Ultrathin Al₂O₃ Coating on LiNi₀.₈Co₀.₁Mn₀.₁O₂ Cathode Material for Enhanced Cycleability at Extended Voltage Ranges

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Abstract: Ni-rich LiNi₀.₈Co₀.₁Mn₀.₁O₂ oxide has been modified by ultrathin Al₂O₃ coatings via atomic layer deposition (ALD) at a growth rate of 1.12 Å/cycle. All characterizations results including TEM, SEM, XRD and XPS together confirm high conformality and uniformity of the resultant Al₂O₃ layer on the surface of LiNi₀.₈Co₀.₁Mn₀.₁O₂ particles. Coating thickness of the Al₂O₃ layer is optimized at ~2 nm, corresponding to 20 ALD cycles to enhance the electrochemical performance of Ni-rich cathode materials at extended voltage ranges. As a result, 20 Al₂O₃ ALD-coated LiNi₀.₈Co₀.₁Mn₀.₁O₂ cathode material can deliver an initial discharge capacity of 212.8 mAh/g, and an associated coulombic efficiency of 84.0% at 0.1 C in a broad voltage range of 2.7–4.6 V vs. Li⁺/Li in the first cycle, which were both higher than 198.2 mAh/g and 76.1% of the pristine LiNi₀.₈Co₀.₁Mn₀.₁O₂ without the Al₂O₃ protection. Comparative differential capacity (dQ/dV) profiles and electrochemical impedance spectra (EIS) recorded in the first and 100th cycles indicated significant Al₂O₃ ALD coating effects on suppressing phase transitions and electrochemical polarity of the Ni-rich LiNi₀.₈Co₀.₁Mn₀.₁O₂ core during reversible lithiation/delithiation. This work offers oxide-based surface modifications with precise thickness control at an atomic level for enhanced electrochemical performance of Ni-rich cathode materials at extended voltage ranges.

Keywords: Al₂O₃ oxide; atomic layered deposition; LiNi₀.₈Co₀.₁Mn₀.₁O₂; Ni-rich cathode material; lithium ion battery

1. Introduction

Lithium ion batteries have been dominantly applied in hybrid electric vehicles (HEVs) and pure electric vehicles (EVs) [1,2], which significantly enhances our living environment. In particular for electric transportation systems and future large-scale applications of stationary grid energy storage, lithium ion batteries are required to provide higher energy and power densities, together with excellent long-term service life and acceptable cost [3]. Performance of lithium ion batteries...
with high Ni content. Capacity fading can be exacerbated, when these Ni-rich LiNi
layers are cycled at broad voltage ranges [22,23]. Oxides are considered common coating materials, because of their low material
cost, simple synthetic procedure, and high effectiveness in protecting internal electrode materials. ALD technique can result
in highly conformal and uniform oxide coating layers at the entire surface of the underlying
substrates, and thus has been considered as an effective method for surface modifications of different
transition metal oxides, LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ cathode materials, leading to undesired electrolyte decomposition and solid electrolyte interphase (SEI) formation at the surface of the cathode. The other reason is the induced phase transition from the initial layered structure to spinel-like and/or NiO-like rock-salt phases at the surface of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ particles, because the formation of Li$^+$ vacancies in high concentration at deep charge destabilizes the initial layered structure of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ [18]. These unfavorable structural transformations are consecutive, and gradually overspread from the surface to bulk Ni-rich layered oxides [17,19]. In addition, the formation of impure phases definitely brings about structural degradation and increased kinetic barrier for lithium ion diffusion, causing capacity fading and inferior rate capability of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ cathode materials [20,21].

