

# Article Enhancing the Storage Performance and Thermal Stability of Ni-Rich Layered Cathodes by Introducing Li<sub>2</sub>MnO<sub>3</sub>

Jun Yang <sup>1</sup>,\*<sup>1</sup>, Pingping Yang <sup>1</sup> and Hongyu Wang <sup>2</sup>

- <sup>1</sup> Shaanxi Key Laboratory of Green Preparation and Functionalization for Inorganic Materials, School of Materials Science & Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China
- <sup>2</sup> Qinghai Provincial Key Laboratory of New Light Alloys, Qinghai University, Xining 810016, China
- \* Correspondence: yangjuncl@sust.edu.cn

**Abstract:** Ni-rich layered cathodes are deemed as a potential candidate for high-energy-density lithium-ion batteries, but their high sensitivity to air during storage and poor thermal stability are a vital challenge for large-scale applications. In this paper, distinguished from the conventional surface modification and ion doping, an effective solid-solution strategy was proposed to strengthen the surface and structural stability of Ni-rich layered cathodes by introducing Li<sub>2</sub>MnO<sub>3</sub>. The structural analysis results indicate that the formation of Li<sub>2</sub>CO<sub>3</sub> inert layers on Ni-rich layered cathodes during storage in air is responsible for the increased electrode interfacial impedance, thereby leading to the severe deterioration of electrochemical performance. The introduction of Li<sub>2</sub>MnO<sub>3</sub> can reduce the surface reactivity of Ni-rich cathode materials, playing a certain suppression effect on the formation of surface Li<sub>2</sub>CO<sub>3</sub> layer and the deterioration of electrochemical performances. Additionally, the thermal analysis results show that the heat release of Ni-rich cathodes strongly depends on the charge of states, and Li<sub>2</sub>MnO<sub>3</sub> can suppress oxygen release and significantly enhance the thermal stability of Ni-rich cathode materials.

Keywords: lithium-ion batteries; Ni-rich cathode; storage performance; thermal stability; Li<sub>2</sub>MnO<sub>3</sub>



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## 1. Introduction

As a renewable and efficient energy storage system, lithium-ion batteries (LIBs) have been widely used in the fields of portable electronic products, intelligent power stations, and electric vehicles (EVs). In particular, the commercialization of EVs requires the development of advanced LIB technology. In this regard, Ni-rich layered oxides are considered as promising cathode materials for lithium-ion batteries due to their high reversible capacity  $(200 \text{ mA h g}^{-1})$  [1,2]. However, a critical obstacle to layered Ni-rich cathodes is the surface instability caused by high chemical reactivity [3]. When exposed to air, Ni-rich oxide cathodes are prone to react chemically with  $CO_2$  and  $H_2O$  in atmosphere, forming Li<sub>2</sub>CO<sub>3</sub>/LiOH impurities on secondary particles. This formed surface contamination of Ni-rich cathode materials exhibits low ionic conductivity. As a result, the interfacial charge transfer resistance increases, resulting in a loss of reversible capacity [4-6]. More seriously, the surface Li-derives impurities accelerate the adverse side reactions between electrolyte and the active cathode surface. The electrochemical oxidation of Li<sub>2</sub>CO<sub>3</sub> produces intermediate free radicals, which react rapidly with the electrolyte solvent to cause electrolyte decomposition, release gaseous products, and form solid-state products on the cathode surface [3]. Meanwhile, the acidic products produced by the chemical decomposition of electrolytes attack cathode surface, resulting in the dissolution of transition metal ions (TMs) [7–9]. These harmful chemical behaviors induced by surface-Li-derived impurities exacerbate the deterioration of electrochemical properties [10-12]. In addition, the thermal instability of Ni-rich cathodes also poses a safety risk for LIBs in practice [13]. In a highly

delithiated layered cathode, metastable Ni<sup>4+</sup> ions weaken the Ni-O bond and improve the reactivity of lattice oxygen, as their covalence increases. Driven by elevated temperature and high delithiated states, the lattice oxygen release is intensified, leading to the reduction of Ni<sup>4+</sup> to Ni<sup>2+</sup> ions, accompanied by the structural degradation from a layered to spinel phase and finally to a rock-salt phase [14,15]. Subsequently, reacting with flammable electrolytes, the highly reactive oxygen species released from the Ni-rich cathode accelerate the combustion of electrolytes to result in thermal runaway and release a large number of harmful gaseous products. Therefore, it is concluded that the unsatisfactory storage performance and thermal stability of Ni-rich cathodes are strongly linked with the structure instability resulting from the high Ni-content and active Ni-O bonds in the layered cathode.

