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Improving the stability properties of 5 V lithium nickel manganese oxide spinel by surface coating with cobalt aluminum oxides for lithium ion batteries



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ABSTRACT

Aluminum cobalt oxide-coated LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cathode materials are synthesized via a wetcoating method. The surface coating of the LNMO with cobalt aluminum oxide (CoAl₂O₄) does not alter its spinel structure, but greatly affects its thermostability. The complete, thin cobalt aluminum oxide coating layer strongly adheres to the host material and possesses a great thermal stability and electrochemical resistance, and it is not damaged in acid or alkali environments. The CoAl₂O₄ coating layer in this work successfully inhibits the dissolution of transition metal ions and maintain the stability of the LNMO structure. This CoAl₂O₄ coating layer also hold back the HF scavenger of the spinel structure in the electrolyte, which leads to enhanced electrochemical properties, especially at high temperatures. Furthermore, the coated LNMO exhibits an obviously improved thermostability compared with bare LNMO.

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1. Introduction

To meet the pressing requirement for electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles, the development of lithium ion batteries with higher working voltages, higher power densities, longer cycling lives, better rate capabilities and more environmentally friendly materials is required [1–3]. Spinel LiMn₂O₄ (LMO) with three-dimensional lithium ion diffusion paths is considered as a prospective alternative for LiCoO₂ for improved Li-ion battery applications due to its unique properties, including low cost, low toxicity, great material abundance and safety, especially under extreme conditions [4]. The Fermi energies and electrode potentials of the spinels are raised by doping with an adequate amount of transition metal ions M (M = Fe, Co, Ni, Cr etc.) to form a solid state solution $LiMn_{2-x}M_xO_4$ [5]. Among these spinel $LiMn_{2-x}M_xO_4$ cathode materials, LiNi_{0.5}Mn_{1.5}O₄ features an excellent performance and a steady charge-discharge cycle [1,4]. The main discharge platform of LiNi_{0.5}Mn_{1.5}O₄ is up to 4.7 V rather than 4.3 V for LiMn₂O₄, which is the value ascribed to the redox of Ni²⁺/Ni⁴⁺. Therefore, the weight energy density of LNMO is higher than that of conventional cathode materials, taking LiCoO₂ [6], LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ [7–9] and LiFePO₄ for examples, because of its higher discharge voltage [10,11]. Spinel LNMO as a possible replacement for the conventional LiCoO₂ cathode material is expected to meet the high energy and high power demands for special instruments and large-scale equipments. It is also one of the few cathode materials that could align with high discharging voltage anode materials, for instance, Li₄Ti₅O₁₂, to assemble batteries with a high power capability without sacrificing energy density [12].

Security is one of the most significant topics for the application of lithium ion batteries, particularly suitable for large-scale applications in EVs and HEVs [13]. According to Xiang's research, the high-voltage cathode material LiNi_{0.5}Mn_{1.5}O₄ occupied the poorest thermostability among delithiated cathodes such as Li $_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$, Li $_xCOO_2$, Li $_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, Li $_xNi_{0.5}Mn_{0.5}O_2$, Li $_xMn_2O_4$, Li $_xNi_{0.5}Mn_{1.5}O_4$ and Li $_xFePO_4$ [14]. This is likely due to the ~ 5 V oxidation potential of the delithiated spinel [14,15]. There are two obvious exothermic peaks located at approximately 130 °C and 180 °C for this 5 V spinel [1]. A great attempt has been made to slow down this safety problem, such as using ionic liquids as the



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electrolyte [16,17] or introducing a nonflammable additive to the electrolyte [18]. However, this additional safety assurance is usually attained at the cost of the battery's electrochemical performance and expense effectiveness. Thus, the best solution has been to coat an isolated layer adhering to the surface of the LNMO particles to prevent thermal runaway generated by the mutual exothermal reactions between the electrolytes and delithiated cathode materials.