Surface modifications, either on particles of active cathode materials or at the surface of the entire cathode, have been demonstrated to improve electrochemical performance for various cathode materials even in harsh operation conditions, such as elevated working temperatures and broad voltage ranges [22,23]. Oxides are considered common coating materials, because of their low material cost, simple synthetic procedure, and high effectiveness in protecting internal electrode materials. Various examples have been reported in the literature [24–28], involving Al$_2$O$_3$, ZrO$_2$, ZnO, TiO$_2$, Cr$_2$O$_3$, SnO$_2$, etc. However, associated electrochemical performance of modified cathode materials is sensitively determined by qualities of the coated oxides in terms of thickness, conformality, uniformity, and integrity. Oxide coatings prepared by atomic layer deposition (ALD) have been demonstrated to considerably enhance electrochemical performance for various cathode materials, involving layered LiCoO$_2$ [29,30], spinel LiMn$_2$O$_4$, and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ [31,32]; Ni-rich LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ and LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ [33,34]; and Li-excess Li[Li$_{1-x}$M$_x$]O$_2$ oxides [35]. The ALD technique can result in highly conformational and uniform oxide coating layers at the entire surface of the underlying substrates, and thus has been considered as an effective method for surface modifications of different

It is well-known that the resultant electrochemical performance of Ni-rich cathode materials is essentially determined on the specific composition of Ni, Co, and Mn elements within these ternary transition metal oxides, LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ [11,14,15]. Higher Ni content results in higher lithium storage capacity of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$, but leads to the undesired formation of Li$^+$/Ni$^{2+}$ cation mixing in the layered structure; the expense of safety in material usage and more complexity in the material preparation [16,17]. Mn and Co dopants have been demonstrated to enhance the structural robustness and cationic ordering for LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ variants, respectively. However, the specific capacity has to be sacrificed, when Mn and Co contents are increased. In order to rapidly promote practical applications of Ni-rich cathode materials for superior lithium ion batteries, poor cycling and thermal stabilities of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ should be urgently addressed, especially for materials with high Ni content. Capacity fading can be exacerbated, when these Ni-rich LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ cathodes are cycled at broad voltage ranges with a high upper cut-off voltage above 4.3 V vs. Li$^+$/Li. One reason is that the intensive oxidation capability of Ni$^{3+}$/4+ redox could aggravate parasitic side reactions during lithiation/delithiation of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ cathode materials, leading to undesired structural transformations and solid electrolyte interphase (SEI) formation at the surface of the cathode. The other reason is the induced phase transition from the initial layered structure to spinel-like and/or NiO-like rock-salt phases at the surface of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ particles, because the formation of Li$^+$ vacancies in high concentration at deep charge destabilizes the initial layered structure of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ [18]. These unfavorable structural transformations are consecutive, and gradually overspread from the surface to bulk Ni-rich layered oxides [17,19]. In addition, the formation of impure phases definitely brings about structural degradation and increased kinetic barrier for lithium ion diffusion, causing capacity fading and inferior rate capability of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ cathode materials [20,21].
cathode materials. Ni-rich cathode materials have been dominantly used for lithium ion batteries to power currently-developed electric automobiles, but still suffer from poor service life, especially in harsh operation conditions, such as at elevated working temperatures and/or in extended voltage ranges. As reported in the literature [33,34], Al₂O₃ ALD coatings contribute to enhanced cycling stabilities of LiNi₀.₅₃Co₀.₂Mn₀.₃O₂, LiNi₀.₈Co₀.₁Mn₀.₃O₂, and LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ by protecting coated Ni-rich oxide particles from parasitic side reactions at the cathode’s surface. However, the insulating property of Al₂O₃ material makes it is necessary to precisely control the coating’s thickness, in order to maximize the electrochemical performance of Ni-rich cathode materials. In addition, it is also urgent to understand structural features and chemical environments between oxide coatings and Ni-rich oxide particles.

The ALD technique was employed in this work to coat ultrathin Al₂O₃ onto Ni-rich LiNi₀.₈Co₀.₁Mn₀.₃O₂ target material (marked as n Al₂O₃ ALD NCM811, then responses to the number of ALD cycles related to the thickness control of Al₂O₃ coating layer). TEM observations were used to examine the structural characteristics of resultant Al₂O₃ coatings and determine the ALD growth rate of Al₂O₃ oxide. XPS spectra were used to study chemical environments of different n Al₂O₃ ALD NCM811 (n = 10, 20 and 50) materials. Electrochemical performance of three n Al₂O₃ ALD NCM811 cathode materials were evaluated and compared with the bare NCM811 cathode in a broad voltage range of 2.7–4.6 V vs. Li⁺/Li. This work offers a high-quality oxide coating for Ni-rich cathode materials by using the ALD method, which significantly contributes to improved electrochemical performance in extended voltage ranges for superior lithium ion batteries.