Surface coating, as a method to enhance structural stability of the commonly used modification, can effectively isolate the surface of the active cathode from the electrolyte to prevent serious interfacial side reactions [16–19]. Moreover, it has been demonstrated that coating can eliminate surface residual Li-derived impurities and inhibit the immigration of active lattice Li<sup>+</sup> into the surface during storage in air, displaying an improved effect on storage performance. However, surface coating has less influence on the reactivity of lattice oxygen in the bulk due to a lack of change in composition and crystal structure, thereby presenting a limited improvement in the thermal stability of layered cathodes. Additionally, a critical concern that also needs to be considered is that the poor interfacial compatibility between coating materials and layered cathode hinders Li<sup>+</sup> ions' fast transport. As another structural optimization strategy, doping can stabilize the lattice oxygen to enhance the cycling and thermal stability of layered cathodes. Nevertheless, the limitation of the solubility of doped ions leads to a generally low amount of doping in the layered cathode. The resulting effect of the low-concentration dopant on the cathode surface has less impact on the surface Ni concentration and surface reactivity, inevitably suffering from being attacked by electrolytes [20–22]. Composition optimization is regarded as a promising strategy for enhancing the structural and thermal stability of layered cathodes, which has been extensively investigated by Sun's group [23]. Mn element has been proven to provide a remarkable enhancement of the thermodynamic stability of layered cathodes. Hence, increasing the stable Mn component (reducing the active Ni component) in the surface composition can significantly reduce the surface reactivity of the layered cathode to achieve excellent structure stability. In our previous study, introducing a low-content layered Li<sub>2</sub>MnO<sub>3</sub> into layered Ni-rich cathode to form the layered solid solution provided markedly improved structural stability of layered cathode at high voltage by suppressing the phase transition [24,25]. As a structural stabilizer, Li<sub>2</sub>MnO<sub>3</sub> not only significantly reduces variations of the unit-cell volume to stabilize the original layered structure of the Ni-rich cathode but also passivates the active surface by increasing Mn content and reducing Ni content on the cathode surface. Despite this, little research has been conducted on evaluating the storage performance and thermal stability of these solid-solution cathode materials.

Based on the above considerations, a low-content  $Li_2MnO_3$  was introduced into the Ni-rich cathode to form a solid-solution cathode, reducing their surface reactivity. The influence of introducing  $Li_2MnO_3$  on storage performance and the thermal stability of layered cathodes were further investigated in this work. The variations in surface/interface structure and electrochemical performance of the Ni-rich cathode during storage in air were explored in detail to build the strong structure–property correlations. Comparatively, the Ni-rich cathode modified with  $Li_2MnO_3$  exhibits a suppressed formation of surface  $Li_2CO_3$  inert layers and low interfacial electrode resistance, which accounts for its inhibitory effect on the deterioration of electrochemical performance. Furthermore, the delithiation potentials and introduction of  $Li_2MnO_3$  on the thermal stability of layered cathodes were investigated with a differential scanning calorimeter (DSC). The solid solution exhibited a relatively low heat release relative to the weak phase transition. This work contributes insights into the storage performance and thermal stability of solid-solution cathodes.

## 2. Materials and Methods

#### 2.1. Sample Synthesis

Ni-rich layered cathode materials were prepared via coprecipitation followed by sintering at high temperatures. Firstly, the hydroxide precursors  $(Ni_{0.8}Co_{0.1}Mn_{0.1})(OH)_2$  were synthesized via a coprecipitation method [24–26]. Sulfates NiSO<sub>4</sub>·6H<sub>2</sub>O, CoSO<sub>4</sub>·7H<sub>2</sub>O, and MnSO<sub>4</sub>·H<sub>2</sub>O were dissolved in distilled water at a molar ratio of 8:1:1 (Ni:Co:Mn) to form a mixed solution with a concentration of 1 M. Then, a reaction base solution ( $pH = 11 \sim 12$ ) was heated at 55 °C under N<sub>2</sub> protection. Then, a 1M mixed solution and a 2M NaOH solution were synchronously pumped to the base solution for the coprecipitation reaction. After the reaction was complete, the products were repeatedly washed with distilled water after collection. Finally, the hydroxide precursor Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>(OH)<sub>2</sub> was obtained by drying at 120 °C for 12 h. Similarly, the precursor (Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>)<sub>0.9</sub>Mn<sub>0.1</sub>(OH)<sub>2</sub> was also synthesized by regulating the ratio of three sulfates via the same process. Then, the precursor powder and LiOH·H<sub>2</sub>O were mixed and sintered at 480 °C for 5 h and at 750 °C for 15 h in a  $O_2$  atmosphere, respectively. Finally, the as-obtained LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> and solidsolution cathode 0.1Li<sub>2</sub>MnO<sub>3</sub>·0.9LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> were denoted as NCM-811-Fresh and LNCMO-1090-Fresh, respectively. Furthermore, the as-synthesized cathode materials were exposed to air for 6 months and denoted as NCM-811-Air and LNCMO-1090-Air.

