Effects of amorphous V_2O_5 coating on the electrochemical properties of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ as cathode material for Li-ion batteries

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Abstract Lithium-rich layered oxide $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ coated with V_2O_5 layers (labeled as $LMNCO@V_2O_5$) has been synthesized and its electrochemical properties as cathode material for lithium ion batteries have been measured and compared with pristine $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ (labeled as $LMNCO$) and $LMNCO-V_2O_5$ composite. As a lithium ions insertion host material, both the V_2O_5 in the $LMNCO@V_2O_5$ and the $LMNCO-V_2O_5$ can reduce the irreversible capacity losses and improve the Coulombic efficiencies of the cathode in the first charge-discharge cycle. However, for improving the cycling stabilities and the high-rate capabilities of the $LMNCO$, the effects of the V_2O_5 coating layers in the $LMNCO@V_2O_5$ are far beyond the effects of the V_2O_5 nanoparticles in the $LMNCO-V_2O_5$. When charge-

discharged galvanostatically at 25 mA g^{-1} between 2.0 and 4.8 V (vs. Li^+/Li), the $\text{LMNCO@V}_2\text{O}_5$ with 3 wt% V_2O_5 exhibits a discharge capacity of 279.5 mAh g^{-1} in the first cycle and maintains a discharge capacity of 269.1 mAh g^{-1} after 50 cycles, with capacity retention of 96.3%. In contrast, the discharge capacity of the pristine LMNCO changes from 251.2 mAh g^{-1} in the initial cycle to 202.2 mAh g^{-1} in the 50th cycle, with capacity retention of 80.2%; and the LMNCO- V_2O_5 shows the same capacity fading trend as the pristine LMNCO, with no obvious improvement in the capacity retention. At high rate of 1250 mA g^{-1} , the discharge capacity of the $\text{LMNCO@V}_2\text{O}_5$ can reach 113.6 mAh g^{-1} , which is much higher than the capacities that the pristine LMNCO and the LMNCO- V_2O_5 can reach. Different effects of V_2O_5 are due to their different roles in the cathode materials. While the V_2O_5 coating layer in the $\text{LMNCO@V}_2\text{O}_5$ can reduce the charge transfer resistance at the electrode-electrolyte interfaces and improve the transportation of lithium ions among the LMNCO particles, the V_2O_5 nanoparticles in the LMNCO- V_2O_5 can only work as a Li^+ ions insertion host material.

Keywords: lithium ion battery; cathode; lithium-rich layered oxide; coating; V_2O_5 .

1. Introduction

Rechargeable lithium ion batteries have been extensively exploited as

energy storage devices for electric vehicles and intermittent renewable energy sources because of their high energy and power densities and long cycle lifetime [1]. To meet the demand for higher energy densities, a family of Mn-based lithium-rich layered oxides (LLOs) with high capacities ($>250 \text{ mAh g}^{-1}$) and high operating potentials ($>4.5 \text{ V}$) has been developed as the cathode materials in recent years [2]. While some researchers proposed that the LLOs are composed of a trigonal LiMO_2 ($\text{M} = \text{Mn, Ni, and Co, etc.}$) phase and a monoclinic Li_2MnO_3 phase, the other researchers believed that the LLOs are actually solid solutions with monoclinic symmetry [3,4].

Although the LLOs cathode materials can achieve very high capacities, they generally have to be electrochemically activated by charging to high potentials (4.6-4.8 V vs. Li^+/Li). During this activation process, oxygen atoms are lost from the materials, causing irreversible capacity losses and low Coulombic efficiencies [3,5]. In addition, high potentials of 4.6-4.8 V are beyond the electrochemical stable windows of normally used electrolytes. These high potentials thus increase the acidity of the electrolytes, lead to side reactions at the electrode-electrolyte interfaces, resulting in poor cycling performances of the LLOs [6]. In order to protect the LLO cathodes from the HF attack, especially when working at the high cut-off voltages, surface modification has been widely applied by researchers due to its simplicity and effectiveness [7-10]. The coating materials include metal oxides [11-14], fluorides

[15-19], carbon [20], phosphates [21-25] and other lithium-containing compounds [26,27].