2. Materials and Methods

2.1. Synthesis of Ni-Rich Layered LiNi₀.₈Co₀.₁Mn₀.₁O₂ Material

In a typical sol (solution)–gel route, stoichiometric amounts of CH₃COOLi·2H₂O, Ni(CH₃COO)₂·4H₂O, Co(CH₃COO)₂·4H₂O, and Mn(CH₃COO)₂·4H₂O were dissolved in 50 mL of distilled water. An extra 3 mol.% of the lithium source was used to compensate for the volatilization of lithium at high heating temperatures. The green sol was obtained after the solvent was completely evaporated, and was then transferred to dry in vacuum at 120 °C for 12 h. Dried gel heat treatments were carried out at 850 °C for 5 h, under pure O₂ flow at a temperature ramp of 5 °C/min. The resultant black LiNi₀.₈Mn₀.₁Co₀.₁O₂ (marked as NCM811) powder was collected after cooling to room temperature.

2.2. Al₂O₃ Coating on LiNi₀.₈Co₀.₁Mn₀.₁O₂ Particles Through Atomic Layer Deposition

The atomic layer deposition of Al₂O₃ coating on LiNi₀.₈Co₀.₁Mn₀.₁O₂ particles was performed in a Savannah 100 ALD system (Cambridge NanoTech Inc., Waltham, MA, USA) at 120 °C, by applying Al(CH₃)₃ (Trimethylaluminum, TMA) and H₂O as precursors with exposure time of 0.01 s, waiting time of 5 s, and purge time of 40 s, respectively. Nitrogen gas was used as the flow gas, and the flow rate was set at 20 sccm. The vacuum condition in the reaction chamber was controlled at 10⁻³–10⁻² torr, and the overpressure threshold for the coating processes was set at 250 torr. Two self-terminating reactions involved in the ALD growth of Al₂O₃ layer are described as follows:

\[
\text{AlOH}^* + \text{Al(CH}_3)_3 \rightarrow \text{Al-O-Al-(CH}_3)_2^* + \text{CH}_4 \tag{1}
\]

\[
\text{Al-CH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + \text{CH}_4 \tag{2}
\]

LiNi₀.₈Co₀.₁Mn₀.₁O₂ particles coated with the Al₂O₃ layer under different ALD cycles were marked as n Al₂O₃ ALD NCM811 (the n corresponds to the number of ALD cycles).

2.3. Characterizations

Crystallographic structures of bare NCM811 and Al₂O₃-coated NCM811 materials were examined by X-ray diffraction (XRD), using a Bruker D8 Advance automatic diffractometer (Bruker, Billerica,
MA, USA) with Cu Kα radiation. Morphologies and energy dispersive spectroscopic (EDS) mappings of different samples were observed by field emission scanning electron microscopy (FESEM) on a Hitachi SU-8010 (Hitachi High-Tech Corp., Tokyo, Japan) and FEI Quanta FEG 250 microscopies (FEI, Hillsboro, OR, USA), respectively, with an acceleration voltage at 15/20 kV in a secondary electrons (SE) detection mode. The Everhart Thornley Detector (ETD) was used to collected electron signals. Detailed structural features of different specimens were captured by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) coupled with selected area electron diffraction (SAED) on a FEI Tecnai G2 T20 equipment (FEI, Hillsboro, OR, USA), at an acceleration voltage of 200 kV. Chemical environments and valent states of cations within different materials were characterized by X-ray photoelectron spectroscopic (XPS) measurements on an ESCALAB 250Xi XPS device (Thermo Fisher Scientific, Waltham, MA USA). All XPS spectra were calibrated according to the binding energy of the C 1s peak at 284.6 eV.