## 2.2. Material Characterization

Powder X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer from a Cu-K $\alpha$  radiation source (Bruker, Germany) to confirm the crystal structure of the cathode material, which was carried out in the 2 $\theta$  range of 10°~100°. The surface chemical environment of the cathode materials was characterized by X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System, PHI Corporation, Lafayette, LA, USA), which was performed on the PHI5000C system with a Mg K $\alpha$  source operating at 14.0 kV and 25 mA. The XPS spectrum deconvolution was performed by using the Avantage software (Thermo Avantage, version 5.9922). The surface morphology of the samples was observed by scanning electron microscope (SEM, JEOL JEM-6390, JEOL, Tokyo, Japan) at a voltage of 25 kV. High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100, JEOL, Tokyo, Japan) equipped with a double-tilt specimen holder was used to observe the microstructure of the materials. Powder samples were placed on a copper microgrid for observation. The element distribution of the sample was observed with an energy dispersive spectrometer (EDS), and the element composition of the sample was analyzed with an inductively coupled plasma-optical emission spectrometer (ICP-OES).

## 2.3. Electrochemical Measurements

Electrochemical measurements were carried out in CR2016-type coin cells. The preparation of electrodes was carried out as follows: The cathode material, conductive material (carbon black), and binder (polyvinylidene difluoride) were homogeneously mixed in N-methyl-2-pyrrolidone (NMP) solvent with a weight ratio of 8/1/1. Then, the slurry was uniformly cast on aluminum foil and vacuum-dried at 80 °C for 10 h. The electrode film was cut into disks with a diameter of 12 mm. In a glove box (O<sub>2</sub> < 0.1 ppm, H<sub>2</sub>O < 0.1 ppm) filled with pure argon, the half cells were assembled with the prepared material (cathode), lithium metal (anode), and Celgard 2300 film (separator). The electrolyte solution was 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethyl methyl carbonate (EMC) at a volume ratio of 1:1:1. The LAND CT2001A Battery Cycler (Wuhan, China) was used for constant current charging–discharging experiments (1 C = 200 mA g<sup>-1</sup>) between 2.0 and 4.5 V vs. Li/Li<sup>+</sup> at room temperature (25 °C). Electrochemical impedance spectroscopy (EIS) measurements were performed on the Solartron 1287 and Solartron 1255B frequency response analyzer systems in the frequency range of 1 MHz to 1 mHz, with an amplitude of 5 mV at room temperature.

## 2.4. Thermal Stability Test

The thermal stability of the cathode material was measured with a differential scanning calorimeter (DSC). DSC measurements of cathode materials were performed as follows: The assembled cells were charged to the specified voltage and kept at constant voltage for several hours to reach the equilibrium state and then disassembled in the glove box under argon. The delithiated cathode was removed from the cells, washed repeatedly with DMC, and dried in a glove box under argon at room temperature. The electrode material was scraped from current collector and weighed, placed with electrolytes in a stainless steel crucible, and sealed. The crucible with the sample was heated in the differential scanning calorimeter with N<sub>2</sub> as the purge and protective gas. The heating conditions were  $25 \sim 350$  °C and 5 °C min<sup>-1</sup>.

