ or LiCoPO₄ not only lowers the pH value of LiNiO₂-based materials, but also purify LiNO₂-based surface from physical adsorption of residue Li₂O/LiOH to enhance the cycle performance at a high voltage. The composite of surface coating of LNMO with V₂O₅ has not been reported. We think that due to ionic conducting property of V_2O_5 , surface coating with V₂O₅ 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 [Ni_{0.5}Mn_{1.5}](OH)₄ was obtained by a co-precipitation method. An aqueous solution of $NiSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot 5H_2O$ with a total transition metal ion concentration of 2.0 M (n_{Ni2+} : n_{Mn2+} = 1:3) was pumped into a beaker (1 L) under an N₂ atmosphere under continuous stirring. At the same time, a solution of NaOH (4.0 M) and desired amount of NH₄OH 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 N₂ atmosphere at 55 °C for 12 h before filtered. The [Ni_{0.5}Mn_{1.5}](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 V₂O₅-coated LiNi_{0.5}Mn_{1.5}O₄, desired amount of NH₄VO₃ was dissolved in 20 mL of water at 80 °C, after adding 2 g LiNi_{0.5}Mn_{1.5}O₄, 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 V₂O₅-coated LiNi_{0.5}Mn_{1.5}O₄. 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% V₂O₅–LNMO, respectively.

2.2. Materials characterization

The XRD data was collected on Rigaku miniflex 600 with Cu Ka 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 Ka 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 asprepared 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.

2.3. Electrochemical measurements

Electrochemical performances of these materials were evaluated with CR2016-type coin cell configuration. The working electrode film was obtained by spreading a slurry of 70 wt% active material, 20 wt% acetylene black, 10 wt% polyvinylidene difluoride (PVDF) binder dispersed in N-methyl pyrrolidione (NMP) solvent onto an aluminum foil. After drying in a vacuum oven at 100 °C overnight, the electrode was punched out and roll-pressed. CR2016-type coin cells were assembled by sandwiching a porous polyethylene separator between the electrode and Li metal foil in a high-purity Ar-filled glove box. The electrolyte was 1.0 M LiPF₆ salt dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a weight ratio of 1:1.

The cells were galvanostatically charged and discharged between 3.0 and 4.9 V at room temperature on battery testers (LAND CT-2001A instrument, Wuhan, China and NEWARE BTS type battery charger, Shenzhen, China). When the rates are higher than 1C (including 1C), a two-step charge process (constant current and constant voltage charge) was employed [34], *i.e.*, following the constant current charge step to the desired voltage, a constant voltage charge process was carried out till the current reduced to one tenth of its initial constant current value. The current values at various rates were pre-set using the theoretical specific capacity 147 mAh g⁻¹ of LNMO. Take 1C for an example, the current density value at 1C was 147 mA g⁻¹. The specific capacity obtained was calculated basing on the composite material mass (V_2O_5 and LNMO) in the electrode. Electrochemical impedance spectra (EIS) were measured with Solartron SI 1287 workstation at a frequency range from 99,999 Hz to 0.009 Hz. All the tests were conducted at 25 °C unless specified. At high temperature cycle test (55 °C), the cells were constant current and constant voltage charged, then constant current discharged between 3.5 and 4.9 V.

3. Results and discussion

Fig. 1(a–f) shows the SEM images of precursor compound $[Ni_{0.5}Mn_{1.5}](OH)_4$, spinel LNMO, 1% V_2O_5 –LNMO, 3% V_2O_5 –LNMO, 5% V_2O_5 –LNMO and 10% V_2O_5 –LNMO, respectively. The precursor $[Ni_{0.5}Mn_{1.5}](OH)_4$ is of a flake-like shape with an average thickness of 50 nm. The LNMO particles are several times larger in the range of 100–300 nm. These polyhedrons show smooth surfaces and well-defined edges, which indicate very good crystallinity of the samples. The morphologies of V_2O_5 coated LNMO samples don't show obvious differences from LNMO, they all showed little fuzzy surfaces and nice crystallinities with similar particle sizes. At higher loading however, for example 10% V_2O_5 –LNMO (Fig. 1(f)), the voids between the LNMO particles are somewhat being filled up and the