Over the past few years, studies of $LiNi_{0.5}Mn_{1.5}O_4$ have been abundantly concentrated on the enhancement of its electrochemical behavior with the following multifarious methods: doping with Ti [19], Ru [20], Cr [21], Cu [22] and Mg [23] in crystal lattices; surface modification with Li₂TiO₃ [24], Bi₂O₃ [25], ZnO [26], FePO₄ [27] and Al₂O₃ [28]; and controlling the morphological and lattice plane [29]. Nevertheless, the heat stability of the LiNi_{0.5}Mn_{1.5}O₄ coexisting with the electrolyte is usually neglected.

In this work, cobalt aluminum oxides with good electrochemical stability, heat stability and resistance to acid and base corrosion are first used to cover the surface of the LNMO via a wet-coating method. Electrochemical performances such as cycling stability and cyclic voltammograms are examined and compared with the bare LNMO. Above all, their heat stabilities in combination with the electrolyte are emphasized and studied to evaluate the cell safety.

2. Experimental

2.1. Materials preparation

The spherical precursor compound [Ni_{0.5}Mn_{1.5}](OH)₄ was obtained via a co-precipitation method. A mixed aqueous solution of MnSO₄·5H₂O and NiSO₄·6H₂O with a total transition metal ion concentration of 2.0 M (n_{Ni2+} : n_{Mn2+} = 1:3) was pumped into a beaker (1L) under N₂ atmosphere with continuous stirring. Meanwhile, a solution of NaOH (4.0 M) and the appropriate amount of NH₃.H₂O as a chelating agent was dropped into the reactor. The temperature, ion concentration, pH, and stirring speed of the solution in the beaker were strictly controlled. The paste-like product was aged in the reactor under an N₂ atmosphere at 55 °C for 12 h before being filtered. The [Ni_{0.5}Mn_{1.5}](OH)₄ powders were washed with distilled water, acetone and alcohol successively several times. After drying at 100 °C, the powder was blended with moderate quantity of LiOH by ball-milling at a rotate speed of 200 rpm for 2 h on a FRITSCH-Pulverisette 14 instrument. The obtained mixture was first burned in ambient air at 800 °C for 20 h, then cooling to 600 °C and kept at this temperature for 20 h to offset for oxygen vacancies before finally cooled slowly to room temperature. To prepare the $CoAl_2O_4$ -coated $LiNi_{0.5}Mn_{1.5}O_4$, a desired amount of $Co(CH_3COO)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 20 mL of water at 80 °C, followed by the addition of 2 g LiNi_{0.5}Mn_{1.5}O₄; the suspension was ultrasonically processed for 30 min before the water was evaporated. The obtained solids were sintered at 400 °C for 5 h to obtain the CoAl₂O₄-coated LiNi_{0.5}Mn_{1.5}O₄. The LNMO samples coated with 2 wt% CoAl₂O₄ were denoted as 2% CoAl₂O₄@LNMO.

2.2. Materials characterization

The XRD data were collected on a Rigaku miniflex 600 with Cu K α radiation scanned from 10° to 90° at 1° min⁻¹ with a step size of 0.02°, operating at 40 kV and 15 mA. Field emission scanning electron microscopy (SEM, HITACHI S-4800) was performed to characterize the morphology of samples, and energy dispersive X-ray spectroscopy as an accessory of the SEM (EDS, OXFORD 7593-H) was carried out to measure elemental distribution on the surface of particles running at 20 kV acceleration voltage. The X-ray photoelectron spectroscopy (XPS) data were gathered on a

Quantum 2000 Scanning ESCA Microprobe spectrometer with focused monochromatized Al K α radiation (1486.6 eV). The pass energies were 60 eV for the survey spectra and 20 eV for particular elements. Transmission electron microscopy (TEM, JEOL-2100) was used to observe the morphologies and evaluate the structures of the as-prepared samples. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was carried out on a Plasma1000 (NSC, China) to measure the metal ion concentration in the electrolyte. A DSC/TG (STA 449 F3 Jupiter Netzsch) was used to estimate the thermal stability of the electrodes together with a 1 M LiPF₆ salt dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a mass ratio of 1:1 (#301 electrolyte, Guotai Huarong, China) from 100 °C to 300 °C at a heating speed of 5 °C/min.

