

Influence of Atmosphere on Electrochemical Performance of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ Electrodes for Li-Ion Batteries

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Abstract. Ni-rich layered materials have been regarded as competitive candidates for advanced lithium-ion batteries due to their high energy density, relatively low cost and environmentally-friendly nature. However, they suffer from serious degradation of cycling performance after exposing to air during their storage. Here we selected $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ as a typical Ni-rich positive material to study the influence upon exposure to ambient air on surface chemical composition and electrochemical performance. TEM confirms the existence of amorphous surface layer after contacting with atmosphere and the thickness is about 3-4 nm. The fresh $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ sample has capacity retention of 94.6% and 93.3% after 50 cycles at 0.2C and 1C, respectively, comparing to the 91.7% and 82.4% of the exposed sample. The charge-discharge curves and electrochemical impedance spectra indicate that exposure to air lead to increased impedance and polarization, which seriously affects $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cycling properties. So, it is very important for Ni-rich cathode materials without contacting with atmosphere directly.

1. Introduction

With the rapid development of electric vehicles (EVs) and energy storage systems (ESSs), the lithium-ion batteries (LIBs) with high energy and power density are in urgent demand. [1-5] However, the energy density of the LIBs is mainly controlled by the electrode materials, especially the cathode materials.[6] Among a large number of cathode candidates, LiCoO_2 has been widely used as a commercialized cathode material for LIBs due to its good cycling properties and excellent rate capability. However, the high cost and environmental concerns of cobalt bring major barrier that impede its large-scale application in high capacity LIBs. [7] Therefore, Ni-rich layered oxides ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$, where $1-x-y>0.5$) have attracted much attention to meet the urgently demand for higher energy and power density for EVs and ESSs. Especially, the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM-811) has been considered as the most promising materials due to its satisfactory energy density, outstanding cycling stability, relatively low cost and eco-friendly nature.[8-10] However, it is well-known that with increase of Ni content in NCM usually leads to high active surface chemistry and poor bulk structural stability, which block its application in commercialized LIBs. Most researches have focused on the improvement of structural stability so far, whereas, the very erratic surface chemistry is also crucial for practical performance of these Ni-rich layered materials. [11-13]



It has been suggested that excess lithium is very necessary for compensating the loss of lithium and achieving stoichiometric Ni-rich layered cathode materials during the high temperature calcining process. However, excess lithium ions, which not migrate into the lattice of bulk materials, usually stop at the surface of the cathode materials. As shown in figure 1, during air storage, the residual lithium ions on particle surface would react with CO_2 , H_2O and O_2 to form an unwanted surface layer composed of Li_2CO_3 or LiOH (Li residuals).[14-16] These residual impurities covering on the material surface will result the easy gelation of the cathode slurry during fabrication, impede the mobility of lithium ions and electrons during cycling and increase the cell impedance.[17] Furthermore, the lithium ions in the sub-surface would also extract from the lattice to react with ambient atmosphere during air storage resulting in surface structural transition. As a result, the inactive surface-layer formation and the structural transition would severely impair the overall performance of the Ni-rich positive electrode material. In generally, it takes a long time to fabricate the cathode materials into a battery, so it is very necessary to have a knowledge of the long-term storage stability of the Ni-rich cathode materials before their extensive application. However, rarely have there been studies reported on the long-time storability of Ni-rich layered oxides.

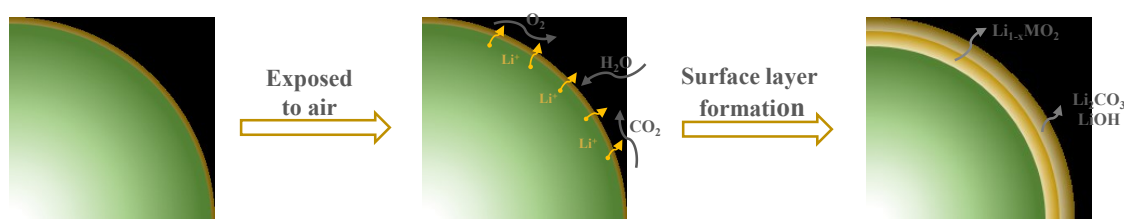


Figure 1. Schematic Illustration of surface layer formation during exposed to air.

In this work, we selected NCM-811 as a typical Ni-rich positive material to examine the effect upon exposure to ambient air on the performance of cathode. The surface chemical composition and the cycling performance are characterized as a function of storage in atmosphere; the results enlighten us that the Ni-rich cathode material is very sensitive to the surrounding environment.

2. Experimental Section

2.1. Synthesis and Characterization

The $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ precursor was prepared via the typical co-precipitation method. Initially, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in distilled water at molar ratio of 8/1/1 and formed 2M metal salts solution. Then, the base solution in flask reactor that contain a certain concentration of NH_4OH was heated at 55°C in water bath kettle, and stirred at 600 rpm under Ar atmosphere. Afterward, the metal salts solution and the mixed solution of 2M NaOH with a desired amount of NH_4OH were pumped into the continuous stirred flask reactor at the same time; the pH was adjusted to 11.0 by adjusting the flow rate of the mixed solution. After complete reaction and aging, the precursor powders were separated by vacuum filtration, washed with deionized water, and vacuum dried at 80°C for 24 h. The dried precursor was mixed with Li_2CO_3 (5mol% excess amount), then sintered at 550°C for 5 h preliminarily and calcined for 15 h at 750°C in O_2 to obtain $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The samples before and after exposing to air were defined as S0 and S1, respectively.

2.2. Material Characterization

The morphologies were observed by field emission scanning electron microscopy (FESEM, FEI QUANTA 250). The surface chemical components were measured by Fourier transform infrared spectrometry (FT-IR) (Hitachi FTIR-8900); Transmission electron microscopy (TEM) was operated upon a JEOL JEM-2100 instrument.

2.3. Electrochemical Measurement

The electrochemical properties were measured in the CR2025 coin type cells for all samples. The working electrodes were prepared by coating slurry containing 10 wt% acetylene black, 80 wt% active materials and 10 wt% PVDF onto a current collector (aluminum foil) and dried at 80 °C for 24h, then punched into discs with 11mm diameter. The electrolyte was 1M LiPF_6 dissolved in ethylene carbonate, ethyl methyl carbonate and dimethyl carbonate (EC/EMC/DMC = 1:1:1 in volume). The cells were assembled in an Ar-filled glovebox and aged for 24h. The electrochemical test was measured between 2.8 and 4.35 V (versus Li/Li^+) on a CT2001A Land instruments. Electrochemical impedance spectroscopy (EIS) was measured by a CHI604D electrochemical workstation with a frequency range of 100 kHz to 0.01 Hz.

3. Results and Discussion

Figure 2 exhibit the morphologies and FT-IR spectra of these two samples of fresh and exposed $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. As shown in figure 2a and b, the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ active materials are packed by a large number of closely contacted primary particles and present a quasi-spherical shape, and we do not find much of a difference between S0 and S1, just the surface seems to be slightly smoother after exposing to ambient atmosphere. Figure 2c illustrates the infrared spectra, it is obvious that the band intensity corresponding to Li_2CO_3 between 860 and 870 cm^{-1} in S1 is much stronger than S0, and the symmetrical absorption peak of Li_2CO_3 in the range of 1430-1500 cm^{-1} also appeared in S1. This indicates that the sample had a violent reaction with CO_2 , H_2O and O_2 when contacted with ambient atmosphere, thus a film composed of Li_2CO_3 and LiOH formed and coated on the particle surface, but the LiOH was not detected in our measurement may be due to its low content. The appearance of this film would result the increase in electrochemical resistance and polarization, affecting the overall performance of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$.

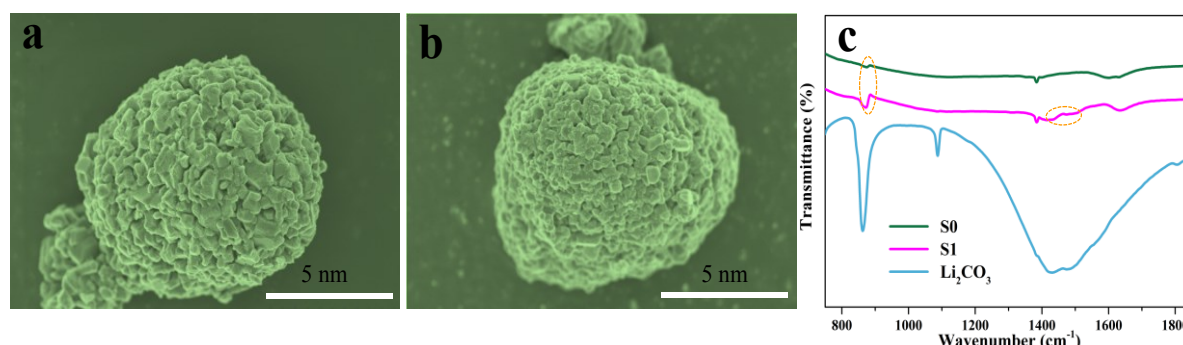


Figure 2. SEM images of (a) S0, (b) S1; FT-IR spectra of S0, S1 and Li_2CO_3

TEM measurements are performed to verify the existence of coating layer on particle surface after exposing to air. TEM images of fresh $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ in figure 3a-b present a smooth and clean surface, and the edges of the particles showed good crystallinity. The lattice fringes of the fresh sample have an interplanar distance of 0.476 nm which is assigned to the (003) planes of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. [18, 19] However, the particle surface shows great changes after exposing to ambient air. As shown in figure 3c, the particle was surrounded by some flocculent materials; the surface was coarse and coated by a rather uniform layer. It is clearly noted in figure 3d that no lattice fringes appeared in this surface layer, indicating that the coating layer is amorphous and the width was about 3-4 nm.

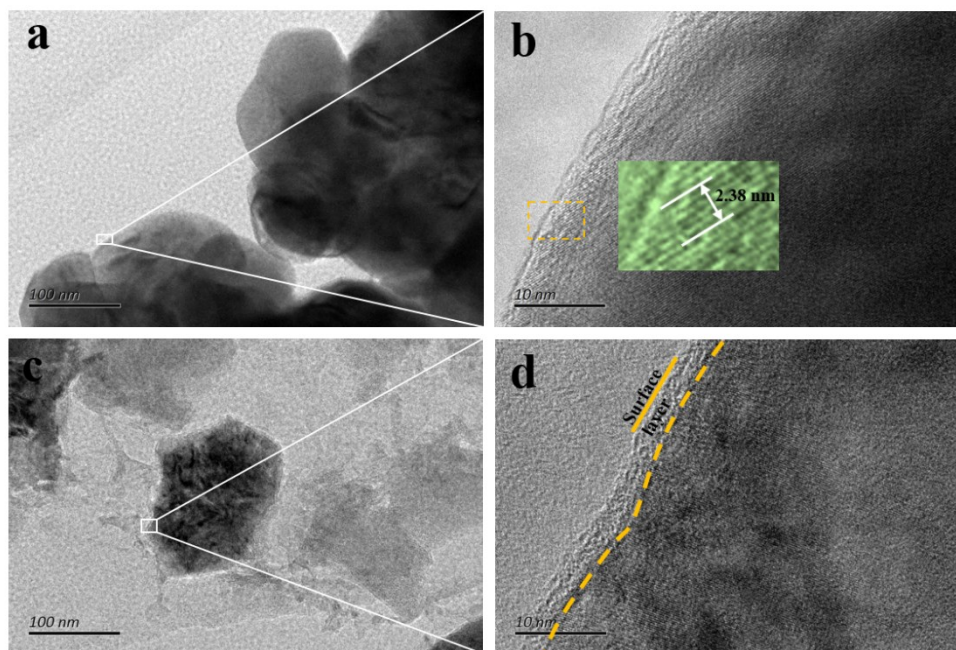


Figure 3. TEM images of (a, b) S0, (c, d) S1

The cycling performance of the two samples at 0.2 C and 1C in 2.8–4.35 V voltage range are shown in figure 4 and the corresponding electrochemical data are listed in Table 1. The two samples display a large difference in the initial discharge capacity. The initial discharge capacity of S0 is 195.9 mAh/g at a current rate of 0.2C, whereas there is only 172.5 mAh/g in S1. After 50 cycles, the reversible capacity of S0 and S1 is 185.3 and 161.0 mAh/g, with capacity retention of 94.6% and 93.3%, respectively. This indicates that the Li_2CO_3 and LiOH coating layer formed after exposing to atmosphere only impacts initial capacity, barely affects the cycle stability. When the current rate reach to 190 mA/g, the S0 also yields a superior cycling performance, with an initial discharge capacity of 172.5 mAh/g and a high capacity retention of 91.7% after 50 cycles. However, the initial discharge capacity of S1 is only 131.4 mAh/g, and the reversible capacity dropped rapidly to 108.3 mAh/g after 50 cycles. As shown in figure 4b, the charging plateau rose considerably with an increase in cycle number because of the polarization caused by Li_2CO_3 and LiOH surface layer. The above cycling results manifest that the coating layer on particles seriously reduces the Li^+ migration rate into the bulk material because of the insulative nature and significantly increases the charge transfer impedance; the cycling properties at higher current rate are extremely reduced.