Fig. 1. SEM patterns of (a) [Ni_{0.5}Mn_{1.5}](OH)₄ and (b) LNMO, (c) 1% V₂O₅-LNMO, (d) 3% V₂O₅-LNMO, (e) 5% V₂O₅-LNMO, (f) 10% V₂O₅-LNMO.

distinction between these particles are not as clear as the pristine LNMO and low-loading coated samples. This implied that coating with 10% V_2O_5 is too thick and might be adverse to electrochemical properties because a thick coating layer increases the resistance for electron transportation among particles and lower its rate capability [35]. The homogeneity of V_2O_5 coating is illustrated by EDS elemental mapping analysis presented in Fig. 2. The vanadium elemental distributions in these samples surfaces are very uniform and their densities increase with the vanadium loading growth during synthesis.

IR spectroscopy, which is an effective technique to identification

of the P4₃32 and Fd3m space lattice of the LNMO [36], is shown in Fig. 3. The vibration at 656 and 427 cm⁻¹ is referred to the dot matrix of P4₃32 spinel. The peaks located at 624 and 593 cm⁻¹ are attributed to the vibration of Mn–O and Ni–O, respectively [1]. The characteristic P4₃32 crystallographic structure lies in a higher intensity band of 593 than 624 cm⁻¹ [37,38]. As the result, the LNMO calcined at 800 °C with annealing at 600 °C reveals the combined dot lattices, which composes of both orderly P4₃32 and disorderly Fd3m spinels [39].

The XRD patterns of the LNMO and V_2O_5 -coated LNMO are shown in Fig. 4. All five samples exhibit sharp diffraction peaks and



Fig. 2. EDS area mappings of V element of samples and corresponding region in SEM plots: (a, b) 1% V₂O₅-LNMO, (c, d) 3% V₂O₅-LNMO, (e, f) 5% V₂O₅-LNMO, (g, h) 10% V₂O₅-LNMO.



LNMO surface and its amount is limited, as shown in XPS data in Fig. 5, likely by the available amount of LiOH and Li_2CO_3 in LNMO surface of air-slake.

As shown in Fig. 5(a), a new peak at approximately 518 eV which is absent in pristine LNMO sample appeared in all the V₂O₅-coating samples, and its intensity increases with the amount of coated V₂O₅. This peak is assigned to V_{2p} and its presence verifies the existence of vanadium on the LNMO surface after V₂O₅-coating. The detailed XPS spectrum about vanadium is shown in Fig. 5(b). The peaks with binding energies of 524.9 and 517.1 eV are assigned to V_{2p1/2} and V_{2p1/3} of V [31]. The peak at 517.1 eV is from both V⁴⁺ and V⁵⁺ ions (V⁴⁺ peak is around 516.7 eV while V⁵⁺ 517.3 eV), its deconvoluting fittings are shown in Fig. 6. At low coating loading, as seen in 1% sample, the V⁴⁺ is about 55.2% in the whole V element. In 3% V₂O₅-LNMO, there is about 30.1% V⁴⁺. When the coating content of V₂O₅ is increased to 5%, V⁴⁺ is only 23.7% and V⁵⁺ becomes the dominant contributor with a content of 76.3%. The moderate constant amount of V⁴⁺ (24%) in V₂O₅ is favorable for electro-



Fig. 4. (a) XRD plots of samples, (b) magnifying graph of (a) in specific zone.