2.4. Electrochemical Measurements

The working electrodes were composed of 80 wt.% active cathode materials, 10 wt.% super p as the conductive carbon, and 10 wt.% polyvinylidenefluoride (PVDF) as the binder. These cathodes were assembled into two-electrode CR2025-type coin cells (Shenzhen Kejing Star Technology Co., LTD., Shenzhen, China), in an Ar-filled glove box (MBraun, Garching, Germany) for electrochemical measurements, with the metallic lithium foil as the reference, and counter electrodes with the glass microfiber (Whatman, Grade GF/B, Little Chalfont, UK) as the separator. The electrolyte was a 1 M LiPF₆ solution dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) at a volumetric ratio of 1:1. The real loading of active material was ~3.5 mg in the cathode with a diameter of 12 mm and a thickness of ~50 nm for all electrode materials. The electrolyte volume used during the coin cell assembly was ~0.5 mL per unit. Galvanostatic charge and discharge were performed at different current densities in a voltage range of 2.7–4.6 V vs. Li⁺/Li on a LAND battery testing system (Jinnuo, Wuhan, China). The current density corresponding to 1 C was 200 mA/g. Electrochemical impedance spectroscopy (EIS) was conducted in a frequency range of 10 mHz–100 kHz with an AC amplitude of 5 mV on the Autolab electrochemical workstation (PGSTAT302N, Metrohm Autolab, Utrecht, The Netherlands).

3. Results and Discussion

3.1. Characteristics of Al₂O₃ Layer Deposited on NCM811 Particles via ALD Coating

As shown in the schematic illustrations in Figure 1a, the ALD growth of Al₂O₃ coating at the surface of NCM811 particles was subjected to a sequence of chemisorption and self-terminating surface reactions (Equations (1) and (2) in Section 2.2). Detailed deposition mechanisms for the different oxides, involving Al₂O₃, ZnO and ZrO₂, can be found in our previous work [12,36–40]. As a result, ultrathin oxide coatings under ALD growth always reveal desirable conformality, uniformity, robustness, and pinhole-free features. Furthermore, thickness of the resultant oxide coatings can be precisely controlled at the Ångström or atomic monolayer level, which is determined by the number of ALD cycles. Accordingly, morphologic and structural differences of pristine NCM811, 20 Al₂O₃ ALD NCM811, and 50 Al₂O₃ ALD NCM811 materials are compared in Figure 1b–j. The pristine NCM811 material (Figure 1b) reveals a distinct aggregation of tremendous primary nanoparticles, which have smooth facets and sharp edges with an average particle size of ~500 nm. Such morphologic features generally indicate the high crystallinity and purity of the prepared NCM811 particles. By contrast, FESEM images of the 20 Al₂O₃ ALD NCM811 particles showed apparent roughness at the entire surface after coating the Al₂O₃ layer in 20 ALD cycles (Figure 1c), implying the conformal and uniform surface modification of the NCM811 substrate. The elemental energy dispersive spectroscopic (EDS) mapping was captured on the selected 20 Al₂O₃ ALD NCM811 particles (Figure 1d), which revealed even distributions of Al, Ni, Co, Mn, and O elements, and thus again demonstrated desirable conformity...
and uniformity of Al₂O₃ coatings at the surface of NCM811 particles. In order to comprehensively understand structural characteristics of the resultant Al₂O₃ layer, 50 Al₂O₃ ALD NCM811 particles with increased coating thickness were examined by TEM observations, and compared to bare NCM811 and the 20 Al₂O₃ ALD NCM811 materials. As shown in Figure 1e, TEM images of NCM811 particles showed consistent contrast throughout the whole observation area, revealing a single solid structure without any surface modifications. HRTEM images of the selected region in Figure 1e, marked by a blue square, showed perfect lattice fringes with a d-space of 0.47 nm (Figure 1h), corresponding to (003) planes in the layered structure of NCM811 oxide. By contrast, TEM images of the 20 Al₂O₃ ALD NCM811 and 50 Al₂O₃ ALD NCM811 particles captured in Figure 1f,g gave rise to distinct contrast differences between the dark NCM811 core and light Al₂O₃ coating shells at the surface, respectively. It was noticeable that the ALD coating contributed to satisfactory uniformity and conformality of the resultant Al₂O₃ layer, which was in accordance with that coated at the surface of different cathode materials reported in the literature [36,38]. The precise thickness was 5.6 nm as shown in the HRTEM image of the 50 Al₂O₃ ALD NCM811 (Figure 1j), corresponding to an Al₂O₃ ALD growth rate of 1.12 Å/cycle. Accordingly, 20 ALD cycles resulted in an Al₂O₃ coating with 2.2 nm thickness as shown in Figure 1i for the 20 Al₂O₃ ALD NCM811 materials. Furthermore, these two HRTEM observations indicated an amorphous feature of the Al₂O₃ coating layer, which was distinguishable from the internal crystalline NCM811 particles. As a result, SEM and TEM images demonstrated the conformational and uniform coating of the Al₂O₃ layer for the surface modification of Ni-rich NCM811 particles through ALD processes, together with thickness control at the sub-nano level.

