Enhanced Electrochemical Performances of Ni-rich Cathode Materials for Lithium Ion Batteries by Mixed Coating Layers

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Abstract

The properties exhibited by Ni-rich cathode materials were enhanced through the mixed coating layers of Li$_3$PO$_4$ and boric acid. The scanning electron microscopy (SEM), the transmission electron microscope (TEM), the differential scanning calorimetry (DSC), the electrochemical Impedance Spectroscopy (EIS), as well as the half-cell and full-cell charge-discharge tests were adopted for characterizing the structure and electrochemical properties exhibited by the cathode materials. As revealed by results, the Li$_3$PO$_4$ and boric mixed coating layers can effectively reduce the surface area and protect the direct contact between cathode material particle surface and electrolyte, meanwhile improving the structural stability and cycle performance. The coating of fast ionic conductor contributes to enhance the specific capacity possessed by the Ni-rich cathode materials accordingly.

Keywords

Ni-rich Cathode, Lithium-ion Batteries, Mixed Coating Layers, Electrochemical properties
1. Introduction

As the fossil energy reserves decrease and the environmental pollution becomes increasingly serious, clean energy becomes more and more urgent.\textsuperscript{1} Recent years, lithium ion batteries (LIBs) have enjoyed a broad application in portable electric devices as well as electric vehicles (EVs) relying on the strong energy density, the low-cost and and environmental friendliness among rechargeable batteries like Li-ion, Na-ion, Li–S, Li–O\textsubscript{2} batteries et al.\textsuperscript{2-5} The key issue in developing EVs lies in using LIBs with a higher specific energy density for satisfying requirement for a long durability during each charge.\textsuperscript{6-8} To be specific, the performances possessed by cathode materials play a depended factor in rechargeable batteries in terms of the long-term durability and performances due to limited capacity.\textsuperscript{9-12} At present, for the nickel-rich layered structure Li\textsubscript{Ni}_{x}Co\textsubscript{y}M\textsubscript{1-x-y}O\textsubscript{2} (0.6 < x < 1, M = Mn or Al) composite oxide, the specific capacity is excellent (more than 200 mAh/g) and the cycle performance is relatively outstanding, making it a proper alternative for LIBs with strong energy density relative to other different cathode materials.\textsuperscript{13} It is capable of providing a higher specific capacity as the content of nickel increases. However, the high content of nickel results in the irreversible surface phase transformation, the deterioration of surface structure as well as the poor cycle performance, especially in the condition of high cut-off voltage.\textsuperscript{21} It is still necessary to solve many problems prior to the full commercialization of the material.

Compared with the normal NCM811, LiNi\textsubscript{0.90}Co\textsubscript{0.05}Mn\textsubscript{0.05}O\textsubscript{2} is a typical nickel-rich cathode material, which exhibits a better commercial application performance.\textsuperscript{15} However, it has some substantial problems, such as the enhanced cation mixing, the dissolving transition metal ions at the high cut-off voltage\textsuperscript{16} and the deteriorative surface structure caused by side reactions. Surface decoration on the particle is a commonly effective approach employed to modify the material including Li\textsubscript{3}PO\textsubscript{4}, SiO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} et al.\textsuperscript{17} Cho et al. reported the SiO\textsubscript{2} coating material for improving the thermal as well as electrochemical properties.\textsuperscript{18} Zhu and Li et al. modified the coating layer by Li\textsubscript{3}PO\textsubscript{4}, which reduced the residual lithium on the surface of NCM811 and...
enhanced the cycle stability. Moreover, researchers keep trying different surface decorations for resolving the inherent problems facing the nickel-rich material. Nevertheless, single coating layer is not sometimes enough to meet the commercial requirements for Ni-rich cathodes.

The work focuses on investigating the structure of the active material surface regarding LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2 primary particles by using lithium phosphate and boric acid, aiming at improving the structural as well as thermal stability, and evaluating its capacity, cycle stability et al. An investigation on performances including structure, thermal stability and electrochemical properties was fully studied. The XPS, XRD as well as HRTEM assisted in observing the change of surface phase before and after the charge and discharge. Although various valuable works have reported LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2 in coating layer, it is believed that the methods and conclusions of this work could contribute to forming significant basis for further investigating the well cycling performance with high nickel (≥0.9) content, which could be used for the industrialization of high energy density lithium-ion battery.

2. Experimental Sections

2.1 Synthesis of NCM9055

All chemicals used in the study exhibited analytical reagents (AR) and came from Aladdin Co., Ltd. The Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2 precursor was provided by Ningbo Ronbay New Energy Technology Co., Ltd. The pristine NCM9055 (LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2) was prepared by mixing Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2 precursor with the LiOH•H_2O at 1:1.04 stoichiometric ratio. The mixture firstly underwent 48 h of calcination at 480 °C, and then underwent 12 h of sintering at 750 °C in flowing oxygen.

2.2 Synthesis of NCM9055-LPO
Firstly, the 1 wt.% H$_3$PO$_4$ (0.04 g, wt.% ≥ 28, without diluted) was dissolved in anhydrous ethanol solution (50 mL), with the obtained solution receiving ten minutes of dispersion. Secondly, after the solution transferred into water bath, 4 g pristine NCM9055 was added in. Thirdly, at 80 °C, the mixture underwent stirring at 300, 400 and 500 rpm, respectively, till the complete evaporation of the solvent. Lastly, the dried power underwent 5 h of heating in a muffle furnace at 500 °C in air. The as-received powders were marked as NCM9055-LPO.

2.3 Synthesis of NCM9055-LPB

Modifying NCM9055-LPO with boric fragments. 0.5 wt.% boric powders were mixed with NCM9055-LPO in a ball mill at a rate of 300 r/min. Then the dried mixture powder underwent 12 h of heating at 200 °C under flowing oxygen atmosphere. We marked the as-received sample as NCM9055-LPB.

2.4 Characterization

Analysis of the crystal information regarding the prepared materials relied on X-ray diffraction (XRD, BRUKER D8A A25) using Cu Kα radiation at 0.02° 2θ/min in the range of 10-80°. General Structure Analysis System (GSAS) software with EXPGUI interface were applied to the Rietveld refinement specific to neutron diffraction. The field-emission scanning electron microscope (FE-SEM, SU8010 HITACHI), the transmission electric microscope (TEM, JEM-2800F JEOL), and the X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) by using Al Kα radiation assisted in observing the surface chemical information regarding the as received samples. With regard to the DSC measurement, we first charged cells to 4.25 V and kept the voltage for certain period, and then disassembled them in the glove box. We scraped the active materials with full charge from electrodes, and used a few electrolytes to seal them into high pressure stainless steel crucible. We conducted the test with the heating rate at 5 °C/min in the range of 30-400 °C. We examined the electrochemical performance exhibited by the prepared materials in CR2032 coin type
cells assembled taking Li metal as the counter electrode in the Ar-filled glove box. Active material, acetylene black, as well as polyvinylidene difluoride (PVDF) were mixed at 97.5:1:1.5 weight ratio, for preparing the cathode electrode in N-methylpyrrolidone (NMP). Subsequently, we pasted the mixed slurry onto the Al current collector. The graphite, acetylene black and PVDF were mixed at 90:5:5 to prepare the anode electrode, with the slurry being pasted onto the Cu foil. Following 12 h of drying treatment at 120 °C under vacuum, we cut the two electrodes into 14 mm disks. The active materials held an average loading of 15.5 mg/cm². The N/P ratio specific to coin-type full cell was controlled at 1.1. We prepared the electrolyte by dissolving 1 M LiPF₆ in EC and DMC (1:1 in volume) solution containing certain FEC. The assembled cells underwent 8 h of aging prior to the electrochemical test. The half cells first received 2 cycles of charge/discharge at 0.2 C-rate (1 C-rate = 200 mAh g⁻¹), followed by the cycling at 0.2 C-rate in 2.5-4.25 V at 25 °C. The full cell first underwent 2 cycles of activation at 0.1 C-rate in 3.0-4.2 V, followed by the long cycles of testing at 1 C-rate. Calculation of all specific capacities was conducted considering the mass of the pristine sample or modified sample. We measured the electrochemical impedance spectrum (EIS) at full-charge state following 0 and 50 cycles in the frequency range of 100-0.005 Hz on an electrochemical working station (Princeton PMC-1000).

3. Results and Discussion

Figure 1 displays the XRD patterns of the pristine (NCM9055) as well as decorated LiNi₀.₉₀Co₀.₀₅Mn₀.₀₅O₂ (NCM9055-LPO and NCM9055-LPB) samples, the diffraction peaks belong to a R3m space group indexed based on the layered hexagonal α-NaFeO₂ structure.²¹ Figure 1 shows the clear separation of the peaks of the 006/102 and 108/110 specific to NCM9055 in the XRD pattern, indicating that their structure is well layered. In the coated samples of NCM9055-LPO and NCM9055-LPB, the four specific peaks remain separated, which implies the irrelevance of the layered structure with the decoration layers on primary particles. The evaluation on the Li⁺/Ni²⁺ mixing degree in NCM materials usually relies on the intensity ratio of I₀₀₃/I₁₀₄. The cation mixing is
lower when the value is higher than 1.2, which demonstrates the less lithium-ion sites occupied by nickel. So, lithium ions can transfer easily in the layered structure. Based on Table 1, the pristine sample NCM9055 and the decorated NCM9055 samples (NCM9055-LPO and NCM9055-LPB) possess the value $I_{003}/I_{104}$ of 2.05, 2.08 and 2.16, respectively, according to the calculation. It means that the cationic order degree regarding the coated NCM9055 samples (NCM9055-LPO and NCM9055-LPB) remains good following the decoration on primary particles.

The Rietveld refinement contributes to the further quantitative analysis (Table 1). NCM9055-LPO and NCM9055-LPB have same lattice parameters, which are not impacted by the decoration layers on the primary particles. Table 1 lists the information in detail on samples including pristine NCM9055, NCM9055-LPO, and NCM9055-LPB samples lattice parameter. As for the cation mixing after calculation, Li$^+$/Ni$^{2+}$ exhibits a cation disorder degree about 0.781% for NCM811-LPO and 1.496% for NCM811-LPB, less than that the previously reported cation disorder degree (> 5%). We can conclude that all the as-prepared samples present a proper cationic order degree, and the decoration basically does not impact the cation mixing in the material.

Figure 2 displays the surface morphology possessed by pristine samples and modified samples, illustrating the uniform distribution of tiny particles on NCM9055-LPO and NCM9055-LPB surface, by contrast the pristine NCM9055 surface is smooth. The HRTEM assisted in further investigating the surface morphology of NCM811-LPB. Figure 2e displays well-organized lattice fringes, indicating the high crystallization of the pristine NCM9055. TEM finds similar morphology with the SEM observations. To support full coverage of Ni-rich NCM with either Li3PO4 or boric, the EDX analysis of Ni, Co, Mn, P, B elements are shown in Figure 3, indicated P and B elements were well coated on the surface of the particles.

The XPS demonstrates the chemical species change regarding pristine and modified sample surface (Figure 4). The C 1s spectra of the pristine NCM9055 and the modified samples (NCM9055-LPO and NCM9055-LPB) are very different. For example, the peak at 289.3 eV matches the MCO$_3$ attributed to residual lithium carbonates at pristine NCM9055 surface. NC9055-LPO and NCM9055-LPB do not see such peak,
which indicates the successful removal of residual lithium species by Li₃PO₄ modification. Additionally, the XPS spectra of O 1s, Al 2p, Li 1s, P 2p, O 1s, and B 1s were provided to characterize the chemical composition of the coated samples as shown in Figure S2.