can all be indexed to cubic spinel LNMO (JCPDS No. 01-010-2162), no impurity such as the rock salt phase $Li_{1-x}Ni_xO$ was observed [34]. Thus it is reasonable to assume the annealing at 600 °C could compensate the oxygen vacancy produced at high-temperature calcination (above 600 °C). In V₂O₅-coating LNMOs, LNMO retains its cubic spinel phase but some weak peaks were evident, as shown in Fig. 4(b). These peaks were indexed as V₂O₅ phase (JCPDS: 00-053-0538) and LiV₂O₅ phase (JCPDS: 01-074-0055). The formation of LiV₂O₅ is from the reaction of V₂O₅ with LiOH and Li₂CO₃ on

chemical property and transport of lithium ion [40]. As the V₂O₅ coating content is increased to 10%, the V⁴⁺ content is 20.3%. The ratio of V⁴⁺ in total V is reduced as the V₂O₅ coating content increases, but the actual amount of LiV₂O₅ formed in the composite materials is also increased.

To characterize the surface structure difference between LNMO and $5\% V_2O_5$ -LNMO particles, we carried out HR-TEM and surface EDS analyses, as seen in Fig. 7. Fig. 7(a) and (b) are high-resolution TEM (HRTEM) images of LNMO and $5\% V_2O_5$ -LNMO particle,



Fig. 5. (a) XPS spectra of pristine samples. (b) XPS analysis of V 2p3/2-1/2 for samples.



Fig. 6. The XPS fitting results of samples: (a) 1% V₂O₅-LNMO, (b) 3% V₂O₅-LNMO, (c) 5% V₂O₅-LNMO, (d) 10% V₂O₅-LNMO.



Fig. 7. (a) HR-TEM image of LNMO, (b) HR-TEM image of 5% V₂O₅-LNMO, (c) the corresponding surface EDS spectrum of 5% V₂O₅-LNMO in the orange area in (b), (d) the element content of (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

respectively, both show clear lattice fringes. The interplanar spacing lattice of them are all 0.48 nm, which is in accordance with the d-spacing of the (111) crystal planes of the $LiNi_{0.5}Mn_{1.5}O_4$. This means that V_2O_5 -coating doesn't alter the basic structure of spinel,

which agrees well with the previously mentioned XRD results. The V_2O_5 coating layer in 5% V_2O_5 -LNMO, from HRTEM, is about 3 nm. Selected area EDS elemental analysis (the orange labeled area in Fig. 7(c)) shown in Fig. 7 (c, d) confirms the surface layer is

composed of vanadium oxide. The presence of Mn and Ni elements is likely due to the penetration of X-ray through the 3 nm layer of V₂O₅. SAED pattern (Fig. S1(b)) related to a flat-lying LNMO nanoparticle in Fig. S1(a) reveals regular hexagonal array of diffraction spots, which is corresponding to the basal plane of spinel structure, with the electron beam in the [1–11] direction. This regular diffraction spots suggest the as-synthesized LNMO sample are of ordered lattice and single-crystal structure. ICP-AES was carried out to identify the exact content of V₂O₅ in composite material. The exact V₂O₅ value in 1% V₂O₅-LNMO, 3% V₂O₅-LNMO, 5% V₂O₅-LNMO and 10% V₂O₅-LNMO is 1.1%, 3.5%, 5.6% and 11.2%, respectively.