Amorphous vanadium pentoxide (V_2O_5) has good electrical conductivity [28] and high Li^+ ions diffusion coefficient [29], and has been proved to be an attractive coating material for lithium ion batteries cathodes [30-37]. Park et al reported that amorphous V_2O_5 impregnated $0.5Li_2MnO_3-0.5LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ exhibited a substantial drop in oxygen evolution during the high voltage charging process. And it was attributed to the vanadium ions in $3d^0$ electronic states which reduced the surface catalytic activities and stabilized the surface oxide ions during their electrochemical oxidation [30]. Also, Lee et al. reported that V_2O_5 coating improved the cyclability of $LiCoO_2$ at high cut-off voltage [31]. Cho reported that coating VOx layer suppressed the Mn dissolution from spinel $LiMn_2O_4$ [32]. Liu et al reported that the rate performance of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was improved by coating V_2O_5 and they attributed this improved performance to the enhanced surface electronic/ionic transport due to the coating [33]. Xiong et al reported that V_2O_5 coating layer was able to reduce the rapid moisture uptake ability and the amount of $LiOH/Li_2CO_3$ impurities at the surfaces of $LiNiO_2$ -based materials [34,35]. M. J. Lee et al reported that V_2O_5 coating could reduce the heat generation and increase the onset

temperature of the exothermic reaction for the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [36].

Here we report the effect of amorphous V_2O_5 layer coating on $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (labeled as LMNCO hereafter in this paper), which is a typical LLO-type cathode material with very high energy density and power density [14]. As an insertion host to accommodate Li^+ ions, V_2O_5 nanoparticles have once been used by Gao et al [38] and Nie et al [39] to improve the low-rate electrochemical properties of LMNCO by forming LMNCO- V_2O_5 composite. But, as far as we know, the effects of amorphous V_2O_5 surface coating on the electrochemical properties, especially the high-rate properties, of LMNCO have not been investigated. In this work, amorphous V_2O_5 coated LMNCO (labeled as LMNCO@ V_2O_5) have been synthesized by a facile wet chemical method and their electrochemical properties as cathode materials for lithium ion batteries have been measured and compared with LMNCO- V_2O_5 composite (labeled as LMNCO- V_2O_5) systematically. The results demonstrate that both the V_2O_5 coating in LMNCO@ V_2O_5 and the V_2O_5 nanoparticles in LMNCO- V_2O_5 can significantly improve the Coulombic efficiencies of the LMNCO in the first cycle. However, for improving the cycling performances and the high-rate capabilities of the LMNCO, the effects of the amorphous V_2O_5 coating layers in LMNCO@ V_2O_5 are far beyond the V_2O_5 nanoparticles in LMNCO- V_2O_5 .

2. Experimental

2.1 Materials synthesis

The pristine LMNCO powders were prepared by traditional co-precipitation method. In a typical synthesis procedure, a solution of the transition metal acetates (0.25 M, with metal ion mole ratio Mn : Co : Ni = 0.54 : 0.13 : 0.13) was added drop by drop into LiOH aqueous solution (0.5 M) under constant stirring. The pH of the solution was ~9 after all the acetates were dropped into the basic solution. The suspension was then transferred into a water bath at 60°C for 6 h for a co-precipitation reaction. The resulting precipitate was washed with deionized water and dried in an oven at 120°C for overnight. Finally, the dried co-precipitated precursor was ground with LiOH·H₂O (5 wt% excess to compensate for the lithium evaporation at high-temperature calcination), fired at 900°C for 20 h in air with a heating rate of 5°C/min, and then cooled naturally.

The LMNCO@V₂O₅ (LMNCO with 3 wt% V₂O₅ coating layer) were prepared as follows: required amount of NH₄VO₃ were dissolved in deionized water at 80°C, followed by dispersing a corresponding amount of pristine LMNCO powders into the NH₄VO₃ solution. (To produce LMNCO@V₂O₅ with 3 wt% V₂O₅ coating, the mass ratio of NH₄VO₃ to the pristine LMNCO powder was controlled at 3.86:100.) The suspension was constantly stirred with a very slow evaporation of water. The obtained substance was heated at the rate of 1°C

/min and calcined in air at 300°C for 5 h.

The LMNCO-V₂O₅ composite, with the weight of the V₂O₅ being 3 wt % of the LMNCO, was obtained by grounding the pristine LMNCO powders with required amount of NH₄VO₃ powder for half an hour to form a well-mixed mixture, which was then heated in air at 300°C for 5 h with a heating rate of 1 °C/min. V₂O₅ nanoparticles were obtained by decomposing NH₄VO₃ powder at 300°C for 5 h with a heating rate of 1 °C/min.