2.3. Electrochemical measurements

The electrochemical performance of these materials was estimated with a CR2016-type coin cell configuration. The working electrodes were obtaineded by rolling out a slurry of 70 wt% active material, 20 wt% acetylene black, and 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 for one night, the electrode was punched out and roll-pressed. The CR2016-type coin cells were fabricated by inserting a porous polyethylene separator between the cathode pole piece and the Li metal foil in a high-purity Ar-filled glove box. The electrolyte was a 1.0 M LiPF₆ salt dissolved in a mixed 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 4.9V at room temperature on battery testers (LAND CT-2001A instrument, Wuhan, China). When the rates were higher than 1C (including 1C), a two-step charge process (constant current and constant voltage charge) was employed [30], i.e., following the constant current charge step to the 4.9 V, a constant voltage charging process was executed until the current was decreased to one-tenth of its initial constant current value. The current values at various rates were preset using the theoretical specific capacity of 147 mAh g^{-1} for LNMO. Take 1C for example: the current density value at 1C was 147 mAg^{-1} . The chargedischarge capacities acquired were calculated based on the LNMO material mass in the electrode. The cyclic voltammogram (CV) measurements were measured on a CHI 660D potentiostat (Chenghua, Shanghai, China) at a scanning speed of 0.1 mV s⁻¹ in a potential range of 3.1–5.0 V. The electrochemical impedance spectra (EIS) were carried out with a Solartron SI 1287 workstation at a frequency ranging from 99999 Hz to 0.009 Hz. All the tests were performed at 25 °C unless additionally specified.

3. Results and discussion

Fig. 1 shows the SEM images of the spinel LNMO (a, b) and 2% $CoAl_2O_4@LNMO$ (c, d). The LNMO are sphere-like particles ranging in size from 4 to 10 μ m. Under high-magnification (Fig. 1(b)), it can be seen that these particles are composed of nano-polyhedrons with well-defined edges and planes, and these polyhedrons have grown together at the vertex and/or plane. Therefore, this particular porous structure offers enough space for the infiltration of the electrolyte and accommodates the volume change to relieve the lattice strain during the intercalation-deintercalation of the lithium ions [31,32]. The SEM of 2% $CoAl_2O_4@LNMO$ with little fuzzy surfaces does not exhibit an obvious difference from bare LNMO; however, the TEM and EDS elemental analysis shown in Fig. 2 clearly presents the difference. Fig. 2 (a, b) and Fig. 2 (c–e) are high-resolution TEM (HRTEM) graphs of the LNMO and the 2%



Fig. 1. SEM patterns of (a, b) LNMO, (c, d) 2% CoAl₂O₄@LNMO.

CoAl₂O₄@LNMO particle, respectively. As shown in Fig. 2(a), the LNMO has a porous structure accordance with the result of the SEM pattern. The SAED pattern (Fig. S1) from the electron beam in the [001] direction, shown as the yellow area in Fig. 2(a), exhibits a sequential array of diffraction spots indicating a classic spinel type structure. This means that the polycrystalline LNMO micron-sized spheres are comprised of monocrystalline nano-sized particles. The ordered crystal lattices in long-range allow for easy insertion and deinsertion of Li ions, which is favorable for the electrochemical properties of a cell with this material. The surface of the LNMO is smooth, while for 2% CoAl₂O₄@LNMO, there is an obvious 8 nm thick coating layer (Fig. 2c-e). In Fig. 2e, the adjacent parallel lattice in the core region corresponds to the typical LNMO spinel materials with interplanar spacing of 0.472 nm, which is in accordance with the distance of the closely packed (111) plane of the LNMO spinel structure. In addition, lattice fingers with interplanar spacing of about 0.468 nm can be viewed in the HRTEM image in the coating layer, corresponding to the (111) interplanar spacing of CoAl₂O₄ spinel.