The initial charge-discharge curves and consecutive discharge cycle profiles at 1C charge rate and 1C discharge rate of the samples LNMO, 1% V₂O₅-LNMO, 3% V₂O₅-LNMO, 5% V₂O₅-LNMO and 10% V₂O₅-LNMO are given in Fig. 8. As shown in Fig. 8(a), all of the charge platform at first cycle are all around 4.75 V expect 10% V₂O₅-LNMO, whose charge platform is up to 4.85 V because of polarization with too thick coating. Their first discharge capacities are 120.9, 121.3, 126.5, 131.5 and 108.2 mAh g⁻¹, respectively. The 5% V₂O₅-LNMO sample shows the highest capacity while the 10% V₂O₅–LNMO the lowest. The discharge curves of these samples are very similar except 10% V₂O₅-LNMO (Fig. 8(b)). These samples (except 10% V₂O₅-LNMO) exhibit a very flat plateau around 4.7 V and their voltages drop quickly at the end of discharge. The 10% V₂O₅-LNMO sample, on the other hand, exhibits a discharge plateau dropped from 4.7 V to 4.6 V, and the voltage drops gradually after that plateau. The platform below 4.5 V accounts for 40% of its discharge capacity, this meaning thick coating layer may increase the resistance for electron transportation and exacerbate the ohmic polarization and electrochemical polarization of materials, which is adverse for electrochemical property, and the active substance (LNMO) in V₂O₅-LNMO composite is also the lowest, so 10% V₂O₅-LNMO exhibits low discharge capacity. These results indicate that low V₂O₅ coating does not bring excess polarization of LNMO, a proper coating can enhance its capacity; a too thick coating layer reduces its capacity. The cycling performance profiles of these materials are shown in Fig. 8(c). After 100 cycles, the discharge capacities of LNMO, 1% V2O5-LNMO, 3% V2O5-LNMO, 5% V₂O₅-LNMO and 10% V₂O₅-LNMO drop steadily from 120.9, 121.3, 126.5, 131.5 and 108.2 mAh g^{-1} to 98.8, 105.4, 115.3, 121.2 and 105.9 mAh g^{-1} , which is equal to 81.7%, 86.9%, 91.1%, 92.2% and 97.8% of their first capacities, respectively. Although the 10% V₂O₅-LNMO has the high capacity retention, its discharge voltage plateau and capacity are relative low. Based upon overall consideration, the 5% V₂O₅-LNMO has the best performance due to the moderate V₂O₅ and LiV₂O₅ coating. The coulombic efficiencies for sample test are shown as Fig. 8(d). The coulombic efficiencies of the initial few cycles is low, especially for the first cycle, which is attributed to the decomposition of #301 electrolyte and catalysis action of Ni and Mn ion in the spinel material [2]. After 10 cycles, its coulombic efficiencies are maintained at around 98.6%. Obviously, the decomposition of electrolyte actually occurred, but was maintained at an acceptable level after 10 cycles, which guarantees our cell a stable cycle performance. Generally, the irreversible capacity loss in the first cycle is related to the formation of a solid surface layer by the oxidation of the electrolyte [41]. The irreversible capacity loss on each cycle is attributable to the oxidation of the electrolyte and the formation of an unstable solid surface film constantly in the following cycles [41]. In order to clarify whether the V₂O₅ makes contribution to the capacity of V₂O₅-LNMO samples, we synthesized V₂O₅ by NH₄VO₃ pyrolysis at 400 °C for 5 h. The charging-discharging process is the same as V₂O₅-LNMO, and the electric current per gram V_2O_5 is the same as that in 5% V₂O₅-LNMO. Therefore, the current density is cal. 20C towards V_2O_5 . The specific capacity of V_2O_5 is only 5.7 mAh g⁻¹ as shown in Fig. S1, while the V₂O₅ content is only 5.6% in 5% V₂O₅-LNMO, so the capacity contribution of V₂O₅ to 5% V₂O₅-LNMO composite is only 0.32 mAh g^{-1} and negligible. This is also the reason that V_2O_5 discharge platform (Fig. 8) in V₂O₅-LNMO composite absent. So, the high capacity of 5% V₂O₅-LNMO is attributed to enhanced ionic conductivities and structural integrity maintained by V₂O₅



Fig. 8. Electrochemical properties of the as prepared samples: (a) the first charge curve at 1C, (b) the first discharge curve at 1C, (c) cycle performance at 1C, (d) coulombic efficiencies of samples at 1C.

protective layer between LNMO and electrolyte.