2.2 Characterization

The crystal structures of the materials were confirmed by Powder X-ray diffraction (Bruker D8 ADVANCE, Germany) using Cu K α radiation (1.54056 Å). XRD spectrum was collected in a range of 2 θ values from 10-80° at a scan rate of 2°/min and a 0.02° step size. The morphology and surface elemental distribution of the particles were observed by a scanning electron microscopy (SEM, QUANTA 200, Holland) coupled with electron dispersive X-ray spectroscopy (EDX), and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2010FEF, Japan). The samples for SEM analysis were fabricated by dispersing a spot of the powders onto the conducting resin and sprayed with little Pt to enhance the electron conductivity of the material. The surface solid-state chemistry of the particles was investigated by X-Ray Photoelectron Spectrometer (XPS, Thermo Scitific ESCLAB

250Xi) with a monochromated Al K α X-ray source (1486.68 eV photons) at a dwelling time of 50 ms. The binding energy ranges from -10 to 1400 eV. Charging of the samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.6 eV. The XPS analysis was done at ambient temperature and pressures typically on the order of less than 10^{-6} Pa. Prior to analysis, the samples were outgassed in a vacuum oven overnight.

2.3 Evaluation of electrochemical performances

Electrochemical characterizations were performed using CR2016 coin-type cell. For the working electrodes preparation, the active materials were mixed with acetylene black and polytetrafluoroethylene (PTFE) binder with a weight ratio = 80:15:5. After being pressed onto a stainless mesh which serves as a current collector, the cathode film was vacuum dried at 60°C for overnight. The cathode loadings are usually about 5 mg/cm². The test cells consisted of cathodes and lithium foil anodes separated by Celgard 2300 micro-porous films, with 1M LiPF₆ (EC:DMC=1:1,v/v) as the electrolyte. The assembly of the cells was carried out in a high-purity Ar-filled glove box. The cells were galvanostatically charged and discharged between 2.0 and 4.8 V (vs. Li⁺/Li) at desired current densities on a battery cycler (Neware CT-3008W-S4, China). The cyclic voltammograms (CV) were measured on an electrochemical station (CHI 660a)

with a scan rate of 0.1mV s^{-1} in a voltage range of 2.0-4.8V. The electrochemical impedance spectroscopy (EIS) measurements of cells were conducted when the cathode materials were half charged after the first charge-discharge cycle, with the frequency range being $10^5\text{-}10^{-2}$ Hz and an AC voltage amplitude of 5 mV. All the electrochemical measurements were performed at room temperature.

3. Results and Discussions

Figure 1a shows the XRD pattern of the pristine LMNCO and the Rietveld refinement of the data. As shown in Fig. 1a, the differences between the calculated and observed curves are minimal, indicating the reliability of the refinement results. While LiMO_2 has been reported to have a trigonal $R\text{-}3m$ structure, with the lattice parameters $a = b = 2.8873 \text{ \AA}$, $c = 14.2901 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ [40], the Rietveld refinement indicates that the pristine LMNCO is composed of a solid solution having $C2/m$ monoclinic symmetry, with the lattice parameters $a = 4.94151 \text{ \AA}$, $b = 8.55407 \text{ \AA}$, $c = 5.02672 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, and $\beta = 109.2625^\circ$. According to the Rietveld refinement, a unit cell of the crystal (Fig. S1a) and the transition metal layer (Fig. S1b) in this layered structured material are shown in the Supporting Information. The transition metal layer is composed of Li, Mn, Co and Ni, which orders, such that the Li/Ni occupies atomic sites S1 and Mn/Co occupies atomic sites S2. The site occupancies are 45.8% Li and 54.2% Ni for S1 sites, 72.9% Mn and 27.1% Co for S2

sites. All the atomic parameters for the pristine LMNCO are given in Table 1.

The XRD pattern of the LMNCO@V₂O₅ is the same as the pattern of the pristine LMNCO, without any XRD peaks of V₂O₅ appearing (Fig. 1b). The absence of V₂O₅ diffraction peaks may be due to the small quantity (3 wt%) and/or the amorphous nature of the V₂O₅ coating in the LMNCO@V₂O₅. It is clear that there is no significant difference between the crystals structures before and after the V₂O₅ surface coating. The heat treatment of the coating process at a relatively low temperature seemed not to allow vanadium doping or forming solid solution between LMNCO and V₂O₅ to occur. Also, no impurities or secondary phase can be observed in this pattern. The XRD pattern of the LMNCO-V₂O₅ (Figure S2a in Supporting Information) is the same as the patterns of the pristine LMNCO and LMNCO@V₂O₅. No XRD peaks of V₂O₅ can be observed, which may be due to the small quantity of the V₂O₅ in the material. V₂O₅ powder using the same synthesis route without adding the pristine LMNCO particles were also synthesized, and its XRD pattern is shown in Figure S2b in Supporting Information. All the diffraction peaks in the pattern can be indexed as V₂O₅ compound with space group of Pmmn (JCPDS 77-2418).