Selected area EDS elemental analysis (the area labeled in orange in Fig. 2 (d) shown in Fig. S2 (e)) confirms that the surface layer is composed of aluminum and cobalt, which further indicates that the coating layer is $CoAl_2O_4$. The existing of the Mn and Ni elements is likely because of the penetration of X-rays through the aluminum cobalt oxide layer.

The EDS area mapping analysis of 2% CoAl₂O₄@LNMO composite material shown in Fig. 3 was carried out to further illustrate the distribution of the CoAl₂O₄ coating layer on the surface of the host LNMO. Fig. 3(b-f) shows that the Co and Al

element distributions completely overlap with those of the Ni, Mn and O elements, indicating that $CoAl_2O_4$ is encapsulated on the LNMO surface uniformly.

The X-ray diffraction (XRD) patterns of the LNMO and the 2% CoAl₂O₄@LNMO were shown in Fig. 4(a). All these samples are assigned to cubic spinel structures. The peaks of the rock salt phase Li_xNi_{1-x}O/NiO (accompanying with oxygen vacancies) peaks at 37.335°, 43.381° and 63.024° [33] does not exist. It is reasonable to speculate that annealing at 600°C could compensate for the oxygen vacancies generated at high-temperature firing (above $600 \circ C$ [2]. CoAl₂O₄ peaks is absent in the 2% CoAl₂O₄@LNMO sample, which may be ascribed to low content coating. XPS characterization was executed for the 2% CoAl₂O₄@LNMO spinel sample to further identify the surface structure of LNMO after CoAl₂O₄ modification. As shown in the detailed XPS spectrum in Fig. 4(c), the peak at approximately 796.3–780.4 eV is assigned to bivalent Co_{2p} , and its presence verifies the existence of Co^{2+} on the LNMO surface following the CoAl₂O₄-coating process. Additionally, trivalent Al³⁺ 2p doublet peaks at lower binding energies (67.5-74.1 eV) in the 2% CoAl₂O₄@LNMO material shown in Fig. 4(d) are also observed. This result means that CoAl₂O₄ is successfully coated on the surface of LNMO.

The first charge-discharge curve and the consecutive discharge profiles of LNMO and 2% $CoAl_2O_4@LNMO$ at 1C at 25 °C are given in Fig. 5(a) and Fig. 5(b), respectively. The first discharge capacities of LNMO and 2% $CoAl_2O_4@LNMO$ are 127.9 and 132.3 mAh g⁻¹, respectively. After 100 cycles, the discharge capacities are 122.4 and 125.7 mAh g⁻¹, with a capacities retention of 95.7% and 95.0%, respectively. The discharge capacity only slightly increases after



Fig. 2. (a, b) HR-TEM images of LNMO, (c-e) HR-TEM images of 2% CoAl₂O₄@LNMO.



Fig. 3. An SEM graph (a) and relevant EDS area mappings of Ni (b), Mn (c), Co (d), Al (e) and O (f) of 2% CoAl₂O₄@LNMO.

coating with CoAl₂O₄, which may be ascribed to the coating layer relieving the interaction between the LNMO host and the electrolyte. The discharge curves of these two samples are very similar, exhibiting a flat plateau at approximately 4.7 V, and their voltages drop quickly at the end of the discharge process [34,35]. These results indicate that the CoAl₂O₄ coating layer does not change the basic spinel structure of LNMO.