Fig. 9 shows the rate performance of the LNMO and V₂O₅coating LNMO cathode material ranging from 0.2C to 10C. The discharge capacity at 1C is even higher than that at 0.5C, which was discussed by Lazarraga [42] and Zhou [34] without clear conclusion. This possibly caused by different charging process between 0.5C and 1C. In our experiment, the cells were galvanostatically charged and discharged on a battery test system between 3.0 and 4.9 V at room temperature at low rates. When the rates higher than 1C (including 1C), a two-step charge process (constant current and constant voltage charge) was employed in order to overcome the polarization of the battery at high rates. In the latter case, following the constant current charge step, the constant voltage charge process was carried out till the current reduced to one tenth of its initial constant value. The discharge capacities of LNMO at 0.2C, 0.5C, 1C, 2C, 5C and 10C are 107 mAh g^{-1} , 101 mAh g^{-1} , 104 mAh g^{-1} 101 mAh g^{-1} , 94 mAh g^{-1} and 87 mAh g^{-1} , respectively. When the current value is returned back to 0.2C, a reversible discharge capacity of 98.6 mAh g^{-1} is obtained, which is only 92.1% of the initial discharge capacity at the same rate. After coating of V₂O₅, the rate performance is improved, especially for the 5% V₂O₅-LNMO, its specific discharge capacities are 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. As the current is back to 0.2C, the discharge capacity returns to 119.2 mAh g^{-1} , which is 96.2% capacity retention of the initial discharge capacity at 0.2C. The capacity of 5% V₂O₅-LNMO at 10C is even higher than that of LNMO at 1C, which means the fast Li ion transportation and stable structure caused by V₂O₅ coating. Fig. 9(b) presents the discharge voltage profiles of the 5% V₂O₅-LNMO electrodes at the current rates of 0.2C-10C over a potential window of 4.9-3.0 V. At the initial rate of 0.2C, the 5% V₂O₅-LNMO electrode show one discharge platforms at 4.7 V. As the discharge current rates increase, the voltage platforms lowered because of the increased electrochemical polarization and ohmic polarization at large current rates [2,3]. When the current is raised up to 10C, the discharge voltage plateau is down to 4.5 V, but it is better than the reported result [43].

Electrochemical impedance spectroscopy is conducted to further illustrate the difference between LNMO and V_2O_5 -coating LNMO in electrochemical polarization and ohmic polarization, as shown in Fig. 10. All the samples are charged at 1C by constant current and constant potential process, and discharged via constant current process for 4 cycles, and then the cathode is charged to full charged state. Their EIS are tested in the range from 99,999 Hz to 0.009 Hz. The Nyquist plots of materials display the similar profile: a semicircle in the high-frequency region (5% and 10% seems to have two semicircles with not clear boundaries) and a linear slop in the low-frequency region; and the equivalent circuits are the same



Fig. 10. EIS spectra of the samples in the frequency range from 99,999 Hz to 0.009 Hz at 25 $^{\circ}$ C. The insets show the equivalent circuits for the EIS measurements.

as insets shown. In the equivalent circuit, the Rs is assigned to electrolyte resistance, while the R1 is ascribed to the cathode surface film (similar to anode SEI layer) and R2 is attributed to direct charge transfer resistance of electrode materials. CPEs represent the double layer capacitance or passivation film capacitance. Ws represents the Warburg impedance. The dotted line is the measured value, while the solid line is the fitted result. It is clearly seen that the equivalent circuit model is adequate for the fitting as each pair of the dotted and solid lines overlap. The fitted values of these components are listed in Table 1. Obviously, the V₂O₅-coating LNMO electrode exhibits a much lower charge-transfer resistance than the pristine LNMO electrode, indicating that V₂O₅ modification of the LNMO material is favorable for electron mobility. V₂O₅

lable 1				
mpedance	parameters	of	electrodes	5.