Figure 2 shows the SEM images of the pristine LMNCO, the LMNCO@V₂O₅, the LMNCO-V₂O₅ and the separately synthesized V₂O₅

nanoparticles, respectively. The image of the pristine LMNCO (Fig. 2a) shows that the particles, with sizes between 200 nm and 400 nm, have regular polyhedron morphologies and very clean surfaces. The SEM image of the LMNCO-V₂O₅ composite is shown in Fig. 2c. We can see from the image that the LMNCO particles in the composite maintain the regular polyhedron morphologies and clean surfaces as the pristine LMNCO. A small amount of irregular nanoparticles can be found in the image, which should be the V₂O₅ in the composite since they look the same as the nanoparticles in the SEM image of the separately synthesized V₂O₅ nanoparticles (Fig. 2d). The SEM image of the LMNCO@V₂O₅ (Fig. 2b) shows that the surfaces of the LMNCO particles are rough and that the particles lost their regular polyhedron morphologies due to the V₂O₅ surface layers coating. To check the uniformity of V₂O₅ coating on LMNCO, the SEM-energy dispersive spectrometry (EDS) was taken on the LMNCO@V₂O₅. The EDS dot-mappings (Fig. 3) show that the V element, like the Mn, Ni and Co elements, is homogeneously distributed in the sample, indicating the uniform distribution of vanadium oxide on the surface of LMNCO. The signal intensity of element V is much lower than those of Mn, Co and Ni due to the small quantity of V₂O₅ in the material. The atomic ratio of V : Mn : Co : Ni measured in the sample is 3.38 : 65.21 : 15.70 : 15.71, which is very close to the theoretical value (3.41 : 65.21 : 15.69 : 15.69) calculated from the 3 wt.% V₂O₅ coated LMNCO. In the

process of making the SEM samples, a little amount of Pt has to be sprayed onto the samples to increase the conductivity, which caused the appearance of Pt peak in the EDS spectrum.

Figure 4 displays the TEM and high-resolution TEM images of the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅, respectively. Figure 4a is the low-magnification TEM image of the pristine LMNCO, and Fig. 4b is the high-resolution image of the circled area in Fig. 4a. It is obvious from these images that the surfaces of the pristine LMNCO particles are very clean, without any coating materials, impurities or dirties. The parallel inter-planar spacing can be measured to be 0.468 nm which can be ascribed to the (001) planes of the Li_{1+x}(TM)_{1-x}O₂ (TM = Mn, Ni, Co, et al) structure with monoclinic symmetry.

Fig. 4c is the high-resolution TEM image of the LMNCO@V₂O₅. As expected, the LMNCO particles are surface coated with uniform layers of V₂O₅. The thickness of the V₂O₅ layer is measured to be around 6 nm. The parallel inter-planar spacing can be measured to be 0.409 nm which can be ascribed to the (110) planes of the Li_{1+x}(TM)_{1-x}O₂ structure with monoclinic symmetry. The image also shows that the V₂O₅ coating layers are amorphous, which confirms the conclusion that we get from the XRD patterns. Low resolution TEM images of the LMNCO-V₂O₅ (not shown) show that the LMNCO particles and the V₂O₅

nanoparticles are two separate components in the composite. From the high-resolution TEM image of the LMNCO particle in the LMNCO-V₂O₅ composite (Fig. 4d), we can see that the surface of the LMNCO particles are very clean, without any coating layers. The parallel inter-planar spacing at the LMNCO particle surface is measured as 0.238 nm which can be ascribed to the (002) planes of the Li_{1+x}(TM)_{1-x}O₂ structure with monoclinic symmetry.

In order to investigate the chemical state of V in the surface coating layers, XPS was carried out on the pristine LMNCO and the LMNCO@V₂O₅. The full range XPS spectra (binding energy from -10 to 1400 eV) of both samples are shown in Figure 5a. For the pristine LMNCO, six main peaks located at about 55, 284, 530, 642, 780 and 854 eV revealed, which correspond to elements Li (1s), C (1s), O (1s), Mn (2p), Co (2p), and Ni (2p), respectively. For the LMNCO@V₂O₅, another peak located at about 517 eV appeared which should belong to the element of V (2p_{3/2}). All the main peaks of the XPS spectrum of the LMNCO@V₂O₅ remain at the same locations as the corresponding peaks in the spectrum of the pristine LMNCO, showing that the coated V₂O₅ thin layer does not change the chemical oxidation states of Mn, Co and Ni in the material. Since the V 2p_{3/2} photoelectron peak is very close to the O 1s peak, Fig. 5a is enlarged and the spectra in the binding energy window between 510 eV and 521 eV is shown in Fig. 5b. According to the literature, the binding energy of V 2p_{3/2} reported

for V_2O_5 (V^{5+} oxidation state) ranges between 517.4 and 516.8 eV; the next oxidation state (V^{4+} oxidation state), represented by V_2O_4 , shows values in the range 515.7-515.4 eV [41]. In Fig. 5b, the V $2p_{3/2}$ binding energy spectrum can be fitted very well by one peak locating at 517.2 eV. This indicates that the vanadium in the surface coating layers is predominantly in the V(V) oxidation state.