The study conducts a systematic investigation on how the mixed coating layer affected the electrochemical performance exhibited by NCM9055. Figure 5 displays the initial charge/discharge profiles regarding the pristine sample and modified sample. Table S1 lists the initial discharge capacity as well as coulomb efficiency specific to all the samples at room temperature, tested at 25 °C in 2.50-4.25 V at 1 C-rate (1 C-rate = 200 mA). As reported by previous research, the side reactions obviously relate to the degradation of capacity in the long cycling term. Hence, it is expected that the Li₃PO₄/Boric coating layer can intensity the cycling stability exhibited by NCM9055. We tested the cycling performance at 1 C-rate in 3.0–4.2 V, finding that NCM9055-LPO displayed a capacity retention of 97% and NCM9055-LPB displayed a capacity retention of 98% after 300 cycles, much higher compared with pristine NCM9055 which was 92% (Figure 5c). Such improvement was more obvious at 45 °C. The capacity retention of the two materials was 89% and 95% after around 300 cycles, respectively, while for the pristine NCM9055, the capacity retention was low at 81% (Figure 5d).

We have performed XRD diffractions on cycled cathode, which shown no obvious changes on crystals as shown in Figure S3. As reported, the generation of cracks on cycled Ni-rich cathode materials leads increasing fade. The cross-sectional SEM on the cycled active materials was provided at Figure S4. Less micro-cracks were found on cycled NCM9055-LPB than that of NCM-LPO and the pristine sample NCM9055, indicated the functions on suppression of side-reaction of Li₃PO₄/boric double layer coating.

Figure 5a displays the charge/discharge voltage distribution. For assessing the rate capability possessed by the modified samples, we measured all samples at different current densities (0.2, 0.5, 1, and 2 C-rate) in the voltage range of 2.5-4.25 V (Figure 5b). All the modified NCM9055 presented a more excellent rate capacity relative to
pristine NCM9055, because of the rapid ionic conductivity possessed by the Li3PO4 coating layer, which speeds up the Li+ diffusion at the material interface. Due to the synergetic effects brought about by Li3PO4 and boric acid, the capacity retention of NCM9055-LPB was obviously high at high current density. At 2 C-rate, the NCM9055-LPB maintained 80.65% (179.6 mAh/g) of the initial capacity. By contrast, the capacity retention of the pristine NCM9055 was only 76.39% (160.2 mAh/g).

To more deeply understand the role played by the decoration layers, the study examined the EIS regarding pristine samples and decoration samples following different cycles (0, 50) within 2.5-4.25V (Figure 6). Figure 6a displays a semicircle together with an inclined line, and Figure 6b has two semicircles together with an inclined line. The 1st semicircle at the high-frequency region denotes the resistance exhibited by cathode electrolyte interphase film (CEI, RCEI), while the second semicircle at the mid-high frequency denotes the charge transfer (Rct), with the inclined lines showing lithium ion diffusion resistance in the cathode material. Figure 6 also shows the inset of equivalent circuit. R0 denotes the cell Ohm resistance between current collector and electrolyte. Generally, NCM9055-LPB sample presented a lower charge transfer resistances (Rct) relative to the pristine sample. Despite room temperature cycling, modified samples maintained their original Rct values at about 0.039 Ω, by contrast, while NCM9055 had an Rct value of 0.025 and 0.050 Ω after 0, 50 cycles, respectively. Clearly, the surface decoration changes the electrode kinetics, resulting in a small polarization. Regarding the undecorated pristine material, Rct increases possibly because of the increase in the polarization along the charge/discharge cycling.

