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# Superiority of Single-Crystal to Polycrystalline $LiNi_xCo_yMn_{1-x-y}O_2$ Cathode Materials in Storage Behaviors for Lithium-Ion Batteries

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ABSTRACT: High nickel content  $\text{LIM}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  (NCM) cathode materials have been attracting increasing attention owing to their significant advantages, but in practical application, because of their poor storage performance their production and transportation cost a lot. The gap between polycrystalline particles can very easily become the site where impurities are first generated; thus, whether the single crystal structure will affect the storage properties of high nickel content NCM materials is worth studying. In this work, we take two typical high nickel content ternary materials,  $\text{LiN}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM811) and Li-Ni<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> (NCM622), as samples to study the differences in properties of single-crystal and polycrystalline materials after storage. Through comparative research, under the same storage



conditions, the single-crystal structure materials have significantly less impurities formed on the surface, the structural stability of materials is obviously better, and they can also exhibit superior electrochemical performance after storage. Particularly for the NCM811 materials with a higher nickel amount, the specific capacity of polycrystalline NCM811 materials basically comes nearly to zero after storage, but the single-crystal structure NCM811 materials can still perform a relatively stable cycle with a certain capacity. It can be concluded from the work that for high nickel content NCM cathode materials, the single-crystal structure can greatly improve its storage performance.

**KEYWORDS:** LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub>, single-crystal, polycrystalline, storage performance, cathode, lithium-ion battery

# INTRODUCTION

With the continuous development of electric vehicles and energy storage, people's demand for high energy density lithium-ion batteries is growing, so there is an urgent need for advanced cathode materials with high specific capacity.<sup>1-3</sup> Among many cathode materials, high nickel content  $LiNi_xCo_yMn_{1-x-y}O_2$  (NCM) materials have become promising cathode materials for their significant advantages in energy density and have attracted widespread attention.<sup>4-6</sup> However, in practical application, the electrochemical performance of nickel-rich oxide cathode materials is not very satisfactory, and they still need to be further improved to meet people's needs.<sup>7</sup> These shortcomings are largely because of the fact that conventional NCM cathode materials are secondary spherical particles formed by stacking many randomly oriented primary nanoparticles, which often undergo volume expansion and intergranular erosion during operation.<sup>8-11</sup> A large number of primary nanoparticles will produce violent microstrain at the boundary of the primary particles when expanding and contracting, which is one of the main causes for the decline in the long-cycle performance of nickel-rich NCM cathode materials.<sup>12-16</sup> With increasing scientific research, people have found that single crystal NCM materials have good performance in terms of cycle, rate, and even high voltage performance.<sup>17–19</sup> For high nickel content ternary materials, another issue that cannot be ignored is their sensitivity to the atmospheric environment. After storage in the air atmosphere for some time, they will deteriorate to a great extent, which seriously affects their electrochemical performance. Therefore, it is often necessary to seal them during production and transportation, which results in a lot of  $\cot 2^{-23}$  Atmospheric water and carbon dioxide will invade the gap between the primary particles and generate impurities on the surface when exposed to air.<sup>24–26</sup> For NCM materials, storage under air conditions will not only change the surface morphology and structure of the materials, but also seriously affect the electrochemical properties. After storage, impurities with poor conductivity will be formed upon the exterior of the materials, which will increase the polarization, and Ni3<sup>+</sup> in the

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#### **ACS Sustainable Chemistry & Engineering** pubs.acs.org/journal/ascecg 104 0.2 104 b а 0.0 103 103 0.0 102 102 -0.5 -0.2 101 101 100 100 DSC (mW/mg) DSC (mW/mg) -0.4 -1.0 99 Mass (%) 99 Mass (%) -0.6 **9**8 98 NCM622-pristine-DSC -1.5 -0.8 CME22 97 NCM622 ristine-DSC 97 622-3 weeks-DSC 96 96 -1.0 -2 0 95 95 SC NCM622-pristine-Mass -1.2 C NCM622-pristi 94 94 -2.5 SC NCM622-3 weeks-Mass -1.4 93 93 PC NCM622-3 we 92 -3.0 92 -1.6 1000 1000 200 400 600 800 200 400 600 800 Temperature (°C) Temperature (°C) 104 104 d 0.0 C 0.0 102 102 -0.5 100 100 -0.5 98 98 OSC (mW/mg) DSC (mW/mg) -1.0 96 96 Mass (%) -1.0 (%) -1.5 94 94 Mass ( SC NCM811-pristine-DSC 92 92 ristine-DSC -1.5 -2.0 90 90 SC NCM811-9 days-DSC 88 -2.5 88 -2.0 SC NCM811-pristine-Mass 86 86 -3.0 SC NCM811-9 days-Mass 84 -2.5 84 82 82 -3.5 1000 0 200 400 600 800 1000 200 400 600 800 Temperature (°C) Temperature (°C)