To compare the electrochemical properties of the pristine LMNCO, LMNCO@ V_2O_5 and LMNCO- V_2O_5 , cyclic voltammetry (CV) was used to investigate the redox reactions occurring during the charge-discharge electrochemical processes for the materials. The cyclic voltammograms of the pristine LMNCO, LMNCO@ V_2O_5 and LMNCO- V_2O_5 in the initial two cycles were recorded in the voltage range of 2.0-4.8 V at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$ and are shown in Figure 6. As shown in Fig. 6a, for the pristine LMNCO, there are two high anodic peaks and one cathodic peak in the initial cycle. The first anodic peak at approximately 4.0 V is associated predominantly with the oxidation of Ni from Ni^{2+} to Ni^{4+} . The second anodic peak at higher potential (4.5-4.8 V) is mainly due to the partial oxidation of Co^{3+} to Co^{4+} and the electrochemical activation reaction that extracts Li_2O from the Li_2MnO_3 component forming MnO_2 [3]. In the second cycle, while the anodic peak at approximately 4.0 V was

maintained, the anodic peak at higher potential disappeared implying that the electrochemical activation process in the first charge is irreversible. The CV features of the LMNCO@V₂O₅ (Fig. 6b) are very similar to those of the pristine LMNCO, without any new anodic or cathodic peaks appearing, which indicates that coating of amorphous V₂O₅ does not lead to new redox reactions in the charge-discharge electrochemical processes. In the initial cycle CV curves of the LMNCO-V₂O₅ (Fig. 6c), except the main anodic peaks at 4.0 V and 4.5-4.8 V, two new anodic peaks appear at 3.21 V and 3.42 V in the charging process, with their corresponding cathodic peaks appearing at 3.12 V and 3.35 V, respectively, in the discharging process. Another cathodic peak can also be noted at 2.27 V, a voltage much lower than the open circle voltage (OCV) of the LMNCO-V₂O₅ material. The CV curves of the synthesized V₂O₅ nanoparticles in the initial two cycles are shown in Fig. 6d. After comparing Figs. 6c and 6d, we are pretty sure that the new redox peaks (labelled with *) that appear in the CV curves of the LMNCO-V₂O₅ composite should belong to the redox reactions of V₂O₅. This result indicates that the V₂O₅ in LMNCO@V₂O₅ and the V₂O₅ in LMNCO-V₂O₅ have different electrochemical actions during the charge-discharge processes, and we suppose that these different electrochemical actions will cause different effects in improving the performances of the LMNCO as Li-ion battery cathodes.

To study the effects of V_2O_5 on the electrochemical properties of $LMNCO@V_2O_5$ and $LMNCO-V_2O_5$, the materials were galvanostatically charge-discharged between 2.0 and 4.8 V as cathode materials for lithium ion batteries. Figures 7a, 7b and 7c show the charge-discharge profiles of the first cycle for the pristine $LMNCO$, the $LMNCO@V_2O_5$ and $LMNCO-V_2O_5$, respectively, at a current density of 25 mA g^{-1} (0.1 C). The three charge-discharge curves are similar and the profile is typical for the Li-rich layered oxide cathodes $Li_{1+x}(TM)_{1-x}O_2$ ($TM = \text{Mn, Ni, Co, et al}$). In the charge process, a sloping region is followed by a prolong plateau at about 4.5 V. While the former (initial sloping region) corresponds to the oxidation of the transition metal in the material, the latter (prolong plateau around 4.5 V) is attributed to the loss of lithium ions and oxygen from this layered oxide cathodes $Li_{1+x}(TM)_{1-x}O_2$ as a net form of Li_2O [3]. The detailed data of these initial charge-discharge cycles for the three materials are shown in Table 2. The discharge capacities are 251.2, 279.5 and 263.3 mAh g^{-1} , with Coulombic efficiencies being 77.4%, 87.8% and 82.7%, for the pristine $LMNCO$, the $LMNCO@V_2O_5$ and the $LMNCO-V_2O_5$, respectively. We can see that, compared with the pristine $LMNCO$, both the $LMNCO@V_2O_5$ and the $LMNCO-V_2O_5$ show increased discharge capacities, much reduced irreversible capacity losses, and higher Coulombic efficiencies. It