## 3. Results and Discussion

#### 3.1. Structure Change of the Ni-Rich Cathode during Storage in Air

Benefiting from the similar crystal structure between layered Li<sub>2</sub>MnO<sub>3</sub> and layered Ni-rich cathodes, Li<sub>2</sub>MnO<sub>3</sub> is easily incorporated into Ni-rich cathodes to form solidsolution cathodes (LNCMO-1090) by coprecipitation followed by sintering at an elevated temperature, as confirmed by structure analysis in our previous research [24,25]. In terms of electrochemical properties, the introduction of Li<sub>2</sub>MnO<sub>3</sub> reduces the ratio of the Ni/Mn microregion in the NCM-811 surface, effectively suppressing the surface side reaction to enhance the cycling performance of cathode materials [24]. In addition,  $Li_2MnO_3$  can significantly inhibit the phase transition of cathodes to improve the structural stability of the cathodes during high-voltage cycling [25]. The elemental components of the synthesized sample were confirmed with an inductively coupled plasma-optical emission spectrometer (ICP-OES). The results (Table S1) showed that the ratio of Ni/Co/Mn in NCM-811 was close to 0.8/0.1/0.1, while the contents of Li and Mn in the LNCMO-1090 sample were relatively increased, which was consistent with the expected calculation results. Experimentally, Ni-rich cathodes (NCM-811 and LNCMO-1090) were stored in the air for 6 months. The change in the crystal structure of cathodes was investigated by X-ray powder diffraction (XRD). All sharp diffraction peaks of NCM-811-Fresh and NCM-811-Air (Figure 1a) could be indexed based on hexagonal  $\alpha$ -NaFeO<sub>2</sub> layered structures with a trigonal (R-3m) space group symmetry [27], and no other obvious peaks appeared in these cathode materials. Furthermore, some weak diffraction peaks were seen in the XRD spectrum of NCM-811-Air after we zoomed in to a diffraction angle range of  $20 \sim 36^{\circ}$  (Figure 1c), which was assigned to Li<sub>2</sub>CO<sub>3</sub> crystals [28]. When exposed to air, Ni-rich cathodes are prone to react chemically with  $H_2O/CO_2$  in the air due to their high surface reactivity, yielding LiOH/Li<sub>2</sub>CO<sub>3</sub> surface impurities. However, no crystalline LiOH was found in the XRD results, which can be attributed to the complete transformation to  $Li_2CO_3$  via a chemical reaction with  $CO_2$  in the air during long-term storage. It is widely accepted that the intensity ratio of diffraction peaks of 003 and 104 crystal planes  $(I_{003}/I_{104})$  can provide the information related to the  $Li^+/Ni^{2+}$  cation mixing. We found that the  $I_{003}/I_{104}$  values of the two samples decreased slightly after storage (Table S2), indicating an increase in cation mixing, which may be linked with the lattice Li<sup>+</sup> ion migration onto the surface and subsequent participation in the formation of Li<sub>2</sub>CO<sub>3</sub> during the storage process. Furthermore, the XRD spectra of LNCMO-1090 before and after storage (Figure 1b) exhibited a set of strong diffraction peaks, highly identical to that of NCM-811. The Rietveld analysis results (Table S2) also indicated that compared with NCM811, introducing the Li<sub>2</sub>MnO<sub>3</sub> component into the layered cathode could decrease the cell parameters a and cell volume V, and increase the c/a value. The decrease in the cell parameter a and the cell volume V can be attributed to the increased content of  $Mn^{4+}$  with a relatively small ionic radius. In addition, the first cyclic voltammetry curves (Figure S1) also showed that the Li<sub>2</sub>MnO<sub>3</sub> component was electrochemically activated in the range of 4.4~4.8 V to produce a wide oxidation peak [29]. The above observations showed that the layered NCM-811 R-3m phase and the layered Li<sub>2</sub>MnO<sub>3</sub> C2/m phase are highly miscible in forming a solid solution due to their similar

lattice parameter and crystal structure. After magnification of the diffraction range of  $2\theta = 20 \sim 36^{\circ}$  (Figure 1d), some diffraction peaks of Li<sub>2</sub>CO<sub>3</sub> crystalline also appeared in the XRD pattern of the stored LNCMO-1090-Air. XRD results showed that the Li<sub>2</sub>CO<sub>3</sub> impurities were inevitably generated on the cathode surface during storage in air owing to the high sensitivity to air. Given that the XRD technique has low sensitivity to surface structural information, the detailed structure information on the cathode surface after storage needs to be further explored to confirm the thickness of the Li<sub>2</sub>CO<sub>3</sub> layers on the cathode materials.



**Figure 1.** XRD patterns and magnifications of cathodes before and after storage: (**a**,**c**) NCM-811. (**b**,**d**) LNCMO-1090.