Figure 1. TG&DSC tests of (a) SC NCM622, (b) PC NCM622, (c) SC NCM811, and (d) PC NCM811 materials before and after storage.

materials will change into Ni2<sup>+</sup>, accompanying the release of Li<sup>+</sup> from the materials.<sup>27</sup> According to research, the poor storage behaviors of high nickel content NCM materials are related to the nature of secondary particles since the primary particle gaps are more likely to be the targets of the components in the air. However,for single crystal materials, the situation is pretty different; it will not be affected by the accumulation of secondary particles. In this case, whether single-crystal ternary materials have better storage performance is worth further studying.

In this work, two high nickel content ternary materials NCM811 and NCM622 were taken as research objects. The storage properties of single crystal and polycrystalline materials with different nickel contents were studied. Through comparative experiments, we found that single-crystal high nickel content ternary materials have better storage performance than polycrystalline materials. Under the same storage conditions, the amount of impurities generated on single-crystal materials is significantly less, and the electrochemical performance can be better maintained.

#### EXPERIMENTAL SECTION

**Material Storage Experiment.** The cathode materials used in the experiments are all commercial materials. In the storage experiment, four kinds of materials were used as the research objects, including single crystal NCM622, polycrystalline NCM622, single crystal NCM811, and polycrystalline NCM811, hereinafter are referred to as SC NCM622, PC NCM622, SC NCM811, and PC NCM811. Four copies were made for each material, and each copy occupied about 5 g of storage. The storage experiments were carried out in a stable temperature and humidity box at 55 °C and 80% relative humidity. According to previous research, it is known that a ternary material with a higher nickel content has poorer stability in atmospheric environment, so the storage time of NCM622 materials was set as 1, 2, 3, and 4 weeks, and the storage period of NCM811 materials was set as 3, 6, 9, and 12 days, respectively. This arrangement can not only ensure that the materials have a certain electrochemical performance during the storage period, but also show the storage performance differences between the materials.

Electrochemical Performance Test. In the electrochemical test, the electrodes of the battery are formulated according to the following ratio. The mass ratio of the positive electrode active materials was 80%, and 10 wt % of the conductive agent acetylene black and 10 wt % of the binder polyvinylidene fluoride were added to the slurry. The N-methyl-1,2-pyrrolidne was used as a solvent to evenly disperse the added materials. After that, it was spread on the aluminum current collector and placed in a vacuum oven of 80 °C to dry overnight. The dried foil was made into circular electrodes with a diameter of 1.2 cm and assembled into 2016 coin-cells. In the assembly of the battery, the as-prepared electrode was the positive electrode, the lithium piece was the negative electrode, a Asahi Kasei separator was the separator, and the electrolyte was LB-301 electrolyte (1 M LiPF6, EC: DMC = 1: 1). The battery was charged with constant current and constant voltage, and the constant current discharge procedure was performed with 200 cycles under a voltage of 3.0-4.3 V.

**Physical Property Test.** After each copy of materials was stored, it was weighed to determine its mass increase during storage. These materials were also thermogravimetrically tested to identify the amount and composition of its weight gain more accurately. Scanning electron microscopy (SEM) was applied to monitor the difference in the exterior morphology of the materials. Transmission electron microscopy (TEM) was applied to distinguish the impurities generated on the surface of the materials more finely. X-ray diffraction (XRD) was applied to differentiate the structural alteration of the materials. Fourier-transform infrared (FT-IR) testing was used help verify the composition of impurities on the surface of the materials. Raman spectroscopy was used to detect the structural changes of the materials and the impurity components generated.