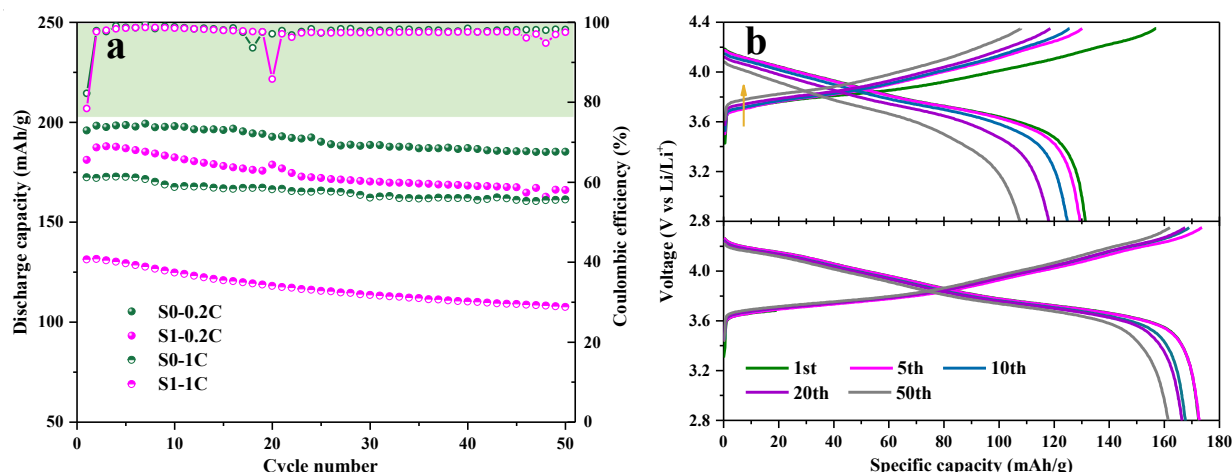


Figure 4. (a) Discharge capacities of the two samples as a function of the cycle number at a current rate of 0.2C and 1C (1C=190 mA/g); (b) charge–discharge curves of S0 and S1 under a current rate of 1C, respectively. All measurements are conducted in the voltage range of 2.8–4.35V vs Li/Li⁺

The EIS tests had been conducted to further investigate the impedance of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ after exposing to air. Figure 5 presents Nyquist plots measured in a charged state of 4.35 V after 1st and 50th cycles at 1C. Generally, the first depressed semicircle in the high frequencies is related to the lithium ion migration through the solid–electrolyte interface (R_f) and another depressed semicircle in the middle frequencies is associated with the charge transfer resistance (R_{ct}) between the electrode and electrolyte, the last sloping tail at low frequencies is related to the diffusion of lithium ion in the solid electrode (Z_w). [20,21] The equivalent circuit model in inset of figure 5 is used for simulating the experimental data and the fitting results are shown in Table 2.

It shows that the R_f values of these two samples are both very small compared to the R_{ct} and do not increase significantly after long cycling, thus the rise of the electrode resistance is predominantly caused by changes of R_{ct} . After 50 cycles, the R_{ct} of S1 increased from 51.7 Ω to 244.1 Ω . We attribute this dramatic variation in R_{ct} to the unstable surface layer which may react with electrolyte more severe than pristine $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. On the other hand, the internal crystalline structure might be destroyed seriously because of the impediment of Li^+ diffusion.

4. Conclusions

We have studied the influence of exposing to air on surface composition and electrochemical performance of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The FT-IR spectra illustrate that contacting with air would induce a violent reaction with H_2O , CO_2 and O_2 and result a covering layer on particle surface. TEM shows that this surface film is amorphous and its thickness is about 3–4 nm. The retentions after 50 cycles at 0.2C and 1C of fresh $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ sample is 94.6% and 93.3%, respectively, much better than that of the exposed sample (91.7% and 82.4%). The results suggest that exposing $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ active material to air has a significant influence on its electrochemical performance, therefore avoiding direct contact with atmosphere is very important in the storage of Ni-rich cathode material and finding effective surface modification methods are also very imperative for the commercialization of Ni-rich cathode materials.

5. Acknowledgment

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6. References

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