	$Rs(\Omega)$	Error%	$R1(\Omega)$	Error%	$R2(\Omega)$	Error%	R1 + R2
LNMO	3.076	0.71	42.12	0.49	17.85	1.0	60.0
1% V ₂ O ₅ -LNMO	2.385	3.7	14.95	4.1	20.15	3.1	35.1
3% V ₂ O ₅ -LNMO	3.062	1.0	13.17	3.86	6.11	0.3	19.3
5% V ₂ O ₅ -LNMO	2.912	1.7	9.62	4.75	3.73	0.42	13.4
10% V ₂ O ₅ -LNMO	2.674	1.6	11.29	3.52	14.7	2.8	26.0



Fig. 9. (a) Rate cycling performance of the samples; (b) discharge profiles of 5% V₂O₅-LNMO at different rates.

an interphase with low electrical resistance is present rather than other inert oxides with lithium ion such as ZnO and MgO [30]. The R1 and R2 values of $5\%V_2O_5$ -LNMO are the lowest among all these samples, which is favorable for electrons transport. V_2O_5 is a protective layer observably inhibits the electrolyte decomposition at the electrode/electrolyte interface to reduce cell impedance [44]. The R2 of $1\% V_2O_5$ -LNMO is nearly same (little bigger) as LNMO, which may be attributed that the V_2O_5 content is too lower to form preferably effect. To some extent, $1\% V_2O_5$ coating is effective, after all the R1 + R2 of $1\% V_2O_5$ -LNMO is lower than that of LNMO. However, the R1 and R2 of $10\% V_2O_5$ -LNMO is bigger than 5% V_2O_5 -LNMO. This could be attributed to that thicker coating layer increases the resistance for electron transportation among particles, which is also responsible for lower discharge capacity and rate capability as shown before [35].

The diffusion coefficient (D_{Li}) of lithium ion can be deduced from the EIS plots in the low-frequency region [9,45]. The calculation equations for the D_{Li} values can be denoted as:

$$Z' = Rs + Rct + \sigma \omega^{-0.5} \tag{1}$$

$$D_{Li} = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma^2$$
 (2)

where T, R, A, n, F, C_{Li} , and ω are the absolute temperature, the gas constant, the surface area, the number of electrons per molecule during redox process, the Faraday's constant, the concentration of lithium ion and the angular frequency, respectively. σ is the Warburg factor which is related to Z'. Fig. 11 presents the $Z' - \omega^{-0.5}$ plots, the relationship between the Z' and $\omega^{-0.5}$ is linear. According to Eqs. (1) and (2), the lithium diffusion coefficients of LNMO and 5% V₂O₅-LNMO are calculated to be approximate 6.73×10^{-9} and 1.27×10^{-8} , respectively. Clearly, the diffusion coefficient of Li ion is greatly improved due to the V₂O₅ coating, which improves the contact between particles of LNMO. According to people's research, coating of cathode with lithium ion conductive oxides could not only enhance the Li⁺ transport rate, but also decrease the electrode polarization during repeated Li⁺ insertion/extraction process [9,46,47]. In our opinion, V₂O₅ worked as lithium ion conductor skeleton, making lithium transport to the surface of each LNMO particle quickly, which is favorable for lithium ion transport.

Fig. 12 shows cycle performance of LNMO and $5\% V_2O_5$ –LNMO electrodes at a high temperature. The cells were cycled at 55 °C and 5C rate. The LNMO sample exhibits a specific discharge capacity of 109.5 mAh g⁻¹ at fifth cycle (stable), the coated 5% V_2O_5–LNMO



Fig. 11. Z' - $\omega^{-0.5}$ pattern in the low-frequency region obtained from EIS measurements of LNMO and 5% V_2O_5–LNMO.



Fig. 12. Cycle performance of LNMO and 5% V_2O_5-LNMO at 5C and 55 $^\circ\text{C}.$

shows a capacity 15% more at about 126.3 mAh g^{-1} at same cycle. The other obvious difference is that the capacity of LNMO drops down quickly in the first few cycles and then gradually, with capacity retention of 85% after 100 cycles, whereas the capacity of 5% V₂O₅–LNMO drops smoothly and retains 92% of the initial capacity after 100 cycles. From these results, we believe that V₂O₅ coating layer can form a stable barrier between LNMO and electrolyte at elevated temperature to prevent the side reactions between them therefore to enhance the electrode high-temperature performance.