Figure 2. SEM images of (a-d) SC NCM622 materials and (e-h) PC NCM622 materials after storage for 1-4 weeks.

#### RESULTS AND DISCUSSION

Storage Properties. According to previous research,<sup>26</sup> the increase in the mass of NCM materials during storage is strongly related to their storage properties. The more the quality increases after storage, the worse the storage property is. Figure S1 shows the weight gain chart after storage of different materials. From the storage comparison of materials with different nickel contents, the mass increase of NCM811 materials with a higher nickel content is much higher than that of NCM622 materials. It is still worth noting that the storage time of the NCM811 material samples is considerably shorter than that of the NCM622 materials. For the NCM811 material, the longest storage time is only 12 days, but the longest storage time of the NCM622 material reaches 4 weeks. It is verified that for NCM materials, the nickel content has a great influence on its storage performance, and when the nickel content is at a higher level, increasing the nickel content will significantly reduce its storage performance.<sup>28</sup> At the same time, by comparing the same-nickel-content materials with different structures, the difference in weight gain between the two is also obvious. Whether it is NCM622 or NCM811 materials, the single crystal structure materials both have significantly lower mass gain, which shows that for NCM materials, the single crystal structure can improve its storage performance.

In order to analyze the impurities generated after storage more accurately, the TG&DSC test (Ar gas atmosphere) was conducted after storage. The test temperature range was from 35 to 1000 °C, and the heating rate during the test was 5 °C/ min. The test results are shown in Figure 1. Through the analysis of the TG&DSC results, it can be seen that among the

four samples used in the experiment, the weight loss of the SC NCM622 material after storage in the TG test is the smallest, which means that the impurity generated during the storage process is minimal. The second smallest reduction in mass is for the PC NCM622 material, and the most mass loss is for the PC NCM811 material, indicating that the amount of impurities generated in the PC NCM811 material during storage is the most. After the same-nickel-content materials are stored for the same time (Figure S2), the weight reduction of the single crystal structure material is significantly smaller. The results are consistent with the mass increase in the experiment. For both NCM622 and NCM811 materials, there were three significant mass declines during the thermogravimetric test. The first two were 200-500 and 670-780 °C, which corresponded to the desorption and decomposition of adsorbed substances and thermal decomposition of  $Li_2CO_3$ <sup>20</sup> In the third stage of mass decline, the situation is different for different nickel content materials. The mass decline of NCM622 materials is after 800  $^\circ\text{C}\textsc{,}$  and that of the NCM811 materials is after 750 °C. These stages correspond to the innate thermal decomposition of the two materials. By comparison, it can be found that the mass reduction of the material after storage mainly occurs in the first stage, indicating that the mass reduction is mainly contributed by the adsorbed substances. Therefore, during storage, the mass increase is mainly because of the adsorption of a large amount of adsorption system impurities (bicarbonate and easily decomposed carbonate) and a small amount of Li<sub>2</sub>CO<sub>3</sub> grime upon covering the materials.

SEM is an effective method to observe the surface properties of materials. In order to study the change of the surface state of



Figure 3. SEM images of (a-d) SC NCM811 materials and (e-h) PC NCM811 materials after 3, 6, 9, and 12 days of storage.

the nickel-based ternary material before and after storage, SEM tests were conducted on the materials before and after the experiment. The SEM images of the pristine materials without storage are shown in Figure S3. From the test results, we can see that for both single crystal and polycrystalline materials, the surface is smooth and flat, without any impurities attached. However, after storage (Figures 2 and 3), the surface state of each materials has changed significantly. For the SC NCM622 materials, at the initial stage of storage (Figure 2a), there are fine impurity particles on the surface. These impurities are all in the shape of small flakes or particles. After 4 weeks (Figure 2d), the grime upon the covering of the SC NCM622 materials continued to grow and became larger particles attached to the surface of the materials. But the original material at this time is still clearly visible, the main body is still clearly exposed, and is not blocked by excessive impurities generated. In contrast, for the PC NCM622 materials, during the first week of the storage experiment (Figure 2e), impurities have been generated among the prime grains of the materials, and these impurities have a tendency to link into pieces, and part of the main body of the active material has been blocked. With the extension of the storage process, by the last week, a thick impurity layer has been formed upon covering the PC NCM622 materials, and these impurities are connected into a block or a large sheet. The original main materials have been blurred and indistinguishable. Under the same storage conditions, the single crystal NCM622 materials generated significantly less impurities during storage. As the nickel content increases, this phenomenon becomes more pronounced. After storage for 3 days (Figure 3a), the SC NCM811 materials have generated a certain amount of grime on their exterior, and the particle size

of these grime is larger than the grime size of the SC NCM622 materials. When the storage time reaches 12 days (Figure 3d), the impurity content upon covering the SC NCM811 materials increased remarkably, but even so, at this time, we can still identify the main body of the SC NCM811 active materials. However, for the PC NCM811 materials, the situation is completely different. After 3 days of storage, the surface of the PC NCM811 materials had grown large-scale strip-shaped impurities, which is very different from the PC NCM622 materials in the initial stage of impurity morphology, and is closer to the PC NCM622 materials in the later storage period, and compared with the original materials (Figure S3d), the main body of the materials has become blurred and unrecognizable. As the storage experiment continued, the surface impurities of the PC NCM811 materials continue to grow, and the impurities connect to each other into a large block, covering the surface of the original materials. When the storage process is completed, the surface of the PC NCM811 materials is completely tightly covered by impurities. From the results of the SEM tests, for ternary materials with a higher nickel content, impurities are more likely to be generated during storage. For materials with the same nickel content, because of the different structures of materials, significantly more impurities are formed upon covering the polycrystalline structure materials during storage. Moreover, the polycrystalline materials are formed by the accumulation of primary particles, so the impurities will grow together after they are generated between the primary particles, and finally completely envelop the body of polycrystalline materials. The single crystal materials are independent of each other, and impurities are

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difficult to connect with each other on the surface, so the original material body will not be wrapped by impurities.

The storage process will cause great changes to the surface morphology of the materials, but it is still unknown whether it will affect the interior of the materials. So the original materials and the materials with the longest storage time were cut for the internal SEM test. Observing the original materials (Figure S4), we can see that the inside of the original single crystal materials are smooth and flat, and the internal particles of the polycrystalline materials are attached to each other, and there are no other components between the particles. After storage (Figure 4), for single crystal materials, the cross-sections are



Figure 4. Cross-section SEM images of (a) SC NCM622, (b) PC NCM622, (c) SC NCM811, and (d) PC NCM811 materials after storage.

still flat and smooth, and there is no obvious change, while the cross-sections of polycrystalline materials are significantly different from the original samples, and the interiors are attacked by impurities to varying degrees. From the SEM figures, impurities can continue to grow along the apertures among the premier particles of the polycrystalline materials, all the way to the interior of the materials, especially in the near surface area. To better distinguish the changes inside the materials, elemental analysis was performed on the cross-section of the materials. From the analysis results (Figure S5), there is almost no C element in the cross-section of the single crystal materials after storage, whereas obvious C element appeared in the cross-section of the polycrystalline materials; this means after storage, there are  $Li_2CO_3$  impurities inside the polycrystalline materials, which matches the cross-sectional SEM test conclusion.

In order to observe the changes of materials after storage at a smaller scale in detail, TEM tests were conducted on the four materials before and after storage. Figure S6 shows the TEM test of the materials before storage. From the TEM results, it can be clearly observed that before storage, the cathode materials with different nickel contents, whether it is a single crystal or polycrystalline structure, the surface of the pristine materials is smooth and flat, and there is no impurity component around the materials. However, after storage (Figure S7), obvious impurities appeared around the four materials. For single crystal materials, there are relatively fewer impurities around the materials, while for polycrystalline materials, the results are much different. In the TEM test, there are many long or massive impurities in the morphology of the stored polycrystalline materials, and a large amount of impurities are generated between the primary particles. These impurities concentrate between primary particles and tightly wrap the polycrystalline cathode materials. The conclusion of the TEM morphology tests is also consistent with that of the SEM tests, indicating that compared to the single crystal NCM materials, the polycrystalline structure NCM materials do have a significant drawback in storage performance, and more impurities will be generated during the storage process. In addition, the degree of structural degradation of the materials can also be judged by observing the phase change behavior of



Figure 5. HRTEM and FFT images of (a) SC NCM622, (b) PC NCM622, (c) SC NCM811, and (d) PC NCM811 materials after storage.

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Figure 6. Electrochemical tests of the different samples before and after storage. The cycling performance, first-cycle charge and discharge curves, and impedance of (a) SC NCM622, (b) PC NCM622, (c) SC NCM811, and (d) PC NCM811 materials before and after storage.

the near surface area after storage. As shown in Figure S8, all the pristine materials have a very good and orderly layered structure, indicating that they all have good crystallinity. Through the high-resolution transmission electron microscopy (HRTEM) and fast Fourier transform (FFT) results shown in Figure 5, it is obvious that four materials have undergone significant phase changes near the surface area after storage, and compared with the single-crystal structure materials, the phase change layer near the surface of the polycrystalline structure materials after storage is significantly thicker, indicating that after the polycrystalline materials are stored, the layered structure of the materials is damaged more seriously. For NCM materials, the phase change on the surface will adversely affect their electrochemical performance,<sup>29</sup> so this also brings hidden danger to the cycle performance of polycrystalline materials after storage.

**Electrochemical Performance.** In order to further explore the effect of storage on single crystal and polycrystalline materials in practical use, electrochemical tests were conducted on the different samples before and after storage. The results of the electrochemical tests are shown in Figure 6. The figure clearly shows that for the ternary cathode materials

with the same nickel content, after the same storage process, the single crystal structure materials are significantly superior to the polycrystalline structure materials in terms of capacity and cycle retention rate. For the NCM622 materials (Figure 6a1-b1), the single crystal materials can still maintain a relatively stable cycle after being stored for 1-2 weeks, whereas the capacity of the polycrystalline materials declined significantly from the beginning, and this trend extends to the end of the entire cycle. The superiority of the electrochemical properties of stored single crystal materials is more obvious in the NCM811 materials (Figure 6c1-d1). When stored for 3-6 days, the SC NCM811 materials can still perform a good cycle, whereas the capacity of the PC NCM811 materials has a cliff-shaped decline from the beginning of the cycle, and continues to maintain at a very low level. When stored for 9-12 days, the SC NCM811 materials can be continuously charged and discharged with a certain capacity. However, the PC NCM811 materials can hardly release capacity, and maintains a capacity close to zero in subsequent cycles, indicating that the materials have completely lost electrochemical activity at this time. Therefore, it is not difficult to see from the analysis of electrochemical performance that for single crystal materials, after a certain period of storage, the electrochemical activity of the materials can be maintained to some extent. However, for polycrystalline materials, especially with a high nickel content, after storage, the electrochemical performance of the materials will be greatly reduced, or even completely lost. To a certain extent, it also reflects the significant advantages of the single crystal structure in storage performance.

It is worth noting that for nickel-based ternary cathode materials, the first-round cycle of stored materials has important evaluation significance. When the ternary cathode materials are placed in the atmospheric environment for a while, a certain amount of adsorptive impurities will be generated on the surface. The ionic and electronic conductivity of these impurities are often low,<sup>30</sup> which will cause some materials to lose electrochemical activity, resulting in the decrease of capacity and initial discharge voltage.<sup>25,31</sup> In this work, the electronic conductivity of the materials before and after storage was measured by a ST-2722 semiconductor resistivity power tester (Suzhou Jingge Electronic Co.,Ltd.). From the test results (Figure S9), all materials have a certain degree of decline in electronic conductivity after storage, and the decline in the conductivity of the SC NCM622 material is the least, while the decline in the conductivity of the PC NCM811 material is the most obvious, which is also consistent with the impurity content generated on the surface of the materials. Comparing the first-cycle charge-discharge curves of different materials after storage (Figure 6a2-d2), it can be observed that the first-cycle discharge capacity of all materials after storage has decreased, and for the same nickel content materials, the discharge capacity of the single crystal materials is obviously higher than that of the polycrystalline materials. At the same time, the first-round discharge voltages of the four materials after storage all decreased to varying degrees, and the severity of the voltage drop was the same as the first-round discharge capacity reduction trend. SC NCM622 has the smallest drop in discharge voltage of 0.0114 V after storage, and the PC NCM811 has the largest voltage drop, which is 0.045 V. In the EIS tests (Figure 6a3-d3), as the storage time increases, the impedance value of the materials will increase significantly. However, when the nickel content is the same,

the impedance of the polycrystalline structure materials is significantly higher than that of the single crystal material, which also shows that the polycrystalline structure materials generate much more impurities on the surface during storage. As can be seen from the impedance test results, the increase in the impedance of the materials after storage is mainly because of the increase in the charge transfer resistance, and the charge transfer resistance is caused by the charge exchange at the interface of the materials and the electrolyte. Therefore, there are more impurities with poorer conductivity on the surface of the polycrystalline materials, so their impedance is significantly larger.

In order to clarify whether new electrochemical reactions occur after storage, the first-round dQ/dV curves (Figure S10) of the materials before and after storage were analyzed. From the figure, we can see that for the pristine materials, the dQ/dVcurves are all consistent with the typical NCM622 and NCM811 materials.<sup>28</sup> No additional redox peak appears in the stored materials between the charge and discharge interval, indicating that the materials do not have new electrochemical reactions. Different from the pristine materials, the oxidation peak of the stored materials will move to a higher potential, and the reduction peak will move to a lower potential, and this phenomenon will become more obvious with the storage time increase, and the deviation extent of polycrystalline materials is significantly greater. The reason for this phenomenon is that after the stored materials get in contact with the electrolyte, it will generate substances with poor conductivity on the surface of the materials, which will increase the degree of polarization of the electrode and the difference between the redox peaks.<sup>26</sup> The results show that the polycrystalline materials generate significantly more impurities after storage, so that the degree of polarization of the electrode is significantly increased. In addition, Figure S10d clearly shows that after storage for a long time, the PC NCM811 materials have almost no redox peaks, indicating that it has basically been deactivated at this time, and no electrochemical reaction has occurred. This also agrees with the cycle performance results shown in Figure 6d1.

Physical Characteristics. The physical properties of the materials before and after storage are also worthy of our attention. In order to further explore the main components of the impurities generated by the materials during storage, FT-IR tests were conducted on the stored materials. The test results are shown in Figure S11. After storage, new absorption peaks appeared mainly at 865, 1435, and 1496 cm<sup>-1</sup>, and some absorption peaks also appeared at 3200-3600 cm<sup>-1</sup>. The absorption peaks at 1435 and 1496 cm<sup>-1</sup> belong to the symmetric and antisymmetric stretching vibration peaks of C-O, and the absorption peak at 865 cm<sup>-1</sup> belongs to the bending vibration absorption of  $CO_{3^{22,32}}$  these absorption characteristic peaks indicate that the materials generate obvious Li<sub>2</sub>CO<sub>3</sub> on the surface after storage. The absorption peak intensity of the polycrystalline materials is obviously enhanced, which means that more impurities are generated on the surface of the polycrystalline materials. The absorption peak at 3200-3600 cm<sup>-1</sup> is generally regarded as the stretching vibration peak of O-H, which mainly comes from LiOH.<sup>33</sup> This shows that not only Li<sub>2</sub>CO<sub>3</sub>, but also a small amount of LiOH may exist in the surface impurities of the materials after storage.