The rate capacities of the LNMO and 2% CoAl₂O₄@LNMO electrodes are compared in Fig. 5(c). The discharge capacity at 1C is even higher than that at 0.5C, which was discussed by Lazarraga [36] and Zhou [30] without a clear conclusion, but could possibly be caused by a different charging process between 0.5C and 1C. In our test, the cells were constant current charged and discharged on a battery test instrument between 3.0 and 4.9V at room

temperature at low rates (<1C). When the currents were higher than 1C (including 1C), a two-step charging course (constant current and constant voltage charging) was carried out in order to overcome the polarization of the battery at high current, that means following the constant current charging process, the constant voltage charging course was executed until the current decreased to one-tenth of its primal constant current value. Notably, the discharge capacity of the 2% CoAl₂O₄@LNMO is higher in all current rate tests. The better rate capability of the 2% CoAl₂O₄@LNMO relative to the LNMO could be ascribed to an improved interface stability after coating with 2% CoAl₂O₄, which relieves the electrochemical polarization and ohm polarization. These results suggest that the CoAl₂O₄ can be used as coating layer for LNMO cathode productions with enhanced electrochemical



Fig. 4. (a) XRD plots of the samples, (b) XPS spectra of 2% CoAl₂O₄@LNMO, (c) XPS analysis of Co 2p3/2-1/2 for 2% CoAl₂O₄@LNMO, (d) XPS analysis of Al 2p3/2-1/2 for 2% CoAl₂O₄@LNMO,



Fig. 5. Electrochemical performance of the as prepared samples: (a) the first charge-discharge curve at 1C, (b) cycle performance at 1C, (c) rate capability of the samples, and (d) cycle performance of LNMO and 2% CoAl₂O₄@LNMO at 5C and 55 °C.



Fig. 6. CVs plots at 25 °C with a scanning rate of 0.1 mV s⁻¹ of (a) LNMO, (b) 2% CoAl₂O₄@LNMO.

performances by enhancing the cycle performance and the rate capability.

Fig. 5(d) shows the cycle performance of the LNMO and 2% $CoAl_2O_4@LNMO$ electrodes at a high temperature. The cells were cycled at 55 °C at 5C. There is little difference between LNMO and 2% $CoAl_2O_4@LNMO$ during the first 70 cycles, but the discharge capacity of LNMO exhibits more serious degradation than that of 2% $CoAl_2O_4@LNMO$ after 70 cycles. The capacity retention of LNMO after 200 cycles is 83%, whereas the capacity retention of 2% $CoAl_2O_4@LNMO$ remains 90%. In short we believe that the $CoAl_2O_4$ capping layer can form a steady protective screen barrier between the LNMO and the electrolyte at high temperatures to inhibit the secondary reactions between them, therefore enhancing the electrode performance at high-temperature.

In order to further identify the reversibility and electrochemical behavior of materials with and without the $CoAl_2O_4$ coating, cyclic voltammograms were executed at a scanning speed of 0.1 mV s⁻¹ in the range of 3.1 V-5.0 V, and the results are depicted in Fig. 6(a) and Fig. 6(b), respectively. Both the intense and sharp reduction/ oxidation peaks of Ni²⁺/Ni⁴⁺ are observed at approximately 4.84/ 4.62 V in LNMO and 2% CoAl₂O₄@LNMO after the first cycle. During the first cycle, the oxidation peak of LNMO is at 4.96 V with a spindle shape, and the oxidation peak decreased to 4.84 V in the following cycle; for 2% CoAl₂O₄@LNMO, the oxidation peak did not exhibit any obvious shifting (only 0.003 V). The smaller oxidization

gap of 2% CoAl₂O₄@LNMO between the 1st and 2nd cycles means less polarization, because CoAl₂O₄ coating holds down the secondary reaction between the electrolyte and NCM.

Fig. 7 presents the concentration of Ni and Mn cations of LNMO and 2% $CoAl_2O_4@LNMO$ cathode pole piece dissolved in the electrolyte. First, the coin cell was charged to a completely delithiated state after 4 cycles at 1C. Then the cell was disassembled to retrieve the electrode material film in an Ar-filled glove box. Second, the film was soaked in 301 electrolyte for



Fig. 7. The ion concentration of Ni and Mn dissolved in the #301 electrolyte for LNMO and 5% $V_{2}O_5$ -LNMO electrodes reserved at 80 °C for 1 day.

1 day with a ratio of cathode electrode materials to electrolyte of 2 mg electrode materials of per milliliter electrolyte at 80 °C. Third, after acid-treating, a metal ion test (ICP) was performed on the above aged electrolyte (shown in second step). The concentration of the Ni and Mn cations of the 2% CoAl₂O₄@LNMO dissolved in the electrolyte is only approx a quarter of that in the LNMO, which indicates that the CoAl₂O₄ coating layer to some extent inhibited the dissolution of the transition metals and maintained a stable LNMO structure. The CoAl₂O₄ coating layer inhibited the HF scavenger of the spinel in electrolyte, leading to improved electrochemical performance.

The DSC/TG was performed on STA 449 F3 Jupiter Netzsch instrument to measure the heat stability of the LNMO and 2% $CoAl_2O_4@LNMO$ electrodes in a 1 M LiPF₆ salt dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a mass ratio of 1:1 (#301 electrolyte, Guotai Huarong, China) from 100 °C to 300 °C at a heating rate of 5 °C/min. The detailed measurement processes were as follows. First, a button cell was charged to the full delithiated state (4.9 V) at 1C rate. Then, the cell was detached to regain the electrode material film in an Ar-filled glove box. Next, the film was washed with DMC and dried at room temperature. Following this, the electrode materials scraped from the pole piece together with the electrolyte were sealed in a gold-plated stainless steel crucible in the glove box. The ratio of electrolyte to electrode material was 1 μ L of electrolyte per milligram of electrode material.

Seen from Fig. 8, the two exothermic peak temperatures for LNMO are at 130.7 °C and 176.2 °C; after coating with 2% CoAl₂O₄ these two exothermic peaks shifted to 139.4 °C and 181.9 °C. These two peaks moved to higher temperature by 8.7°C and 5.7°C. respectively. Furthermore, the total heat quantity for 2% CoAl₂₋ O_4 @LNMO was approximately 180–250 °C, which is 583 J g⁻¹, while that of bare LNMO is up to 969 $[g^{-1}]$. The heat release content of the spinel structure is reduced by 40% after coating with CoAl₂O₄. CoAl₂O₄ works as a protective layer obviously inhibiting the interaction between LNMO and the electrolyte and suppressing the electrolyte decomposition at the electrode/electrolyte interface. It thereby alleviates thermal runaway, stabilizes the host LNMO structure from oxygen release at high temperatures and improves the thermostability of LNMO. The improved thermal stability is very important to the safety characteristics of the battery, which makes the CoAl₂O₄@LNMO composite material promising for practical applications.

4. Conclusions

In summary, a coating layer of $CoAl_2O_4$ on the surface of spinel LNMO is synthetized via a manageable solvent method. The thickness of coating layer is approximately 8 nm thickness. The prepared $CoAl_2O_4@LNMO$ composite exhibits impressive



Fig. 8. DSC profiles of samples in electrolyte at the full de-intercalated states.

thermostability enhanced by the coating layer. The $CoAl_2O_4$ -rich surface layer has been characterized via XPS and TEM. It is found that:

- (1) The CoAl₂O₄-rich layer covering the surface of the LNMO alleviates the metal dissolution of LNMO, which improve the stability of structure.
- (2) The coating layer stabilizes the host LNMO structure eliminating oxygen release at high temperatures, which improves the heat stability between the LNMO and the electrolyte at high voltages. The heat release content of the spinel structure is decreased by 40% after coating with CoAl₂O₄.
- (3) The capacity retention of LNMO at high temperature is enhanced dramatically.

These results indicate that CoAl₂O₄, as a prospective thermally stable secure material, may be used in actual battery production.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.05.021.

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