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Improved electrochemical performances of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material by reducing lithium residues with the coating of Prussian blue

Yan Ding^{a,b}, Bangwei Deng^{a,b}, Hao Wang^{a,*}, Xiang Li^a, Tao Chen^{a,b},

Xinxiu Yan^{a,b}, Qi Wan^a, Meizhen Qu^a, Gongchang Peng^{a,*}.

a Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu

610041, PR China

b University of Chinese Academy of Sciences, Beijing 100049, PR China

*Corresponding Author

E-mail:pgc0102@163.com(G. Peng), wanghao213@mails.ucas.edu.cn(H. Wang). Tel: +86 28 85228839. Fax: +8628 85215069.

Abstract

Reducing the lithium residues on the surface of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM) cathode is one of the most main challenges in Li-ion battery research. To address this task, a surface coating of Prussian blue (PB) of metal-organic framework is applied to NCM cathode to solve this intractable problem via a simple dry-coating method. The transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) results show that the uniform smooth coating can provide a protective shell to block H₂O and CO₂ absorption from the air, suppressing lithium residues formed on the surface. The color change

experiment between PB and Li residuals illustrates PB can react directly with surface residual lithium species. As a result, the amount of residual lithium, such as LiOH and Li₂CO₃, is significantly reduced. The 0.5 wt% PB-modified NCM delivers a high discharge capacity retention of 81% after 500 cycles at 1 C discharge rate and exhibits a superior storage property after storing in air for 14 days. Furthermore, electrochemical impedance spectroscopy (EIS) confirms that the PB-NCM could hinder the impedance increase during cycling. These results clearly indicate that the PB coating layer contributes to the reduction of lithium residues and the creation of thinner cathode-electrolyte interface, improving structural stability and cycling performance of NCM.

Keywords: lithium-ion battery; LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂; Prussian blue coating; lithium residues; storage characteristic

1. Introduction

Lithium-ion batteries (LIBs), as power sources, are rapidly developing from portable electronic devices to electric vehicles (EVs). To meet the extension of cruising range above 300 miles per charge in new energy EVs, nickel-rich layered lithium transition-metal oxides such as Li[Ni_xCo_yM_{1-x-y}]O₂ (M = Mn, and Al; x > 0.5) have attracted significant attention. As one of the most promising cathodes for the next-generation LIBs, it has many excellent advantages such as large reversible capacities, good cycle performance, high operating voltage (> 3.5 V vs. Li/Li⁺) along

with relatively low cost. ^[1-3] However, the presence of a large amount of residual Li on the surface is one of the major problems limiting large-scale application. Firstly, in the synthesis process of Ni-rich layered cathode material, the excess lithium compound is often needed to obtain well-ordered layered structure with lower cation mixing. However, the residual lithium source will react with H₂O and CO₂ to form Li₂CO₃ and LiOH on the surface in ambient air. ^[4-7] These lithium residues often cause side reactions between the electrode material surface and electrolyte, which induce a thicker cathode-electrolyte interface layer (CEI) formed. It would aggravate the deterioration of the electrode surface structure and the electrochemical performance. In addition, the above processes will increase the possibility of gas release simultaneously, leading to safety issues of LIBs. [8-9] Secondly, Li residuals easily react with slurry components during mixing and might turn to gel by the polymerization of N-methyl-2-pyrrolidone (NMP), making it difficult for coating onto the Al foil, thus complicating electrode preparation.

To overcome the above critical problems of Ni-rich cathode materials, many significant efforts have been done to reduce or remove residual lithium on the cathode surface in the recent years. Among them, using the deionized (DI) water or ethanol to remove residual lithium is the simplest method ^[9-10]. However, this process leads to the changes of surface structure, resulting in more NiO production, which destroys the structure seriously in high-nickel ternary materials. ^[11] Another common method is coating inert materials (such as Al₂O₃, La₂O₃ and ZrO₂) on the surface of the cathode to separate the reaction between the cathode and H₂O, CO₂ in air, suppressing lithium

residues formed on the surface. ^[12-14] Nevertheless, this electrochemically inactive protective coating could increased impedance and reduced capacity. In addition, lithium-reactive coating materials such as AIPO₄, Co₃(PO4)₂, and H₃PO₄ are another type of surface modification material. ^[15-17] They are used to react directly with surface residual lithium species (Li₂O, LiOH and Li₂CO₃) to produce Li⁺ compounds Li_xAIPO₄, Li_xCoPO₄, and Li₃PO₄, which provide fast Li⁺ ion conductors and enhance the cycle performance. Although these surface coating methods show a certain degree of improvement in electrochemical performance, most of the process conditions have to undergo wet coating, which is unsuited for industrial production. Therefore, reconsideration of the coating material is necessary in order to decrease the residual lithium on the surface whilst improving the electrode performance, by using a dry process to wrap a weak acidity compound.

Prussian blue (PB) has a stable metal-organic framework, which provides rich sites and transport channels for reversible intercalation/deintercalation of alkali metal ions. ^[18-19] Moreover, it not only contains two redox active centers Fe from Fe-C \equiv N-Fe which can increase the capacity, but also exhibits acidic active sites (H₃O⁺) derived from occupying the alkali metal in PB, which could react with residual lithium on the surface to form a protective layer. ^[20-21] As early as in 2013, Chen et al, ^[22] modified LiMn₂O₄ with Iron Hexacyanoferrate, showing excellent capacity retention, but the reaction at electrode surface was not mentioned. Therefore, we use the metal-organic compounds Fe[Fe(CN)₆] as a surface modifier to lower residual lithium of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NCM) materials with a simple dry-coating method. The **4**/**19** structure, morphology, and cycling performance of pristine NCM materials and PB coated NCM materials will be discussed detailedly in the following part, as well as the storage property.

2. Experiment

2.1 Synthesis and surface modification

NCM was synthesized by means of a high temperature calcination. The $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor (Ningxia Orient Tantalum Industry Co., Ltd.) and LiOH·H₂O (Aladdin) were homogeneously mixed at a molar ratio of 1:1.05. Subsequently, ball-milled evenly at a rolling speed of 250 rpm for 5 h in an All-round planetary micro-miller. And then, there was a two-step calcination process, preheated at 470 °C in dry air for 3 h, and calcined at 835 °C for 12 h. The heating rate was 5 °C min⁻¹. Ultimately, the sample was obtained after naturally cooling to room temperature.

The PB was prepared by a co-precipitation procedure. Briefly, the first step was to add sodium citrate ($C_6H_5Na_3O_7\cdot 2H_2O$, Aladdin) and ascorbic acid (VC, Aladdin) to $Na_4Fe(CN)_6\cdot 10H_2O$ (Aladdin) and $FeC_2O_4\cdot 2H_2O$ (Chengdu West Asia Chemical Co., Ltd.), into deionized (DI) water and mixed uniformly, respectively. The second part included adding HCl-incorporated DI water to the above two solutions, slowly adding the sodium ferrocyanide solution to the ferrous oxalate solution before magnetic stirring for 30 minutes at 40 °C. The third procedure was sealed and placed the solution in the dark for the whole night, then the precipitate was washed with deionized water several times. Finally, the product was put into the freeze dryer until the sample was powdered.

For surface modification, PB and NCM were mixed by a dry process using agate mortar and then heated at 200 °C for 2 h in flowing air gas (0.2 L min⁻¹) to obtain modified material, recorded as PB-NCM.

2.2 Characterization

The crystalline structure and crystal lattice parameters were characterized by powder X-ray diffraction (XRD, X'pert MPD DY1219) with Cu Ka radiation. Fourier transformed infrared spectrum (FTIR, Thermo Fisher Nicolet iS10) was carried out to inspect the existence of functional groups at samples over the range of wave number from 500 to 3000 cm⁻¹. Morphological changes and elements distribution were determined using scanning electron microscopy (SEM, INCA Pen-taFETx3) with energy dispersive spectroscope (EDS) mappings. A high resolution transmission electron microscope (HRTEM, JEOL JEM-2010F) was utilized to further analyze the surface morphologies of samples. The surface chemical compositions of the samples were measured by X-ray photoelectron spectroscopy (XPS, PHI 5600 Physical Electronics). To evaluate pH values, 1 g of cathode materials were immersed into 100 mL of water, and then the pH of the mixtures was measured after continuous stirring for 3 min. The amount of residual lithium was estimated by a titration method, using 0.015 M HCl as a standard solution, phenolphthalein and bromocresol green-methyl red as indicator solution. Karl Fischer Moisture Titrator (915 KF Ti-Touch, Metrohm) was used to determine the water content.

2.3 Electrochemical measurements

Composite positive electrodes were fabricated by 80 wt % active materials (pure NCM or PB-NCM), 10 wt % conductive Super-P and 10 wt % polyvinylidene difluoride (PVDF), which were all dissolved in NMP and pasted onto aluminum foil as uniform as possible. Subsequently, the electrode was dried overnight at 105 °C under vacuum. Then, the coated Al foil was cut into circular electrodes with a diameter of 12 mm. The mass loading of the active material was approximately 1.82 mg cm $^{-2}$. The CR2032 coin cells were assembled in a glovebox filled with Ar gas, which consisted of the active material that was used as a cathode, Li metal as an anode, Celgard 2500 as a separator, and 1M LiPF₆ dissolved in ethylene carbonate (EC)-dimethyl carbonate (DMC)-ethyl methyl carbonate (EMC) (1:1:1 in volume) as electrolyte (Shandong Hairong Power Material Co., Ltd.). Galvanostatic charge-discharge measurements were performed on a battery testing system (Neware CT-4008-5V5ma) in the potential range of 2.8 - 4.3 V (vs. Li/Li⁺). Before cycling tests, cells were activated by galvanostatic charge-discharge at 0.2 C for 3 cycles, where 1 C was set as 160 mA g^{-1} . The electrochemical activities of the cathode were characterized via electrochemical impedance spectroscopy (EIS) using the AUTOLAB PGSTAT302N electrochemical system (Metrohm) in the frequencies ranging from 20 mHz to 100 KHz at the full charge state (4.3 V). The cyclic voltammograms (CVs) were carried out with a potential window of 2.8 - 4.3 V using a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

3.1 Structure and morphology

As seen in Fig. 1, the XRD patterns of the NCM and PB-NCM (0.5 wt%) powders are obtained to investigate the structural changes after the surface coating. It is clearly that the diffraction pattern of the PB-NCM powder is identical to that of the pristine NCM powder. All samples exhibit a typical hexagonal α-NaFeO₂ layered-structure belonging to the space group R3m, and well-grown split doublets of (006)/(102) and (108)/(110) pairs indicate the formation of a well-ordered layer structure.^[23] Diffraction peaks corresponding to PB are not observed in the PB-NCM sample, since the nanosized PB coating content may be too low to be detected. In addition, the lattice parameters of the pristine and the coated samples calculated from the XRD measurements are listed in Table S1. The value of c/a, which is used to evaluate the layered structure of the cathode materials, is almost identical. Thus, the coating layer has almost no influence on the host crystal form of pristine particles. ^[24] Since the value of I(003)/I(104) reflects the cation disorder, and the value of PB-NCM is higher than that of NCM, we conclude that PB-NCM has the lowest level of Li⁺/Ni²⁺ cation mixing.^[25] Therefore, there are reasonable justifications to believe that 0.5 wt% PB-NCM is beneficial to the electrochemical performance.

Fig. 2 (a) shows the surface morphology of 0.5 wt% PB coated NCM. After wrapping with PB, the samples are retained the spherical-like particles well with an average diameter of 10 μ m. Interestingly, the formed PB-NCM microspheres have a relatively rougher surface than the pristine NCM microspheres, this is due to the product of the reaction between PB and the lithium residues, creating more surface pores onto the NCM microspheres.^[26-27] Simultaneously, Some of the particles are **8/19**

covered on the surface of pristine NCM, which is not observed in the coated samples by SEM and could be ascribed to Li residuals (LiOH and Li₂CO₃) (see Fig. S1).^[28] In addition, the elemental mapping is used to further verify the uniformity of the coating layer. Fig. 2b shows the elemental mapping of the 0.5 wt% sample, which demonstrates that Ni, Co, Mn and Fe are homogeneously distributed on the particle surface. The TEM image (Fig. 2c) confirms the presence of amorphous lithium residues attached the surface of pristine NCM. ^[29] As stated in the introduction, the excess lithium is necessarily needed to synthesize a well-ordered layered structure with lower cation mixing. As shown in Eq. (1–4), the active Li₂O and / or Li₂O₂ on the surface of nickel-rich cathode are prone to react with CO₂ and H₂O in air atmosphere, resulting a residual Li layer that consists with Li₂CO₃ and LiOH. ^[4-7]

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \tag{1}$$

$$Li_2O + H_2O \rightarrow 2LiOH$$
 (2)

$$2H_{3}O^{+} + Li_{2}CO_{3} \rightarrow 2Li^{+} + 3H_{2}O + CO_{2}$$
(3)

$$H_3O^+ + LiOH \rightarrow Li^+ + 2H_2O \tag{4}$$

$$PFe[Fe(CN)_6] + 3Li_2CO_3 \rightarrow 2Li_3Fe(CN)_6 + Fe_2O_3 + 3CO_2$$
(5)

$$2Fe[Fe(CN)_6] + 6LiOH \rightarrow 2Li_3Fe(CN)_6 + Fe_2O_3 + 3H_2O$$
(6)

A homogenous coating layer of 5-8 nm which reaction with PB can be observed on the 0.5 wt% sample, according to Eq.5-6. It is obviously noted that no lattice fringes correspond to PB, indicating that the ferricyanide compounds are amorphous. The parallel lattice conforms to the layered materials with interplanar distances of 0.463 nm (Fig. 2d). Along with the XRD and HRTEM results, it is confirmed that PB-NCM 9/19

has a typical (003) crystal plane of the layered phase (space group R3m).

In order to investigate the reaction of Li residuals and PB, the amount of Li residuals in the pristine and coated sample were measured by titration as listed in Table 1. The content of Li residuals is decreased by coating layer in the samples, implying that these species reacts to form other compounds during this process. Furthermore, the NCM powder was suspended in DI water and stirred for 30 minutes, then the solution (12 ml) mixed with PB (0.0025 g) after filtered so that the reaction between PB and lithium residues could be observed more intuitively. The color change is shown in Fig. 3 and Videos S1. The pH value is also one of the critical quality indicators for Li residuals. A low pH value (9.22) of above mixed solution means a decrease of residual lithium, compared with the cathode materials (11.90), and the pristine NCM and PB-NCM (0.5 wt%) suspension are 11.53 and 11.18 after stirred for 3 minutes. (see Fig. S2). Therefore, the reaction of the PB and residual lithium can effectively reduce the amount of residual lithium on the NCM surface.

To investigate the lithium residues on the surface of the NCM and PB-NCM (0.5 wt%), the FT-IR spectra are presented in Fig. S3. According to the previous reports, the band at 3200-3600 cm⁻¹ is considered as the stretching vibration of O-H from LiOH. ^[12] The absorption peaks at about 1390 and 875 cm⁻¹ are assigned to anti-symmetric stretching vibration and out-plane flexural vibration of CO_3^{2-} from Li₂CO₃, respectively. ^[30] The band at 2270–2400 cm⁻¹, which is attributed to the O=C=O antisymmetric stretching vibration, it not observed in PB-NCM, indicating that PB-NCM much more resistant to CO_2 . ^[31] Bands at 2100 cm⁻¹ detected in the **10**/**19**

PB-NCM sample are ascribed to the asymmetric stretching C-N vibrations in $Li_3Fe(CN)_6$ compounds. ^[32] Furthermore, the peaks of O-H and C-O bands for the NCM are prominent than those of the coating samples. It is illustrated that the amount of LiOH/Li₂CO₃ on the surface of NCM could be effectively reduced by PB-coating.

XPS analysis was carried out to investigate the effect of PB coated on the oxidation states of some elements for samples. Fig. 4a shows the Ni XPS spectra for the NCM and the PB-NCM sample, the two peaks at 855.0 eV and 872.3 eV are both attributed to Ni²⁺, assigning to two orbits of Ni 2p3/2 and Ni 2p1/2, while the peaks at ~854.5 eV and ~855.9 eV correspond to the Ni 2p3/2 indicate that the valence state of Ni near the surface is a mixture of Ni²⁺ and Ni³⁺. ^[33] It is noteworthy that the intensity ratio of Ni²⁺/ Ni³⁺ in pristine sample is stronger than that of PB-NCN, indicating the lower cation mixing after NCM coated with PB, which supports the transmission of Li⁺ ions and the improvement of electrochemical performance. It is in good agreement with the results of XRD. The C 1s peaks (Fig. 4b) at 284.6 eV and 289.5 eV belong to adventitious carbon present in the analysis chamber and Li₂CO₃ component, respectively. ^[34] It is obvious that the intensity of the C 1s peak at 289.5 eV is significantly reduced after coating with PB, demonstrating the lower amount of lithium residues on the surface due to the formation of the $Li_3Fe(CN)_6$ by reaction between lithium residues and coating material. Moreover, a noticeable peak at 283.4 eV is ascribed to $Fe(CN)_6^{3-}$ in PB-NCM. The O 1s peaks (Fig. 4c) located at 529.3 eV are attributed to the lattice oxygen, while the peaks at 531.6 eV is related to adsorbed species such as LiOH and Li₂CO₃. ^[35] The intensity of the lattice oxygen peak is 11 / 19

greatly enhanced after PB-coating reveals that the PB coating layer can bring more lattice oxygen and decrease oxygen defects. ^[36] Besides, Fig. 4d and e display the XPS spectrum of the Fe 2p and N 1s for the 0.5 wt% PB-NCM sample, respectively. The peaks at 708.5 eV are attributed to Fe³⁺ which may originate from $Fe(CN)_6^{3-}$. And the N 1s characteristic peaks are detected at 397.8 eV, in well accordance with the results of FTIR, further illustrating the PB is coated on the surface of NCM.

3.2. Electrochemical Results and Discussion.

The as-prepared NCM and PB-NCM materials were used as the cathodes to evaluate their electrochemical performance. Fig. 5a shows the first charge-discharge curves of the samples at 0.2 C (1 C = 160 mA g^{-1}) between 2.8 V and 4.3 V. Five samples display similar and smooth curves, indicating that the PB coating layer brings a minor change during the charge/discharge process. The NCM sample exhibits an initial discharge capacity of 165.2 mAh g^{-1} and 86.6% initial Coulombic efficiency, while the initial discharge capacities of the PB-NCM samples are 169.2 mAh g⁻¹ (0.2 wt%), 175.1 mAh g⁻¹ (0.5 wt%), 172.9 mAh g⁻¹ (1 wt%) and 162.8 mAh g⁻¹ (2 wt%), with Coulombic efficiency values slightly increase to 87.7% in 0.5 wt% coating. In general, the irreversible capacity in the first cycle is attributed to the side reaction between organic electrolyte and electrode to form the CEI. On the one hand, due to the surface modification by PB-coating, the side reactions between the NCM cathode and electrolyte are restrained, leading to the number of irreversible Li⁺ ions decreased. On the other hand, the charge/discharge voltage platform of PB is lower than that of NCM, which limits the great improvement of initial efficiency (see Fig. S4). The 12 / 19

above results suggest that the suitable coating layer leads to the increase of the initial discharge capacity but show a slight effect of elevating the Coulombic efficiency. For the rate capabilities of the NCM and PB-NCM (Fig. 5b), the cells are tested from 0.2 C to 5 C between 2.8 and 4.3 V and then back to 0.2 C, sustaining each rate for five cycles. It is obvious that the discharge capacities of both samples gradually decrease with increasing current density due to the polarization. However, the capacity of PB-NCM (0.5 wt%) has a clear increase compared with the NCM counterpart, showing 171.8, 165.8, 159.5, 150.9 and 133.9 mAh g⁻¹ at 0.2, 0.5, 1, 2 and 5 C, respectively. Such relatively higher discharge capability of PB-NCM is ascribed to the stability of the electrode/electrolyte interface during the charge/discharge process.

To further prove the effect of PB coating layer on the performance of the samples, cycling performance of the NCM and the PB-NCM at 25 °C are showing in Fig. 5c. The samples with 0, 0.2, 0.5, 1 and 2 wt% of PB coating deliver the discharge capacities of 148.1, 149.0, 153.8, 151.9 and 146.4 mAh g⁻¹ after 200 cycles at 1C, respectively. Compared with the NCM, the PB-NCM (0.5 wt%) obtains significantly enhanced capacity retention of 95.8%. Furthermore, long-life cycle performance of PB-NCM (0.5 wt%) and NCM in constant cut-off potential between 2.8 and 4.3 V vs. Li/Li⁺ at 1C is shown in Fig. 5d. Apparently, PB-NCM (0.5 wt%) presents an excellent cycle capacity retention of 81% after 500 cycles. In addition, the corresponding charge-discharge curves are shown in Fig. S5, it directly illustrates that the polarization has been suppressed by coating PB, thereby stabilizing the electrochemical properties of the material. The above results all indicate that the

sample with 0.5 wt % PB coating exhibits the best electrochemical properties including high reversible discharge capacity and large capacity retention (Compared with other coating materials, see Table S2). It is associated with the PB coating layer, because it not only protecting active materials from electrolyte erosion, but also removing lithium residues through forming lithium-reactive coating material Li₃Fe(CN)₆, which has a positive impact on reducing surface impedance and restraining electrolyte decomposition (see Fig. S6). ^[37]

In order to study electrochemical reversibility, the cyclic voltammograms of the pristine and 0.5 wt% PB-NCM sample are recorded in the 2.8 – 4.3 V voltage range at a scan rate of 0.1 mV s⁻¹ (Fig. 6). A pair of anodic/cathodic peaks centers at the voltage range of 3.6 - 4.0 V is found in both samples, which correspond to delithiation/lithiation process in the oxidization/reduction reaction of Ni²⁺/Ni⁴⁺ respectively. The oxidation peaks obviously shift to lower voltage which is generally related to the activation process of the electrode in the first cycle. It can be easily found that oxidation peaks of both samples shift negatively during initial three cycles, and after 100 cycles, the peak positions were shifted towards higher resistance values, while the reduction peaks remain relatively steady. This noticeable change may arise from the changing of polarization.^[38] Compared to the pristine NCM, PB-NCM (0.5 wt%) sample exhibits a smaller shift in the oxidation peaks than in the pristine sample, which might be due to the PB coating layer effectively impede the side reaction between electrolyte and electrode material, bringing a steady cathode-electrolyte interface (CEI) layer and decreasing interfacial impedance between particles and the

electrolyte during cycling. ^[39] According to previous reports, the potential interval value ΔEp is also used to evaluate the electrode polarization. With the cycles continuing, the PB-NCM (0.5 wt%) sample exhibits a smaller value of ΔEp , from 0.118 V (ΔE_1) to 0.056 V (ΔE_2), 0.053 V (ΔE_3) and 0.074 V (ΔE_{100}), whereas the ΔEp value of the pristine sample is large ($\Delta E_1/\Delta E_2/\Delta E_3/\Delta E_{100}=0.276/0.102/0.071/0.086$ V), indicating that the lower polarization are realized on the modified samples. Additionally, the PB-NCM cathode has more sharp oxidation peaks, implying better conductivity on coating material. The above results are consistent with the superior electrochemical properties.

To further investigate the impedance difference of the samples, Electrochemical impedance spectroscopy tests of the pristine and the PB-NCM(0.5 wt%) sample after various cycles at a fully charged state of 4.3 V are shown in Fig. 6c and 6d. Generally, Nyquist plots consist of a typical semicircle in the high frequency region, a similar-semicircle in the middle frequency and a straight line in the low frequency, respectively. The intercept on real axis stands for the ohmic resistance (R_e). The semicircle at high frequency represents surface film resistance (R_f), which is related to the situation of Li ion migration through the CEI film. The similar-semicircle in the middle frequency corresponds to charge-transfer resistance (R_{ct}), reflecting the lithium-transfer rate and interfacial capacitance at the electrode/electrolyte interface. What is more, the oblique line at low frequency means the impedance for Li-ion diffusion inside electrode bulk. ^[40] The simulated impedance parameters using the equivalent circuit are listed in Table 2. It can be clearly seen that both samples show

higher R_f values in the premier cycle than the 100th cycle due to the activation process occurred in the initial cycle, which accordant with CV results. Furthermore, the R_f values of the 0.5 wt% coating sample are always smaller than those of pristine NCM, and maintain stability after 100 cycles, implying that a more stable and thinner CEI layer is established after coating with PB.^[41] As is well known, the surface layers of thickening have components of residual lithium, which increase the interfacial resistance due to their intrinsic insulating properties for both electrons and Li⁺. Thus, it is reasonable to attribute lower R_f values to reduce inactive lithium residues. The R_{ct} of NCM increases from 18.9 Ω at first cycle to 693.7 Ω at the 200th cycle, while the R_{ct} of 0.5 wt% PB-NCM obviously decreases after each cycle due to the effectively suppressing of the cathode surface passivation between the electrode and electrolyte. Combined with the above electrochemical performance and CV results, we conclude that the PB coating layer can inhibit undesirable side reaction between residual lithium and electrolyte, thus strengthening the reversible Li⁺ content and suppressing the impedance increase.

3.3. Storage performance

As for the Ni-rich materials, poor storage performance and rapid moisture uptake have limited its large-scale application. Therefore, it is worth exploring its storage property. We investigated NCM and PB-NCM (0.5 wt%) storage property after 7 and 14 days of exposure in air with a relative humidity of 50% at 25°C. The FTIR results give more evidence of the surface changes on NCM and PB-NCM during the storage, as shown in Fig. 6. Compared with pristine samples, there appears a new adsorbed **16**/**19**

peak at 1430 cm⁻¹ after storage, which are assigned to antisymmetric stretching vibration of CO_3^{2-} from Li₂CO₃. ^[31] The adsorbed band at 3200-3600 cm⁻¹ exists both for the pristine material and the storage materials. Furthermore, although the absorption peaks of Li₂CO₃ show an increasing trend with the extension of storage time, the Li₂CO₃ peaks intensity reduce after modifying by the PB. This means that the formation of Li₂CO₃ is suppressed by PB coating layer. In addition, the forming of LiOH mainly resulted from the reaction between the surface of materials and moisture, so the content of water on NCM and PB-NCM surface before and after 7 and 14 days of exposure in air has been compared in Table 3. In the case of PB-NCM, the water content increased from 2596 to 4740 and 6514 ppm after7 and 14 days storage in air, respectively. While the water content of NCM increased rapidly from 3635 ppm to 6953 and 8440 ppm, respectively. Hence, following the PB coating treatment, less water had been absorbed on the materials surface during the storage process. Fig. S7 presents the SEM images of the pristine samples and the storage materials. Notably, the pristine materials of NCM and PB-NCM have a clear profile (Fig. S7a and S7b). However, after being stored for 14 days, the NCM and PB-NCM samples show a thin layer of transparent substance presenting on the particle surface (Fig. S7c and S7d), which considered to be a mixture of LiOH, LiHCO₃, and Li₂CO₃. ^[42-43] Compared to NCM, the surface of PB-NCM looks relatively distinguishable, this verify the FTIR results.

The first charge-discharge curve and cycling performance of the pristine samples and the storage materials after storage in air for 7 and 14 days are displayed in Fig. 8.

The cathodes of NCM show a large capacity decrease with the extension of storage time. For instance, the initial discharge capacity of NCM are 160.8 mAh g⁻¹ and 152.6 mAh g⁻¹ after 7 and 14 days, respectively. It is obviously lower than that of the PB-NCM samples (170.5 mAh g⁻¹ and 163.2 mAh g⁻¹). Besides, the charging curve of the NCM (14 days) shows a steep increase of voltage up to 3.92 V in the early stage and then subsequently decays to the plateau at 3.83 V. For the PB-NCM (14 days), the charging curve displays a steep increase of voltage up to 3.81 V, but the voltage decay is less subsequently. These results indicate a larger electrochemical polarization for the NCM because more insulating lithium residues is produced after exposing to the air. ^[35] This is coincident with the trends of the moisture uptake. Furthermore, the stored samples PB-NCM (7 days and 14 days) exhibit discharge capacities of 135.6 mAh g⁻¹ and 126.0 mAh g⁻¹ with the corresponding capacity retention of 91.6% and 93.3% after 100 cycles, respectively. In contrast, the capacity retention of NCM after storage in air for 7 and 14 days are only 84.0 % and 77.6%. The improved electrochemical performances are related to PB coating layer, which reduces the lithium residues content and improves the storage property.

4. Conclusions

In this study, we have successfully applied a simple method to synthesize Prussian blue and using them to modify the surface structure of NCM through dry coating at lower temperatures. The PB coating layer can effectively reduce lithium residues content and suppress side reaction between electrode and electrolyte, forming the stable CEI layer and crystal structure, so that the modified material presents better 18/19

capacity retention and longer-life cycling stability than the pure NCM. The TEM, SEM, and XPS analyses confirm the existing of a coating layer on the surface of 0.5 wt% PB-NCM sample. Apart from this, it is demonstrated that the PB coating layer of metal-organic framework contributes to lower polarization of the particles and reduce the charge transfer resistance according to the CV and EIS analyses. Electrochemical tests showed that 0.5 wt% PB-NCM exhibited excellent cycling performance with 81% capacity retention after 500 cycles between 2.8 V and 4.3 V, and superior storage property (126 mAh g⁻¹ discharge capacity at 1C) after storing in air for 14 days. Overall, this facile coating approach shows wide usage for decrease lithium residues and builds a stable interface for cathode materials, which could be employed to other Ni-rich layered oxide cathodes for large-scale production.

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Table(s):

Table 1	Li	residual	s in	the	pristine	and	PB	-NCM	sam	ples.

Sample	Li ₂ CO ₃	LiOH	Total Li			
	(ppm)	(ppm)	(ppm)			
Pristine	6317.60	4093.74	2373.48			
PB-NCM (0.5 wt%)	4156.31	2693.25	1561.50			
Total Li (ppm) =	Atomic weight o molecular weight of	$\frac{\text{of Li}}{\text{Li}_2\text{CO}_3}$ × Li ₂ CO ₃ (ppm)			
+ $\frac{\text{Atomic weight of Li}}{\text{molecular weight of LiOH}} \times \text{LiOH(ppm)}$						

Sampels	Pristine			PB-NCM (0.5 wt%)			
	R _e (Ω)	$R_{f}(\Omega)$	$R_{ct}(\Omega)$	$R_e(\Omega)$	$R_{f}(\Omega)$	$R_{ct}(\Omega)$	
1st	4.1	24.5	18.9	3.3	19.7	11.7	
100th	1.3	13.5	350.7	2.0	18.8	238.1	
200th	2.7	30.3	693.7	1.9	18.8	308.2	
	Č						

Table 2 The impedance parameters of equipment circuit for the pristineand 0.5 wt% PB-NCM samples after different cycles

Somplag	Dricting	7 dava	14 dava
Samples	Pristine	7 days	14 days
	(ppm)	(ppm)	(ppm)
NCM	3635	6953	8440
PB-NCM (0.5 wt%)	2596	4740	6514

7 and 14 days of exposure in air with a relative humidity of 50%

Figures:





















Fig. 5







Figures Captions:

Fig. 1 (a) XRD patterns of NCM and PB-NCM (0.5 wt%) and (b)-(c) enlarged XRD peaks.

Fig. 2 (a) SEM image of PB-NCM (0.5 wt%) microsphere; (b1–b4) EDS mapping of PB-NCM (0.5 wt%); (c) TEM image of NCM and (d) HRTEM image and lattice fringes of PB-NCM.

Fig. 3 Photo images of the reaction between PB and NCM solution after stirring for (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min and (e) 4 min.

Fig. 4 XPS spectra of (a) Ni 2p, (b) C 1s and (c) O 1s for NCM and PB-NCM; (d) Fe 2p for PB-NCM sample, (e) N 1s for the PB-NCM sample, and (f) original XPS survey spectrum for PB-NCM.

Fig. 5 (a) Initial charge and discharge curves of NCM and PB-NCM at 0.2 C; (b) rate capability under variable current rate; (c) cycling performance at 25 °C under a current rate of 1 C and (d) cycling performance at 1 C for the pristine and PB-NCM (0.5 wt%) sample at 25 °C within 500 cycles. All measurements are conducted in the voltage range of 2.8 - 4.3 V vs Li/Li⁺.

Fig. 6 Cyclic voltammograms at a scan rate of 0.1 mV s⁻¹ at 25 °C for (a) pristine and (b) PB-NCM (0.5 wt%) sample, the Nyquist plots of (c) pristine and (d) PB-NCM (0.5 wt%) sample, (e) equivalent circuit used for simulating the experimental impedance data.

Fig. 7 FTIR spectrum of NCM and PB-NCM (0.5 wt%) before and after stored in air for 14 days.

Fig. 8 (a) Initial charge-discharge curves at 0.2 C and (b) cycling performance at 1 C for the pristine and PB-NCM (0.5 wt%) samples after storage in air for 7 days and 14 days.

HIGHLIGHTS

- PB-modified NCM is synthesized by a simple dry-coating method.
- A uniform and thin layer of PB is successfully coated on the surface of NCM.
- PB coating reduces the lithium residues on the surface of NCM.
- 0.5 wt% PB coating enhances the electrochemical properties of NCM.
- PB-NCM sample exhibits superior storage property.