To more accurately investigate whether the storage process will affect the structure of the materials. The XRD tests were conducted on four kinds of samples, and 5 wt % of natural

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Figure 7. XRD results of (a) SC NCM622, (b) PC NCM622, (c) SC NCM811, and (d) PC NCM811 materials before and after storage.

graphite was added to the samples for precise calibration. The test results are shown in Figure 7 and Figure S12. According to the test results, the characteristic peaks of the materials before and after storage have not changed significantly, indicating that the materials still have the R-3m space group structure of  $\alpha$ -NaFeO<sub>2</sub> type.<sup>34,35</sup> Moreover, from Figure S12, the characteristic peaks of (006)/(102) and (108)/(110) of the materials are clearly divided before and after storage, which also shows that the main body of materials still maintains an orderly hexagonal crystal structure.<sup>35</sup> However, after storage, the (003) crystal planes of all materials have a tendency to shift to a lower angle, and with the storage time increasing, the angle of shift is greater. In the XRD analysis of NCM materials, the (003) crystal plane represents the diffraction between adjacent transition metals, and when Li<sup>+</sup> is extracted from the materials,

the repulsion between the adjacent O layers increases, resulting in an expansion of transition metal layers, making the (003) crystal plane shift to a lower angle.<sup>36–40</sup> The principle is also the same during storage. Impurities such as  $\text{Li}_2\text{CO}_3$  will exacerbate the extraction of  $\text{Li}^+$  in the material lattice, which results in the shift of the (003) crystal plane. Therefore, the degree of (003) crystal plane deviation also represents the degree of deterioration of the materials during storage at a certain level. By comparison, it is not difficult to find that among the materials with the same structure, the materials with a higher nickel content have a greater degree of (003) crystal plane deviation, and for the same nickel content materials, the degree of deviation of polycrystalline materials is obvious deeper than the degree of single crystal materials. The XRD test results are also consistent with HRTEM test results. What



Figure 8. Raman results of (a) SC NCM622, (b) PC NCM622, (c) SC NCM811, and (d) PC NCM811 materials before and after storage.

is more, for the stored materials, three new diffraction peaks appear at 21.2, 30.4, and 31.9°. According to the literature, they can be attributed to crystalline  $\text{Li}_2\text{CO}_3$ .<sup>20,22</sup> This also proves that  $\text{Li}_2\text{CO}_3$  impurities are formed upon covering the materials after storage, and the severity of the impurities is completely consistent with the previous analysis. Therefore, compared with the ternary materials with a polycrystalline structure, the single-crystal materials do have significantly better storage performance.

The Raman test is effective in the study of NCM materials. A series of Raman tests (Figure 8) were carried out on the pristine and stored materials. The test results show that the content of  $\text{Li}_2\text{CO}_3$  impurities generated by the stored single crystal materials is remarkably lower. This is also consistent with the previous test results. At the same time, in the Raman test of NCM materials, the ratio of  $A_{1g}/E_g$  is directly related to the structural integrity of the materials. From Figure S13, for NCM materials with the same nickel content, the drop of the  $A_{1g}/E_g$  value of single crystal materials after storage is significantly lower than that of polycrystalline materials, which also shows that single crystal materials have better storage performance than polycrystalline materials.

# CONCLUSIONS

Nowadays, high nickel content NCM materials have become very important cathode materials in the field of lithium-ion batteries. However, the poor storage performance imposes a lot of costs on production and transportation in practical use, which has a certain negative impact on them to some extent. In this work, we take two typical high nickel content ternary materials, LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> and LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>, as research objects, and carefully studied the differences in the electrochemical performance and material structure of single

crystal and polycrystalline materials at the same nickel content after storage. As a result, we found that the single crystal materials have significantly better storage performance than the polycrystalline materials. During storage, impurities of the polycrystalline materials can grow into the interior of the materials along the gap of the primary particles, while impurities on the surface of the single crystal material will not affect the interior of the material. After storage for the same time, the single crystal materials can maintain better structure and electrochemical performance. This research result shows another advantage of single-crystal ternary materials and can provide guidance for further research studies and production.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c05011.

Comparison of weight gain between single crystal and polycrystalline materials; Comparison of TG and DSC; SEM of pristine materials; the cross-section SEM test images of pristine materials; the sectional element analysis tests; the TEM tests of pristine materials; the TEM morphology tests of stored materials; the HRTEM and FFT images of the pristine materials; the electronic conductivity of materials before and after storage; the first cycle dQ/dV curves; the FT-IR test results; the additional XRD test results; the degree of decrease in  $A_{1g}/E_g$  value of different materials before and after storage (PDF)

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#### Notes

The authors declare no competing financial interest.

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