is interesting to note that the discharge profile of the LMNCO-V₂O₅ (Fig. 7c) shows three short plateaus at about 3.4 V, 3.2 V and 2.3 V, respectively, which should belong to the reduction of V₂O₅, with the three plateaus corresponding to the reduction reactions of V⁵⁺/V⁴⁺, V⁴⁺/V³⁺, and V³⁺/V²⁺, respectively. The profile of the first discharge for the synthesized V₂O₅ nanoparticles (Fig. 7d) shows plateaus at exactly the same voltages. In the charge-discharge curves of LMNCO@V₂O₅ (Fig. 7b), no voltage plateaus related to V₂O₅ appear. This indicates that the amorphous V₂O₅ coating layers have different electrochemical properties from the V₂O₅ particles in the LMNCO-V₂O₅ composite.

Figure 8 shows the cycling properties of the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅ at 0.1 C (25 mA g⁻¹) for 50 cycles. Figure 8a shows clearly that the LMNCO@V₂O₅ displays much better cycling performances than the pristine LMNCO and the LMNCO-V₂O₅. The discharge capacity of the pristine LMNCO changes from 251.2 mAh g⁻¹ in the initial cycle to 202.2 mAh g⁻¹ in the 50th cycle, with a capacity retention of 80.2% after 50 cycles. The LMNCO-V₂O₅ shows the same capacity fading trend as the pristine LMNCO, with no obvious improvement in the capacity retention. In contrast, the LMNCO@V₂O₅ exhibits a discharge capacity of 279.5 mAh g⁻¹ in the first cycle and the discharge capacity maintains at 269.1 mAh g⁻¹ after 50 cycles, with high capacity retention of 96.3%.

Figure 8b, c and d shows the charge-discharge curves of the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅ in the 2nd, 10th, 20th and 50th cycle, respectively. For the LMNCO@V₂O₅, the discharge curves are almost overlapped, especially for the first 20 cycles, and this confirms that the coating is beneficial for the voltage stability upon cycling.

The high-rate capabilities of the materials are shown in Figure 9. After initially cycled at 0.1 C rate for activation, the materials were charge-discharged at 1 C, 2 C, 5 C and 10 C, respectively, with each rate cycled for 10 times. It can be clearly seen, from Fig. 9a, that the LMNCO@V₂O₅ shows a more superior rate capability than the pristine LMNCO and LMNCO-V₂O₅. At the charge-discharge rates of 1 C, 2 C, 5 C and 10 C (2.5 A g⁻¹), the discharge capacities of the LMNCO@V₂O₅ can reach 193.5, 172.7, 113.6 and 77.8 mAh g⁻¹, respectively. The typical voltage-specific capacity curves at different high rates for LMNCO@V₂O₅ are shown in Fig. 9b.

To get insight into the effects of the V₂O₅ on the kinetic properties of the cathode materials, electrochemical impedance spectra (EIS) of the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅ were measured and are shown in Figure 10. Fig. 10a displays the Nyquist plots and the equivalent circuit (inset of Fig. 10a) of the materials. As shown in the figure, all the three EIS

spectrums are composed of a depressed semicircle in the high to medium frequency region and a slanted line in the low frequency region. Generally, the intercept of the semicircle at the Z_{real} -axis in high frequency region corresponds to ohmic resistance of the electrolyte (R_e). The semicircle in high-frequency is related to charge transfer resistance (R_{ct}) at the electrode-electrolyte interfaces. The sloped straight line in low-frequency is associated with Li^+ ion diffusion process in the solid phase of electrode materials. In Fig. 10a, it can be seen that, compared with the R_{ct} value of the pristine LMNCO, there is no significant decrease of R_{ct} for the LMNCO- V_2O_5 ; on the contrary, the R_{ct} of the LMNCO@ V_2O_5 is greatly reduced. The R_{ct} values of the pristine LMNCO, the LMNCO@ V_2O_5 and the LMNCO- V_2O_5 are 236.96, 78.47 and 195.76 ohm, respectively. This significantly reduced R_{ct} indicates that the thin V_2O_5 coating layer improves the conductivity of the LMNCO@ V_2O_5 cathode material. In addition to R_{ct} , the apparent Li diffusion coefficient D_{Li^+} also exhibits a noticeable synergistic effect. Fig. 10b displays the relationship between Z_{re} and the reciprocal square root of the frequency ($\omega^{-1/2}$) in the low frequency region, with the slopes of the fitting lines as the Warburg coefficient (σ). Based on the slopes of the straight lines, the lithium ion diffusion coefficients (D_{Li^+}) in the three cathodes can be calculated based on the following equation [42]:

$$D = R^2 T^2 / 2 A^2 n^4 F^4 C^2 \sigma^2 \quad (1)$$

In this equation, R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of electrons per molecule during oxidation, F is the Faraday constant, C is the concentration of lithium ion. As shown in Table 3, the calculated diffusion coefficients of lithium ions (D_{Li^+}) are 1.84×10^{-14} , 4.78×10^{-14} and $1.87 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, respectively, for the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅, indicating that the thin and uniform V₂O₅ coating not only can enhance the electronic conductivity of the LMNCO particles but also is beneficial for the lithium ion diffusions inside the cathode.

The different electrochemical properties of the pristine LMNCO, the LMNCO@V₂O₅ and LMNCO-V₂O₅ show that the V₂O₅ coating layer in the LMNCO@V₂O₅ and the V₂O₅ nanoparticles in the LMNCO-V₂O₅ have different effects on the materials. The V₂O₅ coating layer in the LMNCO@V₂O₅ has three functions in improving the performances of the LMNCO as a cathode material.

(1) As a Li⁺ ions insertion host material (to form Li_xV₂O₅), the V₂O₅ coating layer can increase the discharge capacities and reduce the irreversible capacity loss of the LMNCO, thus increasing the Coulombic efficiencies of the cathode in the first cycles. (2) The uniform V₂O₅ coating layer can serve as a protection barrier that prevents the LMNCO from direct contact with the electrolyte, thus reducing the acidic attack from the electrolyte and improving the cyclabilities of

the LMNCO. (3) As a relatively fast ionic conductor with good electrical conductivity, the thin and uniform V_2O_5 coating layer outside of the particles is beneficial for the transportation of both electrons and Li ions among the LMNCO particles, and thus can enhance the rate capability of the material. On the contrary, the only function that the V_2O_5 nanoparticles in the LMNCO- V_2O_5 composite can have is working as a Li^+ ions insertion host, thus the nanoparticles cannot take any effect on restraining the capacity fading and improving the rate capabilities of the cathode material.

4. Conclusions

In summary, lithium-rich layered LMNCO coated with thin and uniform V_2O_5 layers (LMNCO@ V_2O_5) was successfully synthesized and its electrochemical properties were measured and compared with bare LMNCO and the LMNCO- V_2O_5 composite that has the same amount of V_2O_5 . The V_2O_5 in both LMNCO@ V_2O_5 and LMNCO- V_2O_5 can significantly reduce irreversible capacity losses and improve the Coulombic efficiencies of the material in the first cycle. However, for improving the cycling stabilities and the high-rate capabilities of the LMNCO, the effect of the V_2O_5 in LMNCO@ V_2O_5 is far beyond the V_2O_5 in LMNCO- V_2O_5 . The fact that the V_2O_5 in LMNCO@ V_2O_5 and the V_2O_5 in LMNCO- V_2O_5 have different effects on the electrochemical properties of the LMNCO is due to their different roles in this cathode material. For the V_2O_5 in LMNCO- V_2O_5 , the V_2O_5 nanoparticles work as

lithium ions insertion host material to accommodate the lithium ions that could not be inserted back into the LMNCO particles in the discharge process. For the V_2O_5 in the LMNCO@ V_2O_5 , except as lithium ions insertion host material, the V_2O_5 coating layers can also stable the structure of the LMNCO, protecting the material from the acidic attack of the electrolyte; at the same time, as relatively fast ionic conductors with good electrical conductivity, these V_2O_5 coating layers outside of the LMNCO particles enhance the electronic conductivities of the material and improves the Li^+ ions diffusion rates inside the cathode.

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Figure and table captions

Fig. 1 (a) XRD pattern and its Rietveld refinement of the pristine LMNCO, (b) XRD pattern of the LMNCO@V₂O₅.

Fig. 2 SEM images of (a) pristine LMNCO, (b) LMNCO@V₂O₅, (c) LMNCO-V₂O₅ and (d) the synthesized V₂O₅.

Fig. 3 SEM-energy dispersive spectrometry (EDS) of LMNCO@V₂O₅.

Fig. 4 TEM and high-resolution TEM images of (a, b) pristine LMNCO, (c) LMNCO@V₂O₅ and (d) LMNCO-V₂O₅ composite.

Fig. 5 XPS of (a) pristine LMNCO and LMNCO@V₂O₅ and (b) V 2p_{3/2} binding energy spectrum between 510 eV and 521 eV.

