Improving the electrochemical performance of Ni-rich cathode material $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ by removing the lithium residues and forming Li_3PO_4 coating layer

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Abstract: Ni-rich cathode materials always suffer from surface lithium residues mainly caused by the reduction of Ni^{3+} to Ni^{2+} when exposing to moisture, and severe side reactions between organic electrolyte and highly active Ni^{4+} when fully charged. An appropriate amount of $\text{NH}_4\text{H}_2\text{PO}_4$ is firstly coated on the hydroxide precursor $\text{Ni}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}(\text{OH})_2$ before mixing with Li_2CO_3 . The $\text{NH}_4\text{H}_2\text{PO}_4$ can react with the lithium residues and form a uniform Li_3PO_4 coating layer. X-ray diffraction, scanning electron microscopy, field emission transmission electron microscopy and element mapping are employed to investigate the Li_3PO_4 coating layer. Electrochemical measurements results show that the cycle stability of the synthesized $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ both at room temperature and 55°C has been significantly improved. Its thermal stability has also been greatly enhanced.

Keywords: Li-ion battery; lithium nickel cobalt aluminum oxide; surface lithium; ammonium phosphate; thermal stability.

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1. Introduction

Layered Ni-rich cathode materials such as $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ [1, 2], $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ [3, 4] and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [5, 6] have attracted much attention because of their higher specific capacity and lower cost compared to LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. For the LiNiO_2 -based materials, the average valance of Ni increases from +2 to +3 with the increasing content of Ni. However, the Ni^{3+} ions on the surface of particles are, especially when exposing to moisture, very unstable, leading to the slow reduction of Ni^{3+} to Ni^{2+} accompanied by the generation of lithium residues such as LiOH and Li_2CO_3 [7, 8]. The pH value, an important index for large scale application of Ni-rich cathode materials in lithium ion batteries, is directly related to the amount of lithium residues, i.e. surface alkali. If the pH is too high, it is difficult to make a uniform electrode because of the gelation of the slurry [9]. What's more, the lithium residues can easily react with the HF, a by-product of the decomposition of electrolyte, and produce water that can accelerate the degradation of cathode materials in turn [10]. Another problem that hinders the commercial use of Ni-rich cathode materials is the phase transition from layered to inactive rock salt structure or spinel in charging-discharging process, especially in elevated temperature, which causes the rapid increase of polarization and fast capacity fading [11, 12]. And the thermal stability of Ni-rich materials is critical to safety issues in electro vehicles [13, 14].

Generally, coating a metal oxide layer onto the surface of cathode powders has been proved an effective way to improve the electrochemical properties [15]. However, the widely used coating process is just physically mixing the coating materials with target materials, and then sintering at 500-650 °C, which may leave a lot of coating materials separated and cannot form a uniform coating layer [5, 16, 17]. Some coating materials, such as Al_2O_3 and TiO_2 , might react with the host materials in high temperature ($>700^\circ\text{C}$) and form a surface/bulk doping phase rather than a coating layer [18-20]. Metal phosphates, on the other hand, barely diffuse into the bulk even sintered at high temperature owing to the strong bonding energy of polyanion PO_4^{3-} . Inactive metals phosphates, such as $\text{Co}_3(\text{PO}_4)_2$ [21], $\text{Ni}_3(\text{PO}_4)_2$ [22],

FePO₄ [23] and AlPO₄ [24], have been deeply investigated as coating materials to improve the electrochemical properties of Ni-rich cathode materials. Li₃PO₄, a good ionic conductor, has also been widely studied as coating materials to improve electrochemical performance of cathode materials such as LiMn₂O₄ [25], LiFePO₄ [26], LiNi_{0.4}Co_{0.3}Mn_{0.3}O₂ [27] and LiCoO₂ [28].

Xiong et al. [29] have proposed a method to remove the lithium residues on the surface of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ with (NH₄)₂HPO₄ ethanol solution. Unfortunately, their results show that the assumedly formed Li₃PO₄ is not detected so that the mechanism of improvement is not clarified. V₂O₅ has been also used to remove the lithium impurities on the surface of Ni-rich cathode materials, but the so-called lithium-reactive V₂O₅ still couldn't be directly detected [11]. Herein, taking LiNi_{0.815}Co_{0.15}Al_{0.035}O₂ (NCA) as an example of the Ni-rich cathode materials, we firstly coat NH₄H₂PO₄ on the surface of hydroxide precursor Ni_{0.815}Co_{0.15}Al_{0.035}(OH)₂ before mixing with Li₂CO₃. The results show that NH₄H₂PO₄ can remove the lithium residues and simultaneously form a uniform Li₃PO₄ coating layer in the high temperature sintering process (Fig. 1). The electrochemical properties and thermal stability of this Li₃PO₄-coated Ni-rich material have been largely improved.

2. Experimental

Firstly, 5.0 g commercial hydroxide precursor Ni_{0.815}Co_{0.15}Al_{0.035}(OH)₂ was added into 5.0 mL NH₄H₂PO₄ aqueous solution in a mortar and continuously ground to form homogenous suspension until it was dried. Then stoichiometric Li₂CO₃ was added and thoroughly ground to mix with the coated precursor and the mixture was finally sintered at 750°C for 16 hours under flowing oxygen. The content of NH₄H₂PO₄ is 1 wt%, 2 wt% and 3 wt% to the precursor. For comparison, the bare LiNi_{0.815}Co_{0.15}Al_{0.035}O₂ was prepared with the same process but without adding NH₄H₂PO₄. For convenience, we denoted the pristine and the surface modified materials as P0-NCA, P1-NCA, P2-NCA, P3-NCA and P5-NCA, respectively.

Powder X-ray diffraction (XRD, Rigaku TTR-III) was employed to measure the crystal structures of the as-prepared samples with Cu K α radiation at a scan rate of

$10^\circ \text{ min}^{-1}$ over a 2θ range of $10\text{-}70^\circ$. Morphological studies were carried out using scanning electron microscopy (SEM, JSM-6390LA, JEOL) equipped with an energy dispersive X-ray spectroscope (EDS), and field emission transmission electron microscopy (FE-TEM, JEM-2100F). The pH of the materials was tested as following: 2 g NCA was dispersed into 20 mL deionized water in a centrifuge tube and kept for 10 minutes, then filtered to obtain the clear liquid for the test. After that, the liquid was poured back to the centrifuge tube and kept for one week for another pH test.

The electrochemical properties of the synthesized NCA samples were examined using CR2032 coin type cells with metallic lithium as negative electrode. The positive electrodes were prepared by mixing the NCA powders (84 wt%), carbon black (8 wt%) and polyvinylidene fluoride (PVDF) binder (8 wt%) dispersed in N-methyl-2-pyrrolidone to make slurries. Then the slurry was coated on an aluminum foil and dried at 80°C in an oven overnight. The laminates were punched into round disks with a diameter of 12 mm. A typical electrode disk contained 4.5 mg NCA. The cells were assembled in an Ar-filled glove box (McBraun Labmaster 130) with an electrolyte of 1 M LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC:DEC = 1:1 V/V) and a separator of Celgard 2400 porous membrane.

The cells were cycled on Newware BTS 610 multi-channel battery cycler. The cycle performance was measured at 0.1C rate ($1\text{C}=180 \text{ mA g}^{-1}$) for initial three cycles and then at 0.5C for subsequent cycles in the voltage range of 2.75 - 4.3 V both at 25°C and 55°C . For the rate performance, the cells were tested at 0.1C, 0.5C, 1C, 2C, 5C and 10C for five cycles respectively in the voltage range of 2.75 - 4.3 V. The impedance measurement was conducted on a CHI640 Electrochemical Workstation using electrochemical impedance spectroscopy (EIS) in the frequency range of 0.01Hz-100 kHz. The amplitude of the AC signal was 5 mV.

To check the thermal stability of the cathode materials, the cells, when charged to 4.3V after three cycles between 2.75-4.5V at 0.1C, were disassembled in a glove box and the positive electrodes were thoroughly washed with dimethyl carbonate (DMC). Then the electrodes with trace of electrolyte were tested using C80 micro calorimeter in nitrogen atmosphere with a heating rate of $0.2^\circ\text{C min}^{-1}$ between 30°C

to 300°C.

3. Results and discussion

Fig. 2a shows the X-ray diffraction patterns of the cathode materials. It can be seen that all the samples have good crystallinity and correspond to an α -NaFeO₂ structure with $R\bar{3}m$ space group. Fig. 2b presents the magnified characteristic peaks of Li₃PO₄ (PDF#15-0760) in the 2θ range of 20-26°, which can be detected in P2-NCA and P3-NCA.

Fig. 3 shows the SEM images of the as-prepared NCA samples. With the increasing content of NH₄H₂PO₄, it can be seen the particle surface changed obviously. For the bare NCA particles (Fig. 3a), the primary particles can be seen clearly. However, the needle like particles appeared at the crevice between the surface primary particles (Fig. 3b), and a uniform needle-like coating layer formed with 2 wt% NH₄H₂PO₄ (Fig. 3c). Interestingly, a dense coating layer appeared when the content of NH₄H₂PO₄ reached 3 wt%, but with some little particles adjacent to the surface of the large particle of NCA (Fig. 3d). EDS mapping images of P3-NCA show the element distribution on the surface, from which we can see that Ni (Fig. 3f) and Co (Fig. 3g) distribute uniformly, but the signal of P (Fig. 3h) from the little particles (as mentioned in the red circles) is stronger than that in other areas, which may result from the separate nucleation of Li₃PO₄ when sufficient NH₄H₂PO₄ exists. It can be concluded that, according to the XRD results and SEM images, Li₃PO₄ can in-situ generate during the sintering process and form a uniform coating layer on the surface of NCA cathode materials. The EDS results listed in Table 1 show the molar ratio of the elements Ni, Co, Al and P. It should be noticed that the P element for P1-NCA cannot be detected, which may be because its P content is too little. Note that the EDS results only give the information of the particle surfaces.

Fig. 4 shows the TEM images of P0-NCA, P2-NCA and P3-NCA. It can be seen that the thickness of Li₃PO₄ coating layer for P2-NCA ranges from 45 nm to 120 nm (Fig. 4b), while that for P3-NCA is larger than 200 nm (Fig. 4c). A thin coating layer

can isolate cathode materials from the direct contact with electrolyte and effectively suppress side reactions, but for the thicker one, the diffusion of lithium ions may be hindered to some extent.

The pH tests were carried out as described in the experimental part in order to check, indirectly, the lithium residues. As can be seen in Fig. 5, the pH value decreases with the increasing content of $\text{NH}_4\text{H}_2\text{PO}_4$, which indicates the lithium residues can be removed by $\text{NH}_4\text{H}_2\text{PO}_4$. After soaked in water for one week, the pH values of P0-NCA, P1-NCA and P2-NCA increase rapidly, but P3-NCA just has a moderate increase. This is because the lithium ions in lattice is chemical deintercalated when immersed in water [30], and a dense coating layer can prevent that process. It can be speculated that the removal of lithium residues and the formation of a Li_3PO_4 coating layer are beneficial to the storage ability of Ni-rich cathode materials when exposed to moisture.

The electrochemical properties are shown in Fig. 6. The initial charge-discharge curves at 0.1C between 2.75-4.3 V are presented in Fig. 6a, from which we can see the specific capacity decreased with the increasing content of $\text{NH}_4\text{H}_2\text{PO}_4$, 193.2 mAh g^{-1} , 195.3 mAh g^{-1} , 184.5 mAh g^{-1} , 172.3 mAh g^{-1} for P0-NCA, P1-NCA, P2-NCA and P3-NCA respectively. The cycle performance (Fig. 6b) is significantly improved after modified with $\text{NH}_4\text{H}_2\text{PO}_4$, with the capacity retentions of 70.1%, 70.2%, 88.5% and 92.7% after 100 cycles at 0.5C for P0-NCA, P1-NCA, P2-NCA and P3-NCA, respectively. However, the value of its reversible specific capacity for P3-NCA is considerably lower than other samples due likely to the presence of too much coating material (Li_3PO_4) (Fig. 4c). Furthermore, its rate performance is poorer than other samples as well (Fig. 6d). Therefore, the sample P2-NCA is considered to be the optimal one. Fig. 6c shows the cycle performance of P0-NCA and P2-NCA at 55°C. Clearly, the coated NCA has a much better cycle stability than that of the bare one. As mentioned before, the Ni-rich cathode materials always suffer from structural instability and sever side reactions with electrolyte because of the unstable and highly active Ni^{4+} when fully charged to 4.3 V or higher voltage [10]. A uniform but not dense coating layer can effectively reduce the direct contact between cathode

materials and electrolyte, and suppress the oxidation of electrolyte. There are some researches on the coated NCA in literature, which are compared with our results in Table 2. Obviously, our results are among the best in terms of cycle performance. More importantly, our method allows the simultaneous removal of surface lithium residues and formation of Li_3PO_4 coating layer, which is highly desirable for NCA materials.

For the rate performance, the cells were tested from 0.1C to 10C between 2.75-4.3V (Fig. 6d). As we know, both ionic conductivity and electronic conductivity are critical to good rate capability. For the bare NCA, lithium residues on the surface, including poorly conducting LiOH and Li_2CO_3 , make the NCA particles disconnected from each other. The removal of lithium residues and formation of ionic conductive Li_3PO_4 coating layer can, to some extent, facilitate the Li^+ transport [31]. However, a thick and dense Li_3PO_4 coating layer inevitably hinders the migration of lithium ions because of its limited ion conductivity. That's the reason why P3-NCA exhibits poor rate performance.

Fig. 7 shows the electrochemical impedance spectra (EIS) of the samples at 4.3V after three cycles between 2.75-4.5 V at 0.1C, and fitted by the equivalent circuit to further investigate the effect of lithium residues and Li_3PO_4 coating layer on the kinetics of lithium ions transfer. The obtained fitting values of R1, R2 and R3 are listed in Table 3. Generally, R1 corresponds to the resistance of electrolyte. R2, the first semicircle at high frequencies, is attributed to the charge transfer resistance for the migration of lithium ions through the surface layer on cathode particles. R3, the second semicircle, corresponds to overall contribution of the lithium counter electrode and the cathode surface layer, but in this particular case, we are not able to separate them with data fitting [32]. The inclined line at low frequencies named Warburg impedance is related to Li^+ diffusion through solid state electrode. Clearly, R2 of P1-NCA has a significant decrease after the removal of lithium residues compared with P0-NCA, which indicates the inactive lithium residues has a great impact on the lithium ions transfer through the surface layer. The reduced values for R3 for P1-NCA and P2-NCA may be mainly attributed to the reduction in the resistance of the cathode

surface layer. What's more, the apparent diffusion coefficients of lithium ions ($D_{Li^+}^{app}$) in various NCA have been estimated based on the Warburg impedance data in EIS plot [33, 34]. Similarly, we have derived $D_{Li^+}^{app}$ for our samples and the results are listed in Table 3. These results show that the presence of a Li_3PO_4 coating layer with a suitable thickness can increase the $D_{Li^+}^{app}$. It is obvious that the Li_3PO_4 coating layer can effectively suppress the side reactions, but, if too thick and dense, it obstructs the migration of lithium ions just like the lithium residues and cathode surface layer do.

Thermal stability of the Ni-rich materials is a critical factor in batteries concerning safety issues. Fig. 8 shows the DSC profiles of P0-NCA and P2-NCA electrodes at 4.3V after three cycles between 2.75-4.5V at 0.1C. For both samples, there are two exothermic peaks at 237°C and 286°C, respectively. Unlike other reported results [10, 35, 36], neither the onset temperature of thermal reaction (146°C) nor the exothermic peaks can be deferred by the Li_3PO_4 coating layer, which may depend on the kind of material and experimental conditions [37]. However, the heat generation is considerably decreased from 757 J g⁻¹ to 525 J g⁻¹ for P0-NCA and P2-NCA. This result indicates that the thermal stability of Ni-rich cathode materials can be improved by Li_3PO_4 coating due to the suppression of surface side reactions with organic electrolyte.

4. Conclusions

In this work, removal of the lithium residues and in-situ formation of Li_3PO_4 coating layer have been simultaneously achieved by coating $NH_4H_2PO_4$ on the hydroxide precursor $Ni_{0.815}Co_{0.15}Al_{0.035}(OH)_2$ before mixing with Li_2CO_3 . Thanks to the strong bonding energy of polyanion PO_4^{3-} and good ionic conductivity of Li_3PO_4 , the cycle performance both at room temperature and elevated temperature, and rate capability of NCA have been significantly improved. Moreover, the thermal stability can also be improved by Li_3PO_4 coating due to the suppression of surface side reactions with organic electrolyte. However, a thick and dense coating layer obstructs the migration of lithium ions just like the inactive lithium residues and cathode

surface layer do. This approach is expected to solve, in a simple and economical way, some problems for the applications of Ni-rich cathode materials in advanced lithium ions batteries.

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Figure captions:

Fig. 1 Schematic diagram of the coating process and the role of porous Li_3PO_4 coating layer.

Fig. 2 XRD patterns of as-prepared samples (a), and a magnified range of $20\text{-}26^\circ$ (b).

Fig. 3 SEM images of the P0-NCA (a), P1-NCA (b), P2-NCA(c) and P3-NCA(d); and element mapping of Ni (f), Co (g) and P (h) for P3-NCA (e).

Fig. 4 TEM images of P0-NCA, P2-NCA and P3-NCA.

Fig. 5 The pH values of NCA coated with different amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ after 10 minutes (a) and after one week (b).

Fig. 6 Electrochemical properties of as-prepared samples: initial charge-discharge curves (a), cycle performance at 25°C (b) and 55°C (c), and rate capability (d).

Fig. 7 Nyquist plots of Li/NCA half-cells at 4.3 V and their equivalent circuit.

Fig. 8 DSC profiles of P0-NCA and P2-NCA in the temperature range of $30\text{-}300^\circ\text{C}$.

Table 1. EDS results of P0-NCA, P1-NCA, P2-NCA and P3-NCA.

Table 2. A comparison of electrochemical performance of NCA coated with different materials

Table 3. Fitted R1, R2 and R3 values and the calculated diffusion coefficients of lithium ions of Li/NCA half-cells at 4.3V.

Table

Samples	Ni	Co	Al	P
P0-NCA	82.6	14.0	3.4	0
P1-NCA	81.7	15.3	3.0	0
P2-NCA	78.5	15.9	2.7	2.9
P3-NCA	76.3	14.6	2.9	6.2

Table

Coating materials	Cycle performance Capacity decay rate / cycle		Ref.
	pristine	coated	
Li_3PO_4 -2 wt% (2.75-4.3V)	0.30%@0.5C	0.11%@0.5C	This work
$\text{Ni}_3(\text{PO}_4)_2$ -0.5wt%(2.7-4.3V)	0.47%@0.5C	0.25%@0.5C	[22]
FePO_4 -2wt%-(2.8-4.3V)	0.29%@2C	0.12%@2C	[23]
TiO_2 -0.6wt%-(3-4.3V)	0.20%@1C	0.20%@1C	[18]
MnO_2 -1wt%-(2.8-4.3V)	0.19%@2C	0.12%@2C	[20]
$\text{Li}_2\text{O-B}_2\text{O}_3$ -2wt%-(3-4.3V)	0.25%@1C	0.06%@1C	[17]
LiCoO_2 -3wt%-(2.8-4.3V)	0.24%@2C	0.10%@2C	[19]
AlF_3 -1wt%-(2.7-4.3V)	0.21%@0.5C	0.15%@0.5C	[5]

Table

Samples	R1 / Ω *cm ²	R2/ Ω *cm ²	R3/ Ω *cm ²	$D_{Li}^{pp} / \text{cm}^2 \cdot \text{s}^{-1}$
P0-NCA	2.4	83.1	19.8	8.1*10 ⁻¹³
P1-NCA	2.7	26.5	12.9	6.6*10 ⁻¹²
P2-NCA	2.5	31.1	12.8	5.8*10 ⁻¹²
P3-NCA	2.4	74.1	17.4	1.3*10 ⁻¹²

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