**Figure 1.** (a) Schematics illustration of the Al₂O₃ ALD growth at the surface of NCM811 particles; FESEM images of (b) bare NCM811, and (c) 20 Al₂O₃ ALD NCM811; EDS mapping of (d) 20 Al₂O₃ ALD NCM811; TEM images of (e) bare NCM811, (f) 20 Al₂O₃ ALD NCM811, and (g) 50 Al₂O₃ ALD NCM811; and HRTEM images of (h) bare NCM811, (i) 20 Al₂O₃ ALD NCM811, and (j) 50 Al₂O₃ ALD NCM811.
Al₂O₃ coating effects on changing the crystal structure of Ni-rich NCM811 core were evaluated using XRD patterns of different coated materials, coupled with quantitative analyses from Rietveld refinements. As shown in Figure 2a, the XRD pattern of pristine NCM811 material was well indexed to a layered α-NaFeO₂ structure with a R-3m space group (JCPDS No. 74-0919). It also showed a desirable intensity ratio of characteristic 003 over 104 reflections, i.e., I₀₀₃/I₁₀₄ = 1.48 and distinct peak splitting of two 006/102 and 108/110 doublets, indicating outstanding structural ordering of the layered NCM811 material. The Rietveld refinement on the XRD pattern of pristine NCM811 resulted in lattice parameters of a = 2.8746 Å, c = 14.2102 Å, and V = 101.72 Å³, together with a low estimated Li⁺/Ni²⁺ cation mixing of 3.68% based on a low reliability-factor of R_wp = 6.62% (Table 1). These XRD features all indicate an excellent layered structure of the prepared Ni-rich NCM811 material, in accordance with HRTEM images (Figure 1h). XRD patterns and the associated refinement results of NCM811 particles coated with 10, 20, and 50 Al₂O₃ ALD cycles (Figure 2b–d), respectively, indicating little effects of Al₂O₃ uniformity of surface modifications via oxide ALD coatings. On the other hand, XRD patterns of the ALD NCM811 samples, owing to the amorphous phase. However, the Al₂O₃ coating slightly suppressed the crystal structural of the internal NCM811 host. Coatings thicker than 2 nm, i.e., 20 ALD cycles (20 cycle × 1.12 Å/cycle = 2.24 nm), resulted in a detectable decrease in a, c, and V values, according to the refinement results of the 20 Al₂O₃ ALD NCM811 sample, while the 10 Al₂O₃ ALD NCM811 showed little change in lattice parameters as compared with that in the pristine NCM811 (Table 1). Although the thick Al₂O₃ coating reduced a and c values of the 50 Al₂O₃ ALD NCM811 material, its c/a ratio was almost the same with the NCM811, again indicating high conformity and uniformity of surface modifications via oxide ALD coatings. On the other hand, XRD patterns of the three Al₂O₃-coated NCM811 materials revealed I₀₀₃/I₁₀₄ values equal to 1.54, 1.46, and 1.45 after 10, 20, and 50 ALD cycles (Figure 2b–d), respectively, indicating little effects of Al₂O₃ ALD coating on the structural ordering of internal NCM811 material. The estimated cation mixings within the layered structures of these three samples were all in an acceptable range of 3%–4%, consistent with that of the pristine NCM811 material (Table 1).

