

Providing A Long-term Protection for NCM811 Cathode Material by Al₂O₃ Coating Layer

Jing Wang^{1,2,3}, Qiang Yuan¹, Ran Wang¹, Guoqiang Tan^{1,2}, Yuefeng Su^{1,2,3},
Danhua Li¹ and Feng Wu^{1,2,3}

1 School of Materials Science & Engineering, Beijing Key Laboratory of Environmental Science and Engineering, Beijing Institute of Technology, Beijing, 100081, China

2 National Development Center of High Technology Green Materials, Beijing, 100081, China

3 Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing, 100081, China

Email: wangjingbit98@bit.edu.cn

Abstract. The degradation of Ni-rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode material is successfully suppressed via a facile Al₂O₃ coating method. The coated Al₂O₃ layer on the electrode surface is inactive and amorphous, it does not react with the electrolyte and could provide a long-term protection on the electrode during cycling. The electrochemical performance of the modified NCM811 was improved dramatically both at room and elevated temperature. The capacity retention of pristine NCM811 was enhanced from 81.8% to 91.7% when the coating amount reached to 2 wt% at 25°C and much increased from 68.5% to 87.7% at 55°C. Such excellent high temperature performance clearly confirmed the effect of Al₂O₃ on the structure stability of electrode, it successfully built a favorable protection of the bulk NCM811 from direct contact with electrolyte and suppressed the undesired side reactions.

1. Introduction

Over recent years, the rechargeable lithium-ion batteries (LIBs) have widely used as the power sources for portable electronics, electric vehicles (EVs) and massive energy storage systems (ESSs). Thus, in turn, a lithium-ion battery system with higher energy density, longer cycle life, better safety and lower cost are in urgent demand [1,2] Layered Ni-rich compounds with the general formula LiNi_xCo_yMn_{1-x-y}O₂ (NCM, where $x > 0.5$, $x+y+z=1$) are considered as most promising cathode materials for the next-generation LIBs because of their relatively high capacity ($>180 \text{ mA h g}^{-1}$) and some of them have been applied in electric vehicles [3,4] However, the high content of Ni usually causes rapidly capacity fading and severe structure deterioration, and the major reason is the side reactions between electrode and electrolyte at the electrode surface, such as the dissolution of transition metal ions from the cathode into the electrolyte, and the solid electrolyte interface (SEI) formation on the cathode surface [5,6] Moreover, these harmful side reactions are usually accelerated at high temperature and in the deeply delithiated state at elevated voltages ($>4.3 \text{ V}$).

To overcome the above problems, many works have been performed in recent years, and the method of surface coating is a very effective strategy to improve the cycling stability and thermal stability of the Ni-rich cathode materials. The improvements are mainly ascribed to restricting the direct contact between the electrode and electrolyte, protecting the NCM cathode materials from the attack by HF and reducing the undesired side reactions, thus a stable



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Interface is received during long cycling. Unfortunately, many coating materials are not inactive and easily react with some components of electrolyte, leading to other extra side reactions and can't support as a persistent protect layer during extensive cycling, these materials are called as sacrificial protect layer. Al_2O_3 is chemically inert and is a desirable choice for coating the Ni-rich layered cathode material, and can provide a persistent protection during long cycling. This study therefore explores the effect of Al_2O_3 surface coating on the electrochemical and physicochemical characteristics of a NCM811 cathode.

2. Experimental

2.1. Materials Synthesis

The $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ precursor was synthesized by a conventional co-precipitation method, and then the precursor was mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ (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 NCM811 cathode (denoted as pristine).

To produce the Al_2O_3 coating on the NCM811 cathode, a certain amount of aluminum isopropoxide was dissolved in 15 mL ethanol and then 1 g of the prepared NCM811 powder was slowly added and stirred at a certain speed. The obtained mixture was dried at 60°C and then sintered at 500°C for 5 h. The prepared materials with different coating content were denoted as A-1, A-2 and A-3, respectively.

2.2. Materials Characterization

The crystalline phases of the prepared materials were characterized by powder X-ray diffraction (XRD) at the scan rate of 1° 2 θ /min and ranged from 10° to 90° (Rigaku UltimaIV-185 instrument). The morphologies were observed by field emission scanning electron microscopy (FE-SEM, FEI QUANTA 250). High-resolution transmission electron microscopy (HR-TEM) was operated upon a JEOL JEM-2100 instrument.

2.3. Electrochemical Measurement

The electrochemical properties were measured in the CR2025 coin type half-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 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). 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

X-ray powder diffraction (XRD) was used to measure the crystal structure of different samples. As shown in figure 1a, the peak positions of all materials were indexed to the hexagonal $\alpha\text{-NaFeO}_2$ layered structure with R-3m space group. No any other impurity peaks appeared in the all patterns and the splitting of (006)/(102) and (108)/(110) peaks, indicating that the treatment of aluminum isopropoxide has no influence on the bulk crystalline structure. However, the Al_2O_3 diffraction peaks were not appeared in the three modified samples because of their amorphous structure and low content of Al_2O_3 layer. Furthermore, the lattice parameters of pristine and A-2 are further determined by Rietveld refinement and the results are presented in figure 1b, c.

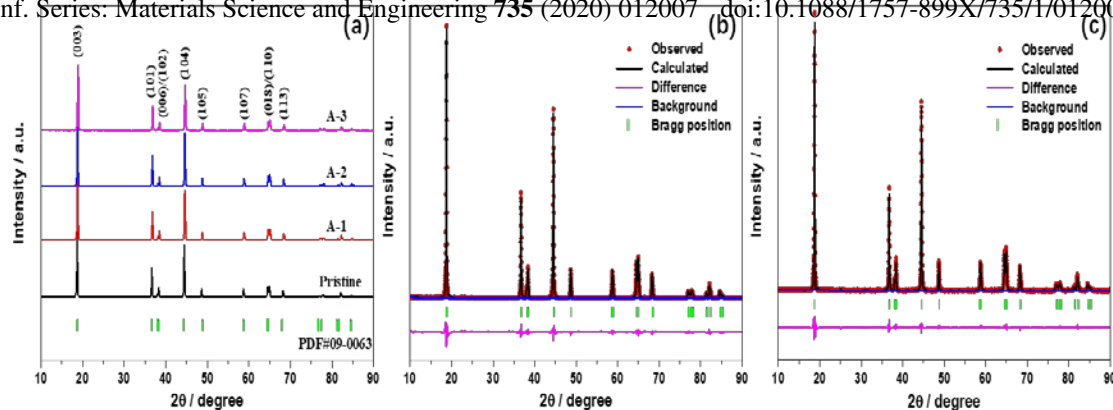


Figure 1. (a) XRD Patterns of Samples and Rietveld Refinement of (b) Pristine and (c) A-2

Table 1. The values of R_p and R_{wp} factors are lower than 15% indicating that the refinement is acceptable. The higher value of c/a than 4.94 shows that all samples preserved a well-defined layer structure after Al_2O_3 modification, moreover, the value of I_{003}/I_{104} (>1.2) reflects a low degree of Li^+/Ni^{2+} cation mixing. In a word, the XRD measurement demonstrated that the Al_2O_3 modification did not destroy the crystal structure on NCM811.

Table 1. Rietveld Refinement Results of NCM and A-2 Materials

Sample	a(Å)	c(Å)	v(Å ³)	c/a	R_{wp} (%)	R_p (%)	I_{003}/I_{104}
Pristine	2.87002	14.18851	101.2102858	4.9437	11	7.09	1.44
A-2	2.870836	14.19216	101.29389	4.9436	13.3	8.49	1.47

Scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HR-TEM) were used to obtain the morphology of different samples and also to verify the existence and distribution of Al_2O_3 on the surface of NCM811 particles. As shown in figure 2, the NCM811 secondary particle has a spherical shape with a particle size of 6-8 μm and is composed of numerous nano-sized primary particles. Through comparing figure 2a to figure 2b-d, we found that there are no obvious changes in the overall morphology before and after modification, which indicates that the Al_2O_3 coating has no influence on the general morphology of NCM811 particles. However, with the increase of coating content, a thin and blurred Al_2O_3 layer has been clearly observed on the surface of the primary particles. Moreover, the EDS mappings of figure 2e-i further confirm the uniform distribution of Al_2O_3 on the particle surface.

Here, the HRTEM measurement was carried out to further investigate the microstructure and the TEM images of the pristine and A-2 samples as shown in figure 2j-m. Figure 2j reveals that the pristine NCM811 is rather smooth and the planar distance in figure 2k is 0.471 nm which corresponds to the (003) plane of pristine NCM811 material. In contrast, there is a clear coating layer on the primary particle surface in the A-2 sample and its thickness is about 2 nm, but any lattice fringes corresponding to Al_2O_3 are not found, indicating that the Al_2O_3 is amorphous.

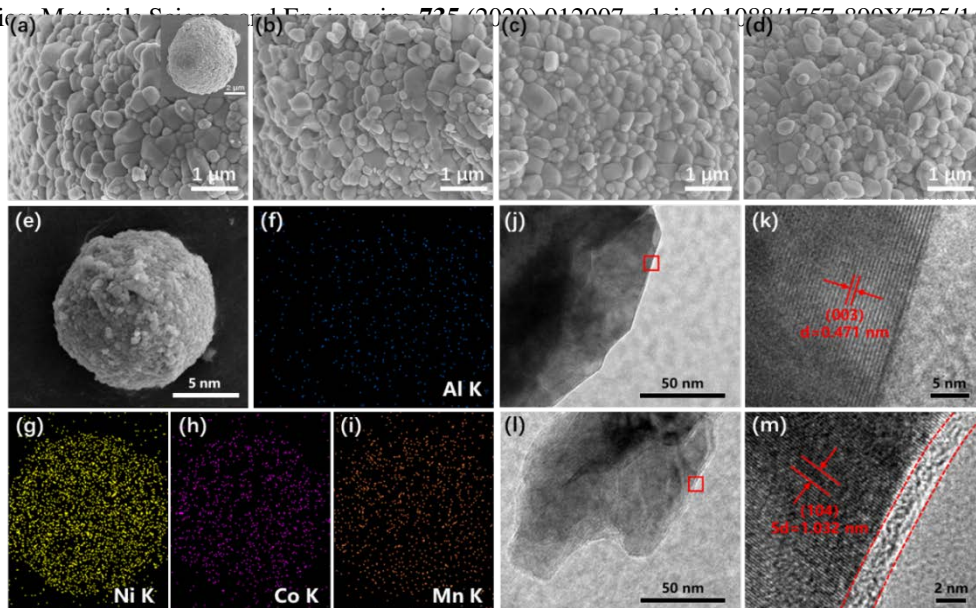


Figure 2. (a-d) SEM Images of Pristine, A-1, A-2 and A-3 Samples, Respectively. (e-i) EDS Mapping of A-2. (j) TEM and (k) HRTEM Images of Pristine $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. (l) TEM and (m) HRTEM Images of A-2.

The electrochemical performances of the pristine and modified samples were then tested as shown in figure 3. Figure 3a displays the initial charge-discharge profiles of all samples at 1C between the voltage range of 2.8-4.35V. Clearly, all samples show a similar electrochemical charge/discharge behavior, indicating that the Al_2O_3 coatings do not induce obvious changes to the bulk of NCM811 material. However, the initial capacities of different samples are decreased with the improvement of Al_2O_3 coating content and are 185.4, 183.6, 182.1 and 172.2 mAh/g for pristine, A-1, A-2 and A-3, respectively. The decreased initial discharge capacity is attributed to the electrochemically inert nature the Al_2O_3 coating layer. Figure 3b illustrates the long cycling performance of the four different samples at the current of 1C between 2.8 and 4.35 V. It is obvious that the capacity stability is significantly improved after Al_2O_3 modification. After 100 cycles, the pristine NCM811 delivers a discharge capacity of 151.7 mAh/g and the capacity retention is 81.8%, however, the other three samples all display a higher discharge capacity than the pristine NCM811, 158.4, 167.5 and 163.7 mAh/g for A-1, A-2 and A-3, respectively, and the corresponding capacity retentions are 89.4%, 91.7% and 92.4%, suggesting that the Al_2O_3 coating layer is beneficial for the structure stability of electrode interface.

Figure 3c, d show the cycling performance of different samples at 55°C. Note that the charge and discharge capacities are all improved at elevated temperature, but the capacity retention is decreased. The capacity retention of pristine NCM811 rapidly decreased from 81.8% of 25°C to 68.5% of 55°C after 100 cycles, implying that the undesired side reactions between electrode and electrolyte is accelerated at higher temperature. However, the effect of Al_2O_3 coating on the cycling stability is more obvious at high temperature, the capacity retention increased from 68.5% of pristine to 87.7% of A-3. But when the coating content beyond 2 wt%, the initial reversible capacity drops dramatically, so we consider that 2 wt% is the optimal coating value.

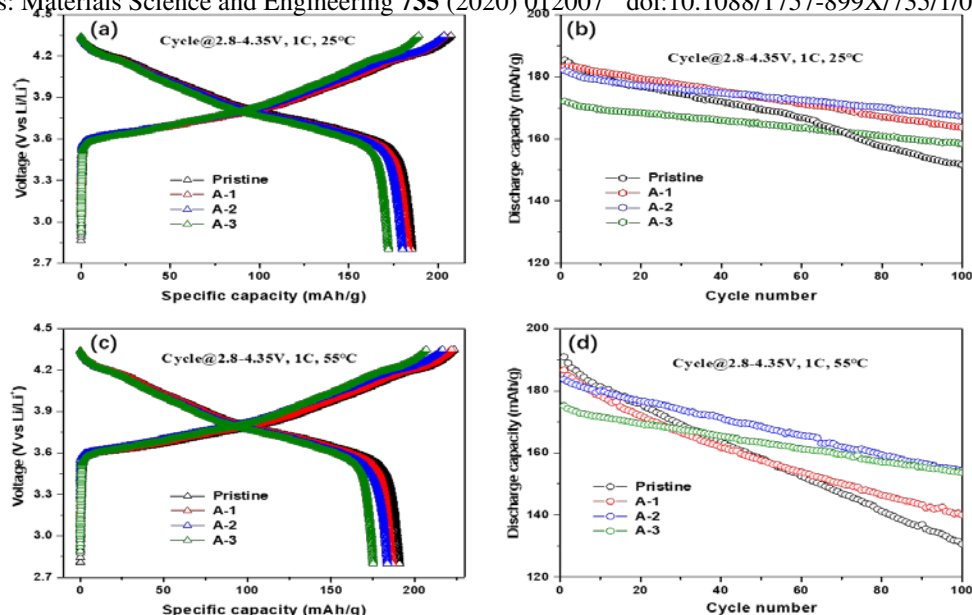


Figure 3. (a) The Initial Charge–Discharge Curves and (b) Cycling Performance at 25°C; (c) the Initial Charge–Discharge Curves and (d) Cycling Performance at 55°C

To further confirm the effect of the Al_2O_3 coating on the electrochemical properties of the NCM samples, EIS measurements were conducted for the pristine and Al_2O_3 modified electrodes during 100 cycles at room temperature, as depicted in figure 4. It can be found that every Nyquist plot contains two semicircles and a slope. The semicircle at high frequency corresponds to resistance of solid electrolyte interphase film (R_f). The second semicircle at middle high frequency refers to charge transfer resistance (R_{ct}), which reflects the transfer speed of Li^+ on the interface of electrode materials. The sloped line at low frequency represents the diffusion rate of Li^+ in bulk electrode and was defined as Warburg impedance. [7] The fitted results of Nyquist plots are shown in figure 4c.

After 1st cycle, the R_{ct} is 13.7 Ω for pristine NCM and similar with 11.6 Ω for A-2, indicating that the Al_2O_3 coating layer does not influence the Li^+ transfer through the electrode interface. However, the R_f for pristine NCM811 is 7.82 Ω , which is more than three times that of A-2, the difference is attributed to the restriction of side reactions that a thin SEI film is formed. After long cycles, both R_f and R_{ct} values for all samples are increased, but the increasing rate is different. After 100 cycles, the R_f and the R_{ct} increased to 54.8 Ω and 554.4 Ω for pristine NCM811, respectively. Such large impedance would result the severe degradation of cycling performance for pristine NCM811. However, the value of R_f and R_{ct} are just 23.1 Ω and 147.2 Ω for A-2, which indicates the long-term protection of Al_2O_3 coating layer on the electrode.

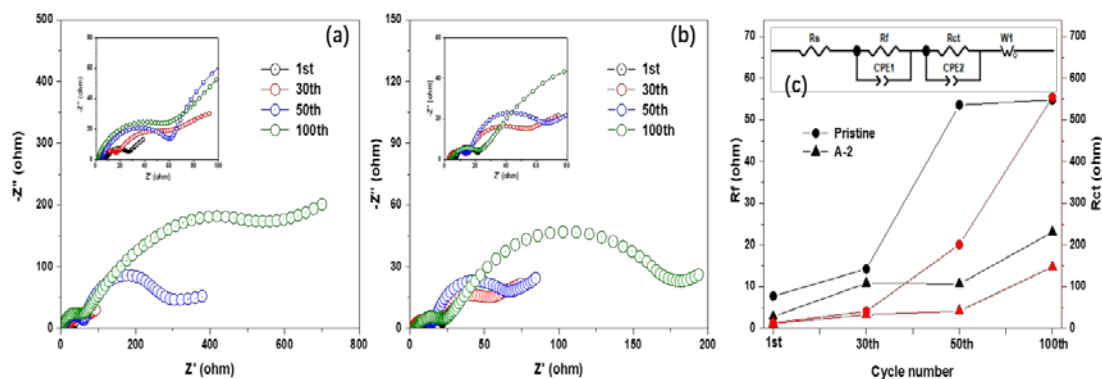


Figure 4. Nyquist Plots of (a) Pristine and (b) A-2 after Different Cycles, (c) the Fitting Results according to the Equivalent Circuit in the Inset

4. Conclusion

We have successfully improved the electrochemical properties of NCM811 via a uniform Al_2O_3 coating layer. According to the XRD, SEM and HRTEM analysis, we know that the Al_2O_3 coating layer does not influence the morphology and crystal structure of the NCM811, and exists as an amorphous phase. From the electrochemical characterizations, we confirm that the presence of Al_2O_3 at the electrode surface can suppress the undesirable side reactions and provide a long-term protection upon cycling due to its inactive nature, thus an improved cycling stability was achieved, especially at elevated temperature. Based on the above results, we believe that this modified NCM811 is very promising to be used in commercial power lithium-ion batteries.

5. Acknowledgment

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6. Reference

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