X-ray photoelectron spectroscopy (XPS) is commonly applied to analyze the valence states and surface chemical environment due to its high sensitivity to the materials [30–32]. Therefore, the surface of cathodes was further examined by XPS. Figure 2a,b show the C 1s XPS spectra of NCM-811 and LNCMO-1090 before and after storage: there are three peaks in the C 1s spectra, referring to C-C (284.6 eV), C-O (286.5 eV), and CO<sub>3</sub><sup>2-</sup> (289.5 eV), respectively. The peak with a binding energy of 284.6 eV arose due to contamination of the material surface with a carbon source, which inevitably occurred in all samples. Another peak with a binding energy of 289.5 eV arose due to a carbon source in the carbonates [3]. For the fresh cathode materials, a very weak  $CO_3^{2-}$  peak appeared in the C 1s spectra of NCM-811-Fresh and LNCMO-1090-Fresh, which can be attributed to the short-time exposure of cathodes to air after synthesis. This result verifies that cathodes have a high surface reactivity and are extremely sensitive to air. After storage in air, NCM-811-Air and LNCMO-1090-Air displayed a strong peak at 289.5 eV, indicating that a large amount of Li<sub>2</sub>CO<sub>3</sub> impurity was generated on the cathode surface during storage. This was also confirmed by the relatively increased content of C and O element and the decreased concentration of other metal elements on the samples' surface after storage (Table S4, Figure S6). Comparatively, the intensity and area of this peak in LNCMO-1090-Air was inferior to those of the peak in NCM-811-Air, demonstrating the lower content of the Li<sub>2</sub>CO<sub>3</sub> impurities on the LNCMO-1090-Air cathode surface. The suppressed effects of the



Li<sub>2</sub>CO<sub>3</sub> impurity formations on the solid-solution cathode (LNCMO-1090) can be attributed to their reduced surface chemical reactivity.

**Figure 2.** The C 1s XPS spectra of cathodes before and after storage: (**a**) NCM-811 and (**b**) LNCMO-1090.

The surface morphology of layered cathodes during storage was observed by scanning electron microscopy (SEM). SEM images of NCM-811 and LNCMO-1090 before and after storage are presented in Figure 3. Both NCM-811-Fresh (Figure 3a) and LNCMO-1090-Fresh (Figure 3c) exhibited micron-scale spheroid secondary particles before storage, which are formed by the aggregation of primary particles of 200–500 nm. After storage for 6 months in air, the size and morphology of NCM-811-Air and LNCMO-1090-Air materials did not change significantly, and they still exhibited micron-scale spheroid aggregates, as shown in Figure 3b,d. Therefore, the storage process has less influence on the surface morphology of layered cathodes, and further characterization of the detailed surface microstructure of the cathode materials by transmission electron microscopy (TEM) is required.



Figure 3. SEM images of cathodes before and after storage: (a,b) NCM-811 and (c,d) LNCMO-1090.

Figure 4 presents the TEM images of NCM-811 and LNCMO-1090 before and after storage. Before storage, NCM-811-Fresh (Figure 4a) exhibited a layered crystal structure, but its surface structure changed to produce a clear interfacial structure. In the insets of Figure 4a, a clear layered structure with a lattice distance of 0.48 nm is apparent in the

bulk region, which belongs to the (003) crystal facets of the rhombohedral phase, while the surface region displays the 0.24 nm lattice fringes that respond to (111) crystal facets of cubic rock-salt phase. As a typical characteristic of the structural degeneration of layered cathodes, the formation of the surface rock-salt phase induced by Ni<sup>2+</sup> ions migrating into Li<sup>+</sup> sites generally occurs during synthesis preparation or exposure to air due to the high surface reactivity [33–35]. In contrast, the LNCMO-1090 cathode (Figure 4b) presented a highly ordered layered structure and consistent lattice fringes measuring 0.48 nm from the surface to the bulk region, which is closely correlated to the relatively stable surface of LNCMO-1090. The increased  $Li_2MnO_3$  phase enriches the Mn-rich region content on the LNCMO-1090 surface, thus improving the surface structural stability of cathodes. Furthermore, it can observed from Figure 4c that thick and dense Li<sub>2</sub>CO<sub>3</sub> layers with a thickness of about 5 nm covered the NCM-811-Air cathode surface after storage. EDS spectrum is helpful to further understand the Li<sub>2</sub>CO<sub>3</sub> layers on the surface of cathodes (Figure S2). The EDS mapping (Figure S2a) showed that the C element had a surfaceenriched distribution in the cathode particles after storage, which was distinguished from other elements of uniform distribution. This result means a thick and dense Li<sub>2</sub>CO<sub>3</sub> layer was formed on NCM-811-Air surface after storage. These Li<sub>2</sub>CO<sub>3</sub> layers also appeared on the LNCMO-1090 cathode surface, but their thickness was remarkably reduced (2~3 nm), as shown in Figure 4d. These results indicated that the generation of  $Li_2CO_3$  impurities was suppressed on the LNCMO-1090 cathode surface, which contributed to the reduced surface reactivity due to its surface increase in the Mn-rich region.