![XRD patterns of different coated materials](image)

**Figure 2.** XRD patterns of (a) bare NCM811; (b) 10 Al₂O₃ ALD NCM811; (c) 20 Al₂O₃ ALD NCM811; and (d) 50 Al₂O₃ ALD NCM811 materials, coupled with rietveld refinement results.
In order to confirm $\text{Al}_2\text{O}_3$ coating formation and its possible impacts on the chemical environments of transition metal cations at the surface of NCM811 particles, characteristic Al 2$p$, Ni 2$p$, Co 2$p$, and Mn 2$p$ XPS peaks of bare NCM811 and three $\text{Al}_2\text{O}_3$-coated NCM811 materials were measured and compared. As shown in Figure 3a, 10 $\text{Al}_2\text{O}_3$ ALD NCM811, 20 $\text{Al}_2\text{O}_3$ ALD NCM811, and 50 $\text{Al}_2\text{O}_3$ ALD NCM811 samples all showed sharp Al 2$p$ XPS peaks, verifying successful $\text{Al}_2\text{O}_3$ coating at the surface of NCM811 particles. These collected Al 2$p$ peaks slightly shifted to higher binding energies at 75.4, 75.6, and 75.7 eV, respectively, compared to 74.6 eV of pure $\text{Al}_2\text{O}_3$ oxide reported in NIST XPS Database, implying possible chemical bonding between the $\text{Al}_2\text{O}_3$ coating layer and NCM811 particles. As reported in the literature [36–40], the oxide coating and substrate in a typical ALD growth can result in a favorable chemical bond of substrate–O–M$_{\text{ox}}$ (M = Al, Zn, Zr, Sn, etc.), this process is illustrated in Figure 1a. However, it is unexpected to see that all the characteristic of Ni 2$p$, Co 2$p$, and Mn 2$p$ XPS peaks captured on three $\text{Al}_2\text{O}_3$-coated NCM811 particles also gave rise to higher bonding energies compared to those of pristine NCM811 particles, when the coating thickness of $\text{Al}_2\text{O}_3$ was gradually increased (Figure 3b–d). These interesting XPS results may be attributed to the tremendous –OH groups that were left at the surface of $\text{Al}_2\text{O}_3$ coating at the end of ALD growth (Figure 1a), which are highly electronegative, and thus probably induce reduced electron cloud densities of Al, Ni, Co, and Mn cations. The thicker $\text{Al}_2\text{O}_3$ coating resulted in increased surface area of $\text{Al}_2\text{O}_3$-coated NCM811 particles as well as the quantity of residual –OH groups at the most outside surface; hence, the inductive effect was enhanced by the increased number of –OH groups, leading to binding energy shifts of different cations to higher values. XPS results indicate a probable chemical bonding between $\text{Al}_2\text{O}_3$ and NCM811, which may facilitate charge transfer and lithium ion diffusion through the oxide coating layer.

![Figure 3. Characteristics XPS spectra captured on the 10 $\text{Al}_2\text{O}_3$ ALD NCM811, 20 $\text{Al}_2\text{O}_3$ ALD NCM811, and 50 $\text{Al}_2\text{O}_3$ ALD NCM811 materials compared to the bare NCM811: (a) Al 2$p$, (b) Ni 2$p$, (c) Co 2$p$, and (d) Mn 2$p$ peaks.](image-url)
3.2. Enhanced Electrochemical Performance of Ni-Rich NCM811 Cathode Materials by Al₂O₃ ALD Coating

Effects of Al₂O₃ ALD coating on improving electrochemical performance of Ni-rich NCM811 cathode material are evaluated in Figure 4, where different cathode materials were subjected to a broad voltage range of 2.7–4.6 V vs. Li⁺/Li. Figure 4a compares resultant cycling performance of the Al₂O₃-coated NCM811 cycled at 0.1 C with bare NCM811 material. The coating thickness of Al₂O₃ layer was optimized at ~2 nm, corresponding to 20 ALD cycles. As a result, the 20 Al₂O₃ ALD NCM811 cathode delivered an impressive discharge capacity of 212.8 mAh/g and an associated initial columbic efficiency of 84.0% in the first cycle, which were both higher than 198.2 mAh/g and 76.1% of the pristine NCM811 without Al₂O₃ protection. Accordingly, the charge/discharge curves of these two cathode materials cycled at 1st and 100th cycles are shown in Figure 4b. The improved electrochemical reversibility with increased specific capacity of the 20 Al₂O₃ ALD NCM811 in the first cycle can be attributed to the conformal surface modification from the Al₂O₃ coating (Figure 1a), which effectively suