

Alleviating the Storage Instability of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ Cathode Materials by Surface Modification with Poly(acrylic acid)

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Cite This: ACS Sustainable Chem. Eng. 2021, 9, 7466–7478





ABSTRACT: The storage stability of the nickel-rich ternary cathode materials deteriorates with the increase of Ni content, which has become a major obstacle in the practical application process of the materials. In this work, a handy and effective surface modification method with poly(acrylic acid) is developed to solve this issue, and the air sensitivity of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ materials is alleviated successfully by the protective poly(acrylic acid) coating. The poly(acrylic acid) coating can not only reduce the surface alkalinity of NCM811 materials but also prevent direct contact between the materials and H₂O/CO₂ in the air. Compared with the pristine materials, the modified materials show smaller weight increase, higher capacity and coulomb efficiency, and less change of morphology and structure after storage in the same conditions (55 °C, 80% RH). The fewer surface impurities, more stable near-



surface structure, and better electrochemical performance for the modified materials benefit from the protective layer constructed by poly(acrylic acid). This work provides a new perspective and possibility for the improvement of storage stability of nickel-rich materials, showing that modifications with other polymers containing acidic groups are also likely to be feasible for nickel-rich cathode materials.

KEYWORDS: LiNi_{0.8}Co_{0.1} $Mn_{0.1}O_2$, Storage stability, Poly(acrylic acid), Cathode, Lithium-ion battery

INTRODUCTION

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Ternary nickel-cobalt-manganese cathode materials (Li- $Ni_x Co_y Mn_{1-x-y}O_2$) with superior performance have received a lot of attention since they were synthesized successfully for the first time in 1999.¹ The advantages of $\text{LiNi}_x \text{Co}_v \text{Mn}_{1-x-v} \text{O}_2$ materials are mainly manifested in high capacity and relatively low cost. Besides, partial substitution of Ni with Co and Mn makes the stability of $LiNi_xCo_yMn_{1-x-y}O_2$ materials better than that of LiNO₂ materials.² Moreover, the rise in nickel content increases the capacity of LiNi_rCo_vMn_{1-r-v}O₂ materials effectively. And the nickel-rich LiNi_xCo_yMn_{1-x-y}O₂ ($x \ge 0.8$) materials have achieved an extremely high reversible discharge capacity up to 200-250 mAh g⁻¹, which have become one of the most prospective high energy density cathode materials for lithium-ion batteries and have great potential in practical application and development.³ However, the nickel-rich LiNi_xCo_yMn_{1-x-y}O₂ materials still suffer from cycling instability, storage thermal instability, and storage instability. Many methods such as doping,⁴⁻⁶ coating,^{7,8} and synergistic strategy of doping and coating^{9,10} have been proposed to improve the cycling stability of nickel-rich LiNi_xCo_vMn_{1-x-v}O₂ materials. In contrast, there is less research on the improvement of storage instability of nickel-rich materials, although the storage degradation mechanism of the materials have been studied

in-depth.¹¹⁻¹⁵ According to the literature,¹⁶⁻²² the storage instability is closely associated with the surface chemical instability of the nickel-rich $\text{LiNi}_x \text{Co}_v \text{Mn}_{1-x-v} \text{O}_2$ materials. First, excess LiOH is added in the manufacturing process of the nickel-rich $\text{LiNi}_x \text{Co}_y \text{Mn}_{1-x-y} \text{O}_2$ materials in order to ensure the complete lithiation of nickel oxide and obtain the materials with excellent cationic ordered structure, thus, residual lithium compounds will remain on the surface of the materials. Second, the surface of nickel-rich cathode materials with strong alkalinity will react with H_2O/CO_2 when exposed to humid air, which causes the generation of surface impurities such as LiOH and Li₂CO₃. These surface impurities not only lead to poor performance of the nickel-rich cathode materials but also probably cause severe safety issues in batteries. Hence, it is essential and of great importance to find effective strategies to remove the residual lithium compounds as well as improve the storage stability of the materials.

 Received:
 February 4, 2021

 Revised:
 May 13, 2021

 Published:
 May 27, 2021



So far, there have been considerable attempts focusing on solving the above-mentioned problems. Xiong et al. used water to remove surface impurities and achieved an improvement in the cycle stability of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) materials.²³ However, the chemical delithiation in the water washing process will cause capacity loss of the materials.^{19,24} What's worse, the water washing method make the NCM811 materials more easily attacked by H_2O and CO_2 when exposed to air.²³ Kong et al. successfully enhanced the storage performance of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ materials by premixing the conductive agent acetylene black with the materials.²⁵ Liu et al. synthesized LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ materials with LiCoO₂ coating, utilizing the air stability of LiCoO2 to make the asprepared materials exhibit better storage stability.²⁶ Besides, Li₃PO₄ was used to build a coating layer on the surface of NCM811 materials by Zhang et al. and significantly alleviated the air instability of the materials.²⁷ According to the above research results, surface modification is an effective and promising strategy to achieve the stable storage of the nickelrich materials. It is well-known that acids can be used to neutralize bases, but simple organic or inorganic acids cannot achieve coating effects. Herein, we propose a method to achieve the removal of the residual lithium compounds and the construction of surface coating by using a polymer organic acid, which may be an innovative and useful strategy to enhance the storage stability of the nickel-rich cathode materials.

In this work, poly(acrylic acid) (PAA) is used to develop an improvement strategy for the storage stability of NCM811 materials. It is well-known that PAA is a polymer with abundant carboxyl groups, which is commonly used as a binder in lithium ion batteries.²⁸⁻³⁰ The PAA coating may have two main functions. First, the carboxyl groups of PAA can react with the residual lithium compounds and lower the alkalinity of the NCM811 materials. Second, PAA constructs a coating layer on the materials, which is related to the interactions between active carboxyl groups of the PAA and species such as active oxygen atoms appearing on the surface of particle^{30,31} and acts as a layer to protect the materials from direct contact with air. The comparative experiments of storage performance carried out in a high temperature and high humidity environment show that the modified materials have fewer surface impurities, more stable near-surface structure, and better electrochemical performance under the same extreme storage conditions. Therefore, taking advantage of the carboxyl groups and film-forming properties of PAA, the purposes of reducing instability and alleviating the deterioration of NCM811 materials in the humid storage environment are successfully achieved.

EXPERIMENTAL SECTION

Preparation of Materials. In order to prepare the NCM811 materials, commercial precursor $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ (Beijing Easpring Material technology Co., Ltd.) and LiOH·H₂O (Aladdin) with a molar ratio of 1:1.05 were mixed uniformly and ground thoroughly in a mortar and then underwent a calcination process in a tubular furnace under an O₂ atmosphere, at 500 °C for 5 h and 750 °C for 15 h.

For the modification process, PAA (\approx Mw 450 000, Shanghai yuanye Bio-Technology Co., Ltd.) was dissolved in 50.0 mL ethanol to obtain a mixed solution by ultrasonic and uniform stirring. Subsequently, 10.0 g the as-prepared NCM811 materials were dispersed into the solution. The mass ratios of the NCM811 and PAA used for modification were 1:0.01, 1:0.02, and 1:0.03,

respectively. Then the mixture was stirred at 80 $^\circ$ C. After constant stirring with a magnetic stirrer for 2 h, the samples were centrifuged and then placed in a vacuum oven at 100 $^\circ$ C and dried for 24 h.

Storage of Materials. The storage process was performed in a Humidity Chamber. Specifically, two groups of the NCM811 and NCM811-PAA samples were placed in the Humidity Chamber, and the temperature and relative humidity were 55 °C and 80% RH, respectively. Each group of samples contained 5.0 g the NCM811 materials and 5.0 g the NCM811-PAA materials. Then a group of the samples was taken out every 3 days, corresponding to the storage time of 3 and 6 days, respectively. The samples were taken out and used for subsequent analysis and tests of the material properties.

Physical Characterization. The pH values of the materials before and after coating modification were measured with a pH meter (Ohaus Starter 2C). The masses of the materials before and after storage were measured by an analytical balance (Mettler Toledo AL204) to record the mass change during the storage. The amount of residual lithium compounds was analyzed by an acid-base titration method. During the titration process, 1.0 g of the materials and 100.0 mL of deionized water were mixed and stirred at a speed of 700 r. min⁻¹ for 5 min in a sealed environment, then the mixture was filtrated to get the filtrate for the following titration. And the titration was carried out with calibrated dilute hydrochloric acid. The morphology of the materials was observed by SEM (scanning electron microscopy, S-4800, Hitachi Corporation). The crosssectional SEM test was carried out with the material particles cut by a Leica EM TIC 3X-Ion Beam Slope Cutter. The samples for the cross-sectional SEM test were made by mixing the materials with binder (polyvinylidene fluoride, PVDF) and solvent (N-methyl-1, 2pyrrolidne, NMP) and then coating on aluminum foil. The elemental distribution and composition on the materials were analyzed by EDS (energy dispersive spectroscopy). In order to detect the coating layer and surface impurities, TEM (transmission electron microscopy, Tecnai F30) was utilized for further observation of the materials. A powder resistivity tester (Suzhou Jingge Electronic Co., Ltd., ST-2722) was used to measure the electronic conductivity of the materials. XRD (X-ray diffraction) was applied to analyze the structural changes during storage. The Raman spectroscopy and the Fourier transform infrared (FT-IR) spectroscopy were applied for detailed analysis of the surface impurities. To obtain the FT-IR spectra, transmittance mode with KBr pellet method was used. Thermogravimetric analysis (TGA) was applied to analyze the impurities components on the stored materials. The TGA was carried out at 35-800 °C in an argon atmosphere.

Electrochemical Tests. Coin cells were used for the electrochemical tests and the coin cell manufacturing process was as follow. The mass ratio of active material, acetylene black, and PVDF in the slurry was 8:1:1. The solvent used for the slurry preparation was NMP. After 8 h of constant stirring with a magnetic stirrer, the slurry was uniformly mixed and then evenly coated on the aluminum foil. Subsequently, the aluminum foil coated with slurry underwent a drying process, in which a vacuum oven was used for solvent evaporation. The vacuum oven temperature was set at 80 $^\circ\text{C}$, and the drying process lasted 24 h. The LB-301 electrolyte used in this work was purchased from Guotai-Huarong New Chemical Materials Co., Ltd. The CR2016 coin cells were finally assembled in a glovebox (M. Braun, Germany) filled with argon. The positive electrode was the prepared electrode mentioned above, and the negative electrode was lithium metal. The current density in the charge and discharge process was 85 mA g^{-1} . Besides, the voltage range of the charge-discharge tests was 3.0-4.3 V (vs Li⁺/Li). The frequency range for the EIS (electrochemical impedance spectra) is $10^{-2}-10^{5}$ Hz, and the impedance measurement was carried out by an Autolab PGSTAT101 cell test instrument. All the above electrochemical tests were conducted in a dry environment at room temperature.

RESULTS AND DISCUSSION

Physical and Electrochemical Properties of Pristine and Modified Materials. The initial charge-discharge cycle

curves of the pristine and modified materials are profiled in Figure S1, the initial discharge specific capacity of the NCM811-PAA-1%, NCM811-PAA-2%, and NCM811-PAA-3% samples are 170.5, 181.6, and 168.2 mAh·g⁻¹, respectively. And the initial discharge capacity of NCM811-pristine is 184.1 mAh·g⁻¹. Hence, the PAA coating is harmful to the discharge capacity of the NCM811 materials, which is probably induced by the poor conductivity of PAA. And among the three modified samples, the capacity of the NCM811-PAA-2% materials is the most similar to that of the original materials. As a result, the modified materials with 2 wt % PAA are selected for the subsequent storage experiment, and the final obtained materials are noted as NCM811-PAA.

The pH values of the materials measured by pH meter are given in Table 1, for the pristine NCM811 materials and the

Table 1. pH Values of NCM811 and NCM811-PAA Materials

sample	NCM811	NCM811-PAA
pH	11.77	11.26

NCM811-PAA materials, the pH values are 11.77 and 11.26, respectively. The lower pH of the modified material means less surface alkaline impurities, and the large amount of carboxyl groups of PAA play an important role in the decrease of pH value after modification. In order to observe the PAA coating on the modified materials, the HRTEM test was conducted. Figure 1 gives the HRTEM images and FFT images. Figure 1a displays the clear lattice stripes and the corresponding FFT image of the NCM811 materials, which suggest that the ordered layer structure of the pristine materials. There is an

amorphous coating on the surface of the NCM811-PAA materials with a thickness of about 5 nm as observed in Figure 1b. The clear lattice stripes indicate that the bulk phase of the materials under the PAA coating maintains a good layered structure. The EDS elemental mapping images (Figure S2) of the NCM811-PAA materials also confirm the formation of the PAA coating layer. As shown Figure S2, the uniform distribution of C indicates that the surface of the modified materials is covered by PAA. The HRTEM and the EDS test results declare the successful construction of PAA coating on the NCM811 materials. Furthermore, the XRD patterns of the NCM811 and NCM811-PAA materials are described in Figure S3, the obvious contrast of (003) and (104) characteristic peaks indicate that both the pristine and modified materials have a typical α -NaFeO₂ structure in the $R\overline{3}m$ space group,² and the characteristic peaks of (006)/(102) show clear peak splitting as well as (108)/(110). The XRD results suggest that the materials have a good hexagonal ordering layered structure before and after the modification.¹⁴

Figure 2a–b show the electrochemical test results at 0.5 C in a voltage range of 3.0–4.3 V (vs Li⁺/Li) of the pristine and modified NCM811 materials. Although the discharge capacity at the first cycle is slightly lower than that of the NCM811 materials, the NCM811-PAA materials exhibit better cycle performance. For further analysis of the difference of electrochemical performance between the NCM811 and NCM811-PAA materials, the AC impedance test of coin cells was conducted at 4.3 V, and the pristine NCM811 materials and the NCM811-PAA materials show similar EIS spectrum (Figure 2c). According to the literature,^{32–35} the semicircle at high frequency corresponds to the solid electrolyte interphase membrane impedance (R_{SEI}) and the



Figure 1. HRTEM and FFT images of NCM811 (a) and NCM811-PAA (b) materials.

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Figure 2. Electrochemical performance of NCM811 and NCM811-PAA materials (a–b); AC impedance maps of NCM811 and NCM811-PAA materials (c); fitted impedance values of the equivalent circuit and corresponding equivalent circuit used for fitting (d).

semicircle at medium frequency is related to the charge transfer impedance (R_{ct}) . Besides, in the low frequency region, there is an oblique line, which is associated with the diffusion of lithium ions in the active material and it can be represented by a Warburg impedance Z_{W} . From Figure 2c, the R_{ct} of the NCM811-PAA materials is larger than that of the NCM811 materials, and the R_{SEI} of the NCM811 materials is significantly larger than that of the NCM811-PAA materials. In order to understand the specific value of the impedance and further explain the influence of PAA coating on the NCM811 materials, we have used the equivalent circuit computing method to obtain the specific values of R_{ct} and R_{SEI} of the materials before and after modification. And the fitting results are described in Figure 2d, the R_{ct} of NCM811 and NCM811-PAA materials are 10.81 and 5.94 Ω , respectively. Besides, the $R_{\rm SEI}$ of NCM811 and NCM811-PAA are 38.26 and 55.89 Ω , respectively. The higher R_{ct} of NCM811-PAA materials is induced by the PAA coating layer with poor conductivity which is adverse to the migration of lithium ions. As a result, there is a slight decrease of discharge capacity for the modified materials. However, the greatly reduced R_{SEI} is also caused by the PAA coating which prevents the materials from directly contacting with electrolyte.²⁸ Thus, the NCM811-PAA materials exhibit more excellent cycle performance.

Storage Performance. The storage stability of the NCM811 and NCM811-PAA materials is investigated by storage experiments carried out in a test chamber with constant conditions (55 °C, 80% RH). The changes of weight during the storage process are shown in Figure S4a, and the weight of the NCM811 and NCM811-PAA materials has increased during storage. The mass increasing rate of NCM811 materials after 3 days of storage is 5.353% and increases to 9.549% after 6 days. And the mass increasing rates of

NCM811-PAA materials after 3 and 6 days of storage are 3.671% and 5.321%, respectively. It is apparent that, in the same storage time, the weight increasing rate of NCM811-PAA materials is much smaller that of the NCM811 materials. According to the literature,^{20,21} the weight increase is mainly caused by the adsorbed H2O, adsorbed carbonate, adsorbed bicarbonate, LiOH, and Li₂CO₃ impurities. Therefore, it can be inferred that the impurities produced in the storage process for the modified materials are less than the pristine materials. Since the surface alkalinity mainly comes from the residual lithium compounds,³⁶ the titration test results are recorded and depicted as the mass fraction of Li contained in per gram of the materials, reflecting the amount of residual lithium compounds on the materials. The alkalinity of the materials obtained by the titration test is shown in Figure S4b, compared with the NCM811 materials, the alkalinity of the NCM811-PAA materials is smaller, and the NCM811-PAA materials have a slower surface alkalinity growth rate in the storage process. Therefore, the smaller weight change and lower surface alkalinity of the NCM811-PAA materials indicate that decrease of surface impurities during storage.

The SEM images of the materials before and after storage are given in Figure 3. The NCM811 and NCM811-PAA materials before storage (Figure 3A1–B2) are similar in appearance with smooth surface and obvious primary particles. After storage for 3 days, for the NCM811 materials, there are many impurities, and owing to the coverage of impurities, the surface of NCM811 materials becomes rough apparently in Figure 3C1–C2. Furthermore, after storage for 6 days, the NCM811 materials are covered with flake impurities in a large area, which cause the disappearance of profile of the primary particles (Figure 3E1–E2). However, for the stored NCM811-PAA materials, the fragmented impurities do not appear, and

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Figure 3. SEM images of NCM811 (A1–A2), NCM811-PAA (B1–B2), NCM811-3 days (C1–C2), NCM811-PAA-3 days (D1–D2), NCM811-6 days (E1–E2), and NCM811-PAA-6 days (F1–F2); cross-sectional SEM images of NCM811-6 days (G1–G2) and NCM811-PAA-6 days (H1–H2).

the NCM811-PAA-3 days and NCM811-PAA-6 days maintain good integrity, which can be clearly seen from (Figure 3D1-D2, F1-F2). In order to observe the change of the interior of material particle, the pristine materials and the materials after storage for 6 days were cut for the cross-sectional SEM analysis. From Figure S5, the NCM811 and NCM811-PAA materials all have smooth cross sections. After storage, the NCM811-PAA particle shows no apparent change in the interior, while there are some impurities appearing in the internal section of the particle of NCM811-6 days (Figure 3G1-H2). Along the space between the primary particles, impurities gradually grow to the inside of the NCM811 materials and finally result in different degrees of impurity attack in the internal section of NCM811-6 days. The difference in the morphology of NCM811-6 days and NCM811-PAA-6 days observed in the TEM test results is more obvious. As shown in Figure S6a-b, no impurity exists on the pristine NCM811 materials, but there are a large number of the impurities formed on the surface of NCM811 after being stored for 6 days. In contrast, from Figure S6d, there is no fragmented impurities on the surface of NCM811-PAA-6 days. The TEM characterization results are in consistent with the SEM images as well as the analysis of weight change and surface alkalinity, which suggests that fewer impurities are generated for the NCM811-PAA materials after storage.

Figure 4 displays the results of electrochemical performance tests performed on the stored materials. The initial charge and discharge curves of the NCM811 and NCM811-PAA materials before and after storage are described in Figure 4a-b. And, the specific values of capacity and coulomb efficiency are listed in Table 2. The specific charge capacity of NCM811 materials decreases from 184.1 to 132.7 mAh·g⁻¹ after being stored in the extreme environment for 3 days, eventually dropping to only 53.3 mAh·g⁻¹ for NCM811-6 days. Moreover, the corresponding coulomb efficiency for the first cycle of NCM811 materials sharply decreases from 80.8% to 72.3% after 3 days of storage and finally reduces to 39.0% after 6 days of storage. The reduction of the capacity and coulomb efficiency indicate that the electrochemical performance of NCM811 materials drop significantly after storage, which is probably caused by the moisture and impurities absorbed on the materials as well as the occurrence of adverse reactions between the impurities and electrolyte in the batteries.³⁷ By comparison, the degree of capacity deterioration for the NCM-PAA materials is much smaller after the same storage time. As given in Table 2, the initial specific discharge capacity of NCM811-PAA decreases from 181.6 to 147.8 mAh·g⁻¹ after storage for 3 days and then drops to 115.8 mAh·g⁻¹ after 6



Figure 4. Initial charge and discharge curves of NCM811 (a) and NCM811-PAA (b) materials before and after storage; cycle performance of NCM811 and NCM811-PAA materials after storage for 3 (c) and 6 days (d); AC impedance maps of NCM811 and NCM811-PAA after storage for 3 (e) and 6 days (f).

 Table 2. Initial Cycle Charge and Discharge Performance of

 NCM811 and NCM811-PAA Materials after Storage

materials	charge capacity (mAh g ⁻¹)	discharge capacity (mAh g ⁻¹)	Coulomb efficiency (%)
NCM811- 3 days	183.5	132.7	72.3
NCM811-PAA- 3 days	195.0	147.8	75.8
NCM811- 6 days	136.7	53.3	39.0
NCM811-PAA- 6 days	186.2	115.8	62.2

days. And the coulomb efficiency of NCM811-PAA-6 days is 62.2%, which is obviously higher than that of the NCM811-6 days. Moreover, the voltage drop of the NCM811 and NCM811-PAA materials after storage are also depicted in Figure 4a-b. The discharge voltage decreases with the storage time, which is mainly induced by the adsorbed substances and impurities with low conductivity as well as the isolated cathode particles caused by impurities.²⁵ After storage for 6 days, for the NCM811 materials, the voltage drop is 0.3305 V, while the voltage drop of the NCM811-PAA materials is only 0.2362 V. After undergoing the same storage time, the reduction of the initial discharge voltage of the NCM811 materials is much larger than that of the NCM811-PAA materials. Figure 4c-d show the cycle performance of the stored materials, and the NCM811-PAA materials possess higher discharge capacity during the cycling process after storage. The rate performances of the materials before and after storage for 6 days as depicted in Figure S7 also confirm the higher capacity of the NCM811-PAA materials after storage, even at the high rate. Above all, compared with the NCM811 materials, the higher capacity and coulomb efficiency along with the smaller voltage drop for the NCM811-PAA materials after storage imply that the modified materials still possess better electrochemical performance after

being stored in the humid environment, which probably benefits from the fewer impurities induced by the PAA coating.

The AC impedance test was conducted to further analyze the electrochemical performance of the stored materials. As described in Figure 4e–f, after being stored in the high temperature and humidity environment, the impedances of the NCM811 and NCM811-PAA materials gradually increase. And it is obvious that the impedance of NCM811 materials is larger than that of the NCM811-PAA materials after storage. The sharp increase of R_{ct} is probably induced by the substantial surface impurities generated during the storage process, which are usually poor ion/electron conductors and can seriously hinder the interface charge exchange between the materials and the electrolyte.²⁵ The R_{SEI} , by contrast, shows a smaller increase which is probably associated with the increasing reactions between the electrolyte and the impurities.³⁷

In order to further analyze the changes of conductivity after storage, the Li⁺ diffusion coefficient (D_{Li^+}) was calculated and the electronic conductivity was measured. The specific values of D_{Li^+} were calculated from the EIS plots of the materials according to the following equations:^{27,38,39}

$$D_{1i^{+}} = R^2 T^2 / 2A^2 n^2 F^4 C^2 \sigma^2 \tag{1}$$

$$Z' = R_{\Omega} + R_{ct} + \sigma \omega^{-1/2} \tag{2}$$

where *R* stands for the gas constant, *T* represents the thermodynamic temperature, *A* stands for the active surface area of the electrode, *n* is the total number of electrons which is transferred in the electrochemical reaction, *F* is the Faraday constant, *C* represents the molar concentration of Li⁺ in the cathode material, and σ is the Warburg coefficient and its value is equal to the slope of Z' vs $\omega^{-1/2}$ as shown in Figure S8. The corresponding values of σ and D_{Li^+} obtained from the above equations are listed in Table 3; the D_{Li^+} values of the two materials before storage are in the same order of magnitude, but the D_{Li^+} of NCM811-PAA materials (2.15 × 10⁻¹⁴ cm².

Table 3. D_{Li^+} and σ Values of NCM811 and NCM811-PAA Materials before and after Storage for 6 Days

	before storage		after storage for 6 days		
sample	σ	$D_{{ m Li}^{+}} ({ m cm}^2 \cdot { m S}^{-1})$	σ	$D_{{ m Li}^+} ({ m cm}^2 \cdot { m S}^{-1})$	
NCM811	1.88	4.60×10^{-12}	310.51	2.19×10^{-15}	
NCM811-PAA	2.05	3.87×10^{-12}	45.03	2.15×10^{-14}	

 $\rm S^{-1})$ is bigger than that of the NCM811 materials (2.19 \times $10^{-15}~\rm cm^2 \cdot S^{-1})$ after storage for 6 days, and the difference of the $D_{\rm Li^{*}}$ values between the two stored materials is an order of magnitude. The higher $D_{\rm Li^{*}}$ value for the NCM811-PAA materials after storage means better ionic conductivity and reveals that the PAA coating can efficiently inhibit the generation of impurities with poor conductivity and stabilize

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the structure of the cathode materials during the storage process.⁴⁰ The electronic conductivity of the materials was obtained by a powder resistivity tester, and the results are described in Figure S9. Before storage, the electronic conductivity of NCM811-PAA materials is smaller than that of the NCM811 materials due to the existence of PAA coating layer, and all the materials experience varying degrees of the electronic conductivity decline after storage because of the gradual generation of impurities. Then the NCM811-PAA materials show better electronic conductivity after the same storage time, which is also associated with the formation of fewer surface impurities on the NCM811-PAA materials. The higher ionic conductivity and electronic conductivity for the NCM811-PAA materials are in accordance with the results of the AC impedance test, which also explain the better



Figure 5. FT-IR spectra of NCM811 and NCM811-PAA materials after storage (a–b); XPS spectra of Ni 2p of the materials before and after storage: NCM811-pristine (c), NCM811-PAA (d), NCM811-6 days (e), and NCM811-PAA-6 days (f).



Figure 6. Partially enlarged XRD patterns of (003) of NCM811 and NCM811-PAA materials after storage (a-b); Rietveld refinement results of the materials before and after storage: NCM811-pristine (c), NCM811-PAA (d), NCM811-6 days (e), and NCM811-PAA-6 days (f).

electrochemical performance for the stored NCM811-PAA materials compared with the stored NCM811 materials.

Physical Characterization. The changes in weight, surface alkalinity, morphology, and electrochemical properties of the pristine materials and modified materials after being stored in a humid environment have been explored to compare the storage stability of the NCM811 and NCM811-PAA materials in the previous section. Herein, physical characterization is used to analyze the changes of surface impurities as well as the structure of the materials before and after storage and thereby further explain the improved performance of NCM811-PAA materials.

The FT-IR spectra (Figure 5a–b) have been recorded to study the impurities. The absorbed peak arising from the stretching vibration of O–H at $3200-3600 \text{ cm}^{-1}$ is assigned to LiOH.¹⁴ After storage, there are three new adsorbed peaks including the peak assigned to the out-of-plane bending vibration absorption of CO_3^{2-} at 865 cm⁻¹ and the peaks assigned to the symmetrical and antisymmetric stretching

vibration of CO_3^{2-} at 1438 and 1496 cm⁻¹. Therefore, all these new characteristic absorption peaks are ascribed to Li₂CO₃.^{11,21} It can be observed in Figure 5a-b that the intensity of the absorption peaks increases with the storage time, which implies the continuous generation of Li₂CO₃ during the storage process. And the intensity of the Li₂CO₃ characteristic absorption peaks of the NCM811-PAA materials is weaker than that of the NCM811 materials after storage, which suggests fewer Li₂CO₃ impurities for the NCM811-PAA materials. The normalized Raman spectra (Figure S10) of the NCM811 and NCM811-PAA materials before and after storage for 6 days also confirm the fewer LiOH and Li₂CO₃ impurities for the modified materials after the same storage process. As shown in Figure S10a, for the NCM811 materials, new peaks appear after storage, and the peaks at 200 and 1100 cm⁻¹ are ascribed LiOH and Li₂CO₃, respectively.⁷ And the rapid increase in the intensity of the characteristic peaks of LiOH and Li₂CO₃ indicates that the impurities sharply increase with the storage time for the NCM811 materials.

However, from Figure S10b, there is only a new and weak peak attributed to Li2CO3 for the NCM811-PAA materials after storage. Therefore, the results of Raman spectroscopy correspond to the results of FT-IR analysis. Besides, the TG test was used to further analyze the components of the materials after storage. And, the TGA results are depicted in Figure S11; the mass loss above 800 °C is induced by the decomposition of active materials, and the mass losses below 800 °C are mainly caused by the adsorbed species and Li_2CO_3 impurities. Specifically, the adsorbed species desorption occurs in the temperature range of 200-500 °C, and the decomposition of Li₂CO₃ occurs at 668-780 °C.^{20,21} From Figure S11, the differences in the mass losses of the NCM811 and the NCM811-PAA materials after storage are noticeable, especially for the materials after storage of 6 days, which imply fewer impurities on the modified materials after storage. Furthermore, the TG results are consistent with the analysis of the changes of weight and surface alkalinity as well as the SEM results mentioned above. The fewer impurities also explains the alleviated capacity degradation of NCM811-PAA materials during the storage process.

The XPS spectra of Ni 2p of the NCM811 and NCM811-PAA materials before and after storage are used to analyze the transformation of Ni3+ to Ni2+ in the surface region and depicted in Figure 5. After storage, the content of Ni^{2+} increase while the content of Ni^{3+} decreases, which is caused by the reduction of unstable Ni^{3+} to more stable Ni^{2+} on the surface of the materials when exposed to air.⁴¹ After storage for 6 days, the Ni²⁺ content of the NCM811-PAA materials is much lower than that of the NCM811 materials. The area ratios of $Ni^{2+}/$ Ni³⁺ of the NCM811 and NCM811-PAA materials are 0.1344 and 0.1369 and become 0.2898 and 0.2156 after storage, respectively. The smaller change of the area ratio of Ni²⁺/Ni³⁺ for the NCM811-PAA materials indicates that the more severe transformation of Ni^{3+} to Ni^{2+} on the surface of NCM811 materials and the reduction process of Ni³⁺ to Ni²⁺ on the NCM811-PAA materials is probably inhibited. The transformation of Ni³⁺ to Ni²⁺ not only promotes the production of active oxygen species, driving the generation of Li₂CO₃/LiOH impurities, but also aggravates the degree of cationic disorder, leading to the formation of NiO rock-salt phase.^{41,42} As a result, the alleviated transformation of Ni³⁺/ Ni²⁺ shown in the XPS results suggests that the PAA coating plays an important role in reducing the LiOH and Li₂CO₃ impurities and preserving the structure of the materials during storage.

In order to obtain the structural information and investigate the structural changes, XRD tests were carried out on the materials after storage. From Figure S12a-c, both the NCM811 and NCM811-PAA materials have no obvious change in the bulk structure after storage, the obvious peak splits of (006)/(102) and (108)/(110) indicate that the materials maintain ordered hexagonal layered structures after storage.^{14,21} As shown in Figure S12d, for the NCM811 materials, four small peaks at 21.26°, 30.46°, 31.94°, and 34.18° are new peaks after storage and are attributed to the crystal Li_2CO_3 .^{11,20,21} Apparently, for the NCM811 materials, the intensity of the peaks of crystal Li₂CO₃ increases with the storage time. However, for the NCM811-PAA materials after storage, the characteristic peaks belonging to Li₂CO₃ are not obvious, and the intensities of the Li₂CO₃ characteristic peaks are much smaller than that of the NCM811 materials, which declare that fewer impurities are generated during the storage process for the modified NCM811 materials once again. In the

partially enlarged patterns of the (003) crystal plane (Figure 6a-b), there is an apparent shift of the (003) characteristic peak of the NCM811 materials after storage, which is associated with the extraction of Li from the materials. Specifically, the characteristic peak for the (003) crystal plane shifts to a lower Bragg angle with the increase of the transition metal layer spacing.⁴³⁻⁴⁵ The formation of the impurities containing Li such as LiOH and Li2CO3 promotes the extraction of lattice Li during the storage process, leading to the increase of the transition metal layer spacing and, then, causing the shift of (003) peak.^{21,25} Therefore, as shown in Figure 6a-b, for the NCM811 materials, the diffraction peak shift increases with the storage time. And, the (003) peak shift angle for the NCM811-PAA materials is much smaller than that of the NCM811 materials, which reveals that the NCM811-PAA materials experience less extraction of Li during storage and have fewer impurities. In order to clarify the changes of crystal structure and lattice parameters of the materials more clearly, the Rietveld refinements of XRD patterns for the NCM811 and NCM811-PAA materials before and after storage for 6 days are described in Figure 6c-f, and the specific lattice parameters are listed in Table 4. The small

Table 4. Rietveld Refinement Results of XRD Patterns for NCM811 and NCM811-PAA Materials before and after Storage for 6 Days

sample	a (Å)	c (Å)	c/a	Rwp (%)	Rp (%)
NCM811-pristine	2.8720	14.1699	4.9337	2.63	1.69
NCM811-PAA	2.8722	14.1736	4.9346	2.48	1.60
NCM811-6 days	2.8706	14.1875	4.9424	2.51	1.75
NCM811-PAA-6 days	2.8701	14.1752	4.9389	2.34	1.60

values of Rp and Rwp suggest that the final refined results are reliable. For the NCM811 and NCM811-PAA materials, there is no significant difference in the lattice parameters, which confirms that the PAA coating process does not cause damage to the crystalline structure of the NCM811 materials. The value of c/a represents the degree of cationic mixing, and the cationic disorder is associated with the Ni³⁺/Ni²⁺ transformation and the extraction of Li from the materials induced by the formation of impurities such as Li₂CO₃ and LiOH^{46,47} during storage. The values of c/a of the materials increase after storage, indicating that the cationic disorder in the layered structure increases with the storage time. For the NCM811-PAA materials, the value of c/a is smaller than that of the NCM811 materials after storage, which indicates that the degree of cationic disorder is alleviated. And it further proves that the decrease of transformation of Ni³⁺ to Ni²⁺ and the reduction of impurities, conforming to the XPS analysis and the investigations of impurities mentioned above.^{16,20,41} The XRD patterns and corresponding Rietveld refinement results suggest that the NCM811-PAA materials experience smaller change of structure and fewer generation of impurities.

The high-resolution transmission electron microscope (HRTEM) images and the corresponding fast Fourier transformation (FFT) images of the materials after storage for 6 days are shown in Figure 7. The bulk structure of the NCM811 materials maintains an ordered layered structure after storage for 6 days, while a phase change layer appears in the near-surface area, which is concluded from Figure 7a and the FFT images of regions 1 and 2. The original ordered

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Figure 7. HRTEM and FFT images of the materials after storage: NCM811-6 days (a) and NCM811-PAA-6 days (b).

structures in the near-surface region of the NCM811 materials becomes polycrystalline disordered structure after storage. And the formation of polycrystal area is associated with the rock salt phase and Li_2CO_3 crystal impurity layer. The transformation of the crystal structure is induced by the extraction of lithium ions,²⁵ which is also reflected in the shift of (003) peak observed in the studies of XRD mentioned above in Figure 6a–b. From Figure 7b, a good structural consistency is still maintained for the NCM811-PAA materials after storage for 6 days, and the near-surface region shows a good layered structure. For the NCM811 and NCM811-PAA materials after storage for 6 days, the difference of the near-surface structure is mainly caused by the surface impurities, the extraction of Li⁺, and the transformation of Ni³⁺ to Ni²⁺ in the near-surface region.^{16,20,48} For the NCM811 materials, the transformation of Ni^{3+} to Ni^{2+} confirmed by XPS (Figure 5c, e), the extraction of Li⁺ confirmed by the shift of (003) peak in the XRD patterns (Figure 6a-b), and the impurities confirmed by FT-IR, TG, XRD, etc., eventually lead to the surface structure changes and the formation of a crystalline mixed region with the original layered structure, the rock-salt phase, and impurities.^{25,48} Because of the decreased surface impurities, the inhibited transformation of Ni³⁺ to Ni²⁺ and the alleviated degree of lithium ions extraction, a well-order layered structure is maintained from the near-surface to the bulk region for the NCM811-PAA materials during the storage process, which proves the better structure stability during storage after PAA coating and further declares the improvement of the storage performance for the modified materials.

CONCLUSIONS

In this work, PAA is used for the surface modification of NCM811 materials to improve the storage performance of NCM811 materials, which is illustrated in Figure 8. The experimental results confirm that the protective PAA layer is successfully constructed on the materials. Moreover, PAA can reduce the surface alkalinity of the materials to a certain extent during the modification process. When the materials are stored under the same conditions (55 °C, 80% RH), fewer surface impurities are generated on the NCM811-PAA materials, and the degradation of electrochemical performance as well as the change of structure are alleviated effectively. All these results demonstrate the improvement of storage performance of the NCM811 materials after the surface modification process with PAA. Overall, the stable PAA coating layer makes NCM811 materials less sensitive to humid air, and thus result in



Figure 8. Schematic illustration of PAA modification.

significant alleviation of air sensitivity and great enhancement of storage performance of the materials. Moreover, other polymers which are similar to PAA and contain acidic groups such as carboxyl groups are also likely to be feasible for the alleviation of instability of nickel-rich materials in the air. This surface modification strategy exhibits potential application prospects in enhancing the storage stability of the nickel-rich cathode materials.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c00802.

Initial charge and discharge curves of NCM811 before and after modification; EDS elemental mapping images of NCM811-PAA materials; XRD patterns of NCM811 and NCM811-PAA materials; weight increasing rate of NCM811 and NCM811-PAA during storage and surface alkalinity of NCM811 and NCM811-PAA before and after storage; cross-sectional SEM test images of NCM811 and NCM811-PAA materials; TEM images of NCM811 and NCM811-PAA materials before and after storage; rate performance of NCM811 and NCM811-PAA materials before and after storage; linear fitting of Z' vs $\omega^{-1/2}$ in the low-frequency region for the NCM811 and NCM811-PAA materials before and after storage; electronic conductivity of NCM811 and NCM811-PAA before and after storage; Raman spectra of NCM811 and NCM811-PAA materials before and after storage for 6 days; TG test results of NCM811 and NCM811-PAA materials after storage; XRD patterns of NCM811 and NCM811-PAA materials before and after storage (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of National Key Research and Development Program of China (2017YFB0102000), National Natural Science Foundation of China (21875195, 22021001), Fundamental Research Funds for the Central Universities (20720190040), and the Key Project of Science and Technology of Xiamen (3502Z20201013).

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