Figure 4. TEM images of cathodes before and after storage: (a,c) NCM-811 and (b,d) LNCMO-1090.

## 3.2. Changes in Electrochemical Properties of Ni-Rich Cathodes during Storage

To further clarify the change of interfacial structure, we characterized the layered Nirich cathodes before and after storage using electrochemical impedance spectroscopy (EIS). The impedance spectrum (Figure 5) includes two semicircles in the high-frequency and medium-frequency region and an oblique line in the low-frequency region. The impedance curve intercepting with the Z' axis at the highest frequency refers to ohmic resistance ( $R_s$ ), the semicircle in the high-frequency region is related to the impedance generated by  $Li^+$  passing through the surface film of electrodes ( $R_f$ ), the second semicircle in the medium-frequency region is the impedance caused by the interface charge transfer ( $R_{ct}$ ), and the low frequency area oblique line is related to the diffusion behavior of lithium ions in the material phase [36,37]. The equivalent circuit diagram in Figure 5 can be used to analyze and fit the impedance spectrum, and the fitting results are shown in Table S3. The results indicated that LNCMO-1090-Fresh had a slightly larger R<sub>ct</sub> value compared to NCM-811-Fresh, which is related to the increased inactive Mn component on the surface [38]. Notably, the electrode impedances of NCM-811-Air and LNCMO-1090-Air after storage had an obvious increase in Rf and Rct values compared to that of NCM-811-Fresh and LNCMO-1090-Fresh before storage. Surface Li<sub>2</sub>CO<sub>3</sub> impurity layers on cathodes accelerate the harmful side reactions at the interface between electrolytes and the active surface of cathodes to produce the cathode-electrolyte interphase (CEI) layer, thereby hindering Li<sup>+</sup> diffusion to generate a  $R_f$  [39–41]. Meanwhile, the interfacial side reaction causes the surface to undergo a severe structural transformation to greatly impede the charge transfer process. As shown in Table S3, the increases in both Rf and Rct value for LNCMO-1090 during storage were remarkably lower than those for NCM-811, indicating the suppressed interfacial side reaction resulting from the thinner Li<sub>2</sub>CO<sub>3</sub> impurity layers on the LNCMO-1090 surface. The electrode impedance of cathodes after storage increased due to the significant change in their surface/interfacial structure, which drastically affected the electrochemical performance of the layered cathodes.



**Figure 5.** The Nyquist plots and the corresponding equivalent circuit model (inset) of the cathodes charged to 4.3 V before and after storage: (a) NCM-811 and (b) LNCMO-1090.

Furthermore, the variation in the electrochemical performance of layered cathodes during storage was investigated. Figure 6a,b show the first charge and discharge curves of NCM-811 and LNCMO-1090 cathode materials before and after storage. An obvious change in the charge–discharge curves was observed in the cathode materials after storage, and the specific capacity at the intersection between charging and discharging curves decreased, indicating that severe polarization behavior occurs in the cathode materials after storage [7,42]. Compared with NCM-811 (Figure 6a), LNCMO-1090 (Figure 6b) demonstrated a smaller change in decreasing capacity at the intersection of charge–discharge curves, mean-