Fig. 13 exhibits the concentration of Ni and Mn cations of LNMO and 5% V₂O₅–LNMO dissolved in the electrolyte. Firstly, the cell was charged to fully delithiated state after 4 cycles at 1C, then the cell was disassembled to get electrode materials film in an Ar-filled glove box. Secondly, the film was soaked in 301 electrolyte with a ratio of electrode materials to electrolyte was 2 mg electrode materials of per 1 mL electrolyte at 80 °C for 1 day. Thirdly, after acid-treating, the storage electrolyte was conducted metal ion test. The concentration of Ni and Mn cations of 5% V₂O₅–LNMO dissolved in the electrolyte is much lower than that of LNMO, which indicates that the V₂O₅ coating layer successfully inhibited the dissolution of transition metals and maintained LNMO a stable structure. This V₂O₅ protective coating suppressed HF scavenger of spinel in electrolyte, leading to enhanced electrochemical properties.

The schematic illustrations of the V_2O_5 -coated LNMO composite and the mechanism of its role as a Li⁺-conductive protective layer to suppress the side interfacial side reactions are presented in Fig. 14. According to previous literature reports, Ni⁴⁺ ions formed at



Fig. 13. The concentration of Ni and Mn cations dissolved in the electrolyte for LNMO and 5% V₂O₅–LNMO electrodes stored at 80 °C for 1 day.



Fig. 14. Schematic illustrations of the V_2O_5 effects as a Li⁺-conductive coating layer to suppress the unfavorable interfacial side reactions between V_2O_5 -LNMO composite and electrolyte.

the deintercalation state of the cathode $(Li_{1-x}Ni_{0.5}Mn_{1.5}O_4)$ are active in the liquid electrolyte and can catalyze the oxygenolysis of the electrolyte, which is the major reason for the capacity fading of LNMO during the cycle performance at high temperature [41,48,49]. In this work, V₂O₅ as a protective layer observably inhibits the electrolyte decomposition at the electrode/electrolyte interface and thereby improves the structure integrity and capacity retention during long-term charge-discharge cycles. Furthermore, unlike oxide coatings which may be adverse for the transportation of Li⁺, V₂O₅ could offer a two-dimensional path for Li⁺ and Li⁺ -transfer velocity is improved, which improves the rate capability of LNMO. As previously reported, the failure of LNMO cells could be mainly ascribed to transition metal dissolution (especially Mn^{3+}) and diffusion to the anode leading to the damage to the solid electrolyte interface (SEI) of the anode and the increased cell impedance relative to oxidative decomposition of the electrolyte [50,51]. Surface coating can stabilize the surface structure of cathode materials and alleviate metal-ion dissolution [52]. In this work, Li⁺-conductive V₂O₅ is available to coat on the surface of the LNMO cathode. With this protective layer, transition metal dissolution of LNMO is effectively reduced, the side reaction between the electrode and the electrolyte is suppressed, and lithium ion diffusion coefficient is improved.

4. Conclusions

In summary, we have demonstrated a simple method coating a thin layer of V₂O₅ on spinel LNMO surface. The V₂O₅ coating forms a close contact to LNMO particles. The V₂O₅ layer not only works as an isolating layer to prevent LNMO cathode from HF corrosion in electrolyte but also modifies the lithium ion diffusion of LNMO because this thin coating layer is made of lithium ion conductor V_2O_5 . The D_{Li} lithium ion diffusion coefficient values of 5% V₂O₅-LNMO is roughly twice of that of the pristine LNMO. The electrochemical performance of the vanadium oxide coated depends on the coating thickness, i.e., the amount of coating on LNMO surface. We found that the optimal coating content of V_2O_5 is 5wt%. The 5% V₂O₅-LNMO shows remarkable rate capability, and its discharge specific capacity retention is much improved compared with pristine LNMO. Furthermore, it has superior electrochemical property at elevated temperature and high rates, making it a promising cathode material for high-voltage lithium ion batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.01.087.

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