The thermal stability exhibited by NCM cathode material at the charged state decides whether the lithium battery is safe in practice. Figure 7 displays the DSC results specific to the pristine sample and modified sample at 4.25 V. The primary exothermic peak specific to pristine NCM9055 could be seen at 217.83 °C, and the reaction heat flow was high at 1620.2 J/g. The primary exothermic peaks specific to NCM9055-LPO and NCM9055-LPB could be seen at 221.93 °C and 221.23 °C, respectively. Besides, the reaction heat flow specific to two modified samples presented an obvious decrease
to 893.3 J/g and 903.9 J/g. NCM9055 surface with a high instability cannot contact with electrolyte directly. Based on the change, due to the existence of the coating layer, the reactivity at the interface lowered effectively. What’s more, the boric coating layer decrease the surface area of primary particles, which reduced the contact area between particle surfaces and electrolyte. Furthermore, the mixed coating layer Li$_3$PO$_4$/Boric prevented the release of oxygen from bulk phase, contributing to raise the exothermic reaction occurrence temperature as well as reduce the reaction heat.

4. Conclusions

In summary, a simple but effective synthesis method is adopted for preparing the Li$_3$PO$_4$ and boron decorated nickel rich NCM9055 cathode material. The material exhibited an outstanding electrochemical performance, and the largest discharge capacity is 213.4 mAh/g at 0.2 C-rate, when the cut-off voltage reaches 4.25V. It maintains a capacity retention of 98% at 25 ℃ and 95% at 45 ℃ after 300 cycles, 6% and 14% higher relative to the pristine material, respectively. In the charge-discharge cycle, mixed decoration layer remarkably suppresses rock-salt phase generation which weakens the material stability. Relative to pristine material, such material also has the function of promoting the movement of Li ions inside cathode material. Taken together, lithium phosphate surface decoration has dual positive effect as it enhances the stability and capacity possessed by the NCM9055 material as well as contributes to its commercial application.
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Figure Captions

Figure 1 The XRD of NCM9055, NCM9055-LPO, and NCM9055-LPB.
Figure 2 The SEM images about a) NCM9055, b) NCM9055-LPO, c, d) NCM9055-LPB; and the TEM images of e) NCM9055-LPB.
Figure 3 The EDX analysis of NCM9055, a) SEM of NCM9055, b) Ni elements, c) Co elements, d) Mn elements, e) P elements, f) B elements.
Figure 4 XPS results for NCM9055, NCM9055-LPO and NCM9055-LPB.
Figure 5 a) The initial charge/discharge curves, b) the rate performance, and c) the cycling performance exhibited by the full-cell for NCM9055, NCM9055-LPO and NCM9055-LPB in 3.0-4.2 V at 1 C-rate at 25 °C. d) The cycling performance exhibited by the full-cell for NCM9055, NCM9055-LPO and NCM9055-LPB in 3-4.2 V at 1 C-rate at 45 °C.
Figure 6 The results of EIS at charged state after 5 (a) and 50 (b) cycles at 1 C-rate.
Figure 7 The differential scanning calorimetry traces which display the heat flow when the electrolyte reacts with pristine, NCM9055, NCM9055-LPO, and NCM9055-LPB charged to 4.25 V.
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Table 1. The Rietveld refinement analysis data of samples

| Compound          | a/Å  | c/Å  | c/a | D₀₀₃ /nm | D₁₀₁ /nm | D₁₀₄ /nm | D₀₀₃/D₁₀₄ | I₀₀₆ | I₀₁₂ | I₁₀₁ | Cell Volume/Å³ | Crystal Density g/cm³ | Mixing Ratio | Ni/Li | Li/Ni |
|-------------------|------|------|-----|---------|----------|----------|-----------|------|------|------|-----------------|------------------------|-------------|-------|-------|
| NCM9055-LPO       | 2.88 | 14.28| 4.94| 109.7   | 66.7     | 49.0     | 255.93    | 2.05 | 4.1  | 10.1 | 31.3            | 101.67                  | 4.72        | 3.807%| 2.538%|
| NCM9055-LPB       | 2.87 | 14.20| 4.94| 116.3   | 69.6     | 51.5     | 276.42    | 2.08 | 3.6  | 10.1 | 30.2            | 101.64                  | 4.67        | 3.995%| 0.781%|