Fig. 6 CV of (a) pristine LMNCO, (b) LMNCO@V₂O₅, (c) LMNCO-V₂O₅ and (d) the synthesized V₂O₅ nanoparticles in the initial 2 cycles in the voltage range of 2.0-4.8 V at a scan rate of 0.1 mV·s⁻¹.

Fig. 7 The charge-discharge profiles of (a) pristine LMNCO, (b) LMNCO@V₂O₅, (c) LMNCO-V₂O₅ and (d) the synthesized V₂O₅ nanoparticles in the first cycle at a current density of 25 mA g⁻¹ between the voltage of 2.0 and 4.8 V.

Fig. 8 (a) The cycling properties of pristine LMNCO, LMNCO@V₂O₅ and LMNCO-V₂O₅ at 0.1 C for 50 cycles, and the charge-discharge curves of (b) pristine LMNCO, (c) LMNCO@V₂O₅ and (d) LMNCO-V₂O₅ at 0.1 C in the 2nd, 10th, 20th and 50th

charge-discharge cycle.

Fig. 9 High-rate capabilities of pristine LMNCO, LMNCO@V₂O₅ and LMNCO-V₂O₅: (a) capabilities of the materials at different rates, and (b) typical charge-discharge curves at different high rates for LMNCO@V₂O₅.

Fig. 10 (a) Nyquist plots and equivalent circuit (inset) and (b) the relationship between Z_{re} and $\omega^{-1/2}$ in the low frequency region of pristine LMNCO, LMNCO@V₂O₅ and LMNCO-V₂O₅.

Table 1. The atomic parameters of the pristine LMNCO according to the Rietveld refinement of the XRD pattern. The R factors of the structure refinement $R_{wp} = 0.74\%$, $R_p = 0.47\%$. According to the refinement data, the lattice parameters $a = 4.94151 \text{ \AA}$, $b = 8.55407 \text{ \AA}$, $c = 5.02672 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, and $\beta = 109.2625^\circ$.

Table 2. Electrochemical data of pristine LMNCO, LMNCO@V₂O₅ and LMNCO-V₂O₅ in the initial charge-discharge cycles.

Table 3. Impedance parameters of pristine LMNCO, LMNCO@V₂O₅ and LMNCO-V₂O₅.

Figure 1a

Figure 1b

Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 3

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 6c

Figure 6d

Figure 7a

Figure 7b

Figure 7c

Figure 7d

Figure 8a

Figure 8b

Figure 8c

Figure 8d

Figure 9a

Figure 9b

Figure 10a

Figure 10b

Table 1

Table 1 The atomic parameters of the pristine LMNCO according to the Rietveld refinement of the XRD pattern. The R factors of the structure refinement $R_{wp} = 0.74\%$, $R_p = 0.47\%$. According to the refinement data, the lattice parameters $a = 4.94151 \text{ \AA}$, $b = 8.55407 \text{ \AA}$, $c = 5.02672 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, and $\beta = 109.2625^\circ$.

	x	y	z	Occupancy
Co (4g)	0	0.17264(26)	0	0.2709
Mn (4g)	0	0.17264(26)	0	0.7291
Ni (2b)	0	1/2	0	0.5417
Li (2b)	0	1/2	0	0.4583
Li (2c)	0	0	1/2	1
Li (4h)	0	0.6782(19)	1/2	1
O (4i)	0.2361(15)	0	0.20861(97)	1
O (8j)	0.2456(11)	0.32720(39)	0.23130(53)	1

Table 2

Table 2. Electrochemical data of the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅ in the initial charge-discharge process

Materials	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Irreversible capacity loss (mAh g ⁻¹)	Coulombic efficiency (%)
Pristine LMNCO	324.5	251.2	73.3	77.4
LMNCO@V ₂ O ₅	318.2	279.5	38.7	87.8
LMNCO-V ₂ O ₅	318.4	263.3	39.5	82.7

Table 3

Table 3. Impedance parameters of the pristine LMNCO, the LMNCO@V₂O₅ and the LMNCO-V₂O₅ materials.

Samples	R _e (Ω)	R _{ct} (Ω)	σ (Ω cm ² s ^{-1/2})	D _{Li+} (cm ² s ⁻¹)
Pristine LMNCO	4.86	236.96	111.11	1.84×10 ⁻¹⁴
LMNCO@V ₂ O ₅	3.97	78.47	68.92	4.78×10 ⁻¹⁴
LMNCO-V ₂ O ₅	4.35	195.76	110.06	1.87×10 ⁻¹⁴