ing a slightly weak polarization in LNCMO-1090-Air. Additionally, the onset potential of the first delithiation of NCM-811 significantly increased after storage (Figure 6a), but it had no obvious change in the LCNMO-1090 cathode (Figure 6b). These observations are closely correlated with the lower electrode impedance of LNCMO-1090-Air, which can ascribed to the thinner surface  $Li_2CO_3$  layer on cathode materials after storage. Consequently, a slight decrease in both charge/discharge capacity and overall Coulombic efficiency was observed in NCM-811-Air and LNCMO-1090-Air after storage (Figure S7). As shown in Table 1, NCM-811-Fresh and LNCMO-1090-Fresh materials delivered the reversible capacities of 224 mAh  $g^{-1}$  and 207 mAh  $g^{-1}$  , but their capacities after storage decreased to 219 mAh g<sup>-1</sup> and 201 mAh g<sup>-1</sup>, respectively. Furthermore, the cycling performance of the cathode materials before and after storage was evaluated at 0.1C. Figure 6c,d show that NCM-811-Fresh and LNCMO-1090-Fresh before storage exhibited excellent cycling stability, with a capacity retention of 82.2% and 84.6% after 50 cycles, respectively (Table 1). The excellent cycling stability of fresh cathodes was also confirmed by the small variation in the charge and discharge profiles during cycling (Figure S3a,c). However, the surface Li<sub>2</sub>CO<sub>3</sub> impurities on the cathode materials chemically reacted with electrolytes, leading to continually thickening CEI layers and serious degradation of the surface structure of the electrode. Therefore, the layered Ni-rich cathodes after storage exhibited deteriorated cycling performance, and the reversible capacities rapidly decreased to 117 mAh  $g^{-1}$  for NCM-811-Air and to 126 mAh g<sup>-1</sup> for LNCMO-1090-Air after 50 cycles, which amounts to 53.4% and 62.9% of initial capacities, respectively. Despite the decay in the capacities as aggravated by surface Li<sub>2</sub>CO<sub>3</sub> impurities reacting with electrolyte, LNCMO-1090 exhibited a relatively slow deterioration of cycling performance to NCM-811, which was apparent in the change in the charge–discharge curves during cycling (Figure S3b,d). Additionally, the rate capability of layered cathodes before and after storage was estimated, as shown in Figure 6e,f. After the rate was increased from 0.1C to 2C, the reversible capacities of NCM-811-Fresh and NCM-811-Air decreased to 138 mAh  $g^{-1}$  and 94.5 mAh  $g^{-1}$ (Figure S4a,b), which accounted for 62% and 43%, respectively, of their initial capacities at 0.1C (Figure S5a). For LNCMO-1090, the reversible capacities of fresh and stored cathodes drop to 144 mAh  $g^{-1}$  and 125 mAh  $g^{-1}$ , respectively, when the rate was increased to 2C (Figure S4c,d), which is 70% and 58% of the initial capacity at 0.1C (Figure S5b). Although the rate capability of cathode materials deteriorated after storage, LNCMO-1090 exhibited a slower capacity decay compared to NCM-811, which can be attributed to the relatively stable surface structure of LNCMO-1090.



**Figure 6.** Comparison of electrochemical performance of cathode materials before and after storage. (**a**,**b**) The first charge/discharge profiles at 0.1 C. (**c**,**d**) Cycling performance at 0.1 C. (**e**,**f**) Rate capability.

Sample		First Discharge Capacity (mAh g <sup>-1</sup> )	50th Discharge Capacity (mAh g <sup>-1</sup> )	Capacity Retention (%)
NCM-811	Before storage	224	184	82.2
	After storage	219	117	53.4
LNCMO-1090	Before storage	207	175	84.6
	After storage	201	126	62.9

**Table 1.** The first discharge capacity and 50th discharge capacity before and after storage and the capacity retention after 50 cycles at 0.1 C of the cathode materials of NCM-811 and LNCMO-1090.

## 3.3. Thermal Stability of Ni-Rich Layered Cathodes

The safety features of LIBs are also a significant indicator for their practical application, which depend strongly on the thermal stability of cathodes [43-45]. It is well known that the thermal stability of charged NCM cathodes is closely related to their compositions [46]. The higher the Ni content in the layered cathode is, the worse thermal stability, the lower initial temperature for its structural transformation, and the faster the oxygen release rate. Enriching the Mn content in the layered cathodes is an effective method to improving the thermal stability of the cathodes [23,47–49]. An elevated temperature leads to the delithiated layered cathodes suffering serious structural transformation, which is accompanied by the release of oxygen which accelerates the combustion of electrolytes and results in serious thermal runaway or even explosion [50–54]. Firstly, the heat release of the cathodes with varied delithiation states was evaluated using a differential scanning calorimeter (DSC). The delithiation states of NCM-811 cathodes were controlled by changing the charge voltage. The heat release of NCM-811-4.3V, as shown in Figure 7a, responding to the structure transformation and oxygen release [31,55], began to occur when the temperature rose above 200 °C, and a weak peak appeared at 220 °C. With further elevated temperatures, more severe structure degradation resulted in greater oxygen release, thereby accelerating the combustion of electrolytes to generate a peak at approximately 272 °C. The total heat release of NCM-811-4.3V during the exothermic reaction was recorded to be 1270 J  $g^{-1}$ . In higher delithiation states, the initiation of heat release of NCM-811-4.5V and NCM-811-4.8V moved to a lower temperature below 200  $^{\circ}$ C, and the peak shifted to a lower temperature of 205 °C. For the whole exothermic reaction during elevating temperature, the heat release of NCM-811-4.5V and NCM-811-4.8V was recorded to be 1312 J  $g^{-1}$  and 1336 J  $g^{-1}$ , respectively. The heat release of the delithiated Ni-rich cathodes increases with the increased charge states. The higher delithiation induces a greater production of Ni<sup>4+</sup> ions in the cathodes and more substantial oxygen release, which was soundly confirmed by the more obvious exothermic peak of NCM-811-4.5V and NCM-811-4.8V at 203 °C. Furthermore, the influence of introducing Li<sub>2</sub>MnO<sub>3</sub> on the thermal stability of the cathodes was evaluated by DSC (Figure 7b). When charged to 4.5 V, NCM-811-4.5V showed a clear exothermic peak for phase transition at about 200  $^{\circ}$ C, while this peak became very weak and flat in LNCMO-1090-4.5V. This result indicates that introducing Li<sub>2</sub>MnO<sub>3</sub> reduces the oxygen release and impedes the phase transition behavior of the cathodes. Meanwhile, the heat release of the delithiated cathodes decreased from 1312 J  $g^{-1}$  of NCM-811 to 891 J  $g^{-1}$  of LNCMO-1090. LNCMO-1090 exhibited excellent thermal stability compared to NCM-811. Introducing layered  $Li_2MnO_3$  into Ni-rich layered cathodes increases the stable Mn component (reducing the active Ni component) to significantly reduce the chemical reactivity and inhibiting the oxygen release in the formed solid-solution cathode, thereby enhancing the structural stability and thermal stability of the layered cathode.



**Figure 7.** (a) The DSC curves of the NCM-811 cathode with different charge states. (b) The DSC curves of the NCM-811 and LNCMO-1090 cathodes with charge state of 4.5 V vs. Li/Li<sup>+</sup>.

## 4. Conclusions

In conclusion, the effects of introducing Li<sub>2</sub>MnO<sub>3</sub> on the storage performance and thermal stability of the Ni-rich cathode were investigated. The physical characterization results indicated that a thick and dense Li<sub>2</sub>CO<sub>3</sub> layer is produced on the surface of the Ni-rich layered cathode after storage for 6 months in the air due to its high surface reactivity. This Li<sub>2</sub>CO<sub>3</sub> impurity layer increases the electrode impedance and accelerates the cathode-electrolyte side reaction, resulting in severe structural degradation and electrolyte decomposition. Consequently, Ni-rich cathodes after long-term storage exhibit a remarkable deterioration in the reversible capacity, cycling stability, and rate capability. Introducing Li<sub>2</sub>MnO<sub>3</sub> into Ni-rich cathode can increase the Mn component and reduce the Ni component on cathode surface, thereby reducing its surface reactivity and sensitivity to air. Therefore, the formed solid-solution cathode (LNCMO-1090) exhibited a significant inhibitory effect on the deterioration of electrochemical performance after storage in air. In particular, LNCMO-1090 after storage still maintained a relatively superior rate capability with a high reversible capacity of 125 mAh  $g^{-1}$  at 2C, which can be attributed to the thinner Li<sub>2</sub>CO<sub>3</sub> impurity layer forming on the LNCMO-1090 surface. Furthermore, DSC test results showed that the heat release of the Ni-rich cathode strongly depended on the delithiation states (charge voltage), which is closely linked with oxygen release. Introduction of Li<sub>2</sub>MnO<sub>3</sub> had a remarkably suppressive effect on oxygen release from the Ni-rich cathode. Therefore, LNCMO-1090 demonstrated greater thermal stability compared with NCM-811. This work introduces a new method for improving the structural and thermal stability of Ni-rich layered cathodes.

**Supplementary Materials:** The following supporting information can be downloaded at https:// www.mdpi.com/article/10.3390/en17040810/s1: Table S1: ICP results for the chemical composition of the cathodes powders; Table S2: Rietveld analysis results of the cathodes; Table S3: Fitting values of the EIS curves of the cathodes; Table S4: Analysis of the relative content of surface elements from XPS results; Figure S1: The first CV curves of the cathodes; Figure S2: EDS mapping of NCM-811-Air; Figure S3: The charge/discharge profiles at different cycles of cathodes before and after storage; Figure S4: The charge/discharge profiles at different rates of cathodes before and after storage; Figure S5: The capacity retention at different rates of cathodes before and after storage; Figure S6: The broad spectrum of XPS for NCM-811 cathodes; Figure S7: Comparison of the electrochemical performance of cathode materials: (a,b) Coulombic efficiency of cycling performance and (c,d) Coulombic efficiency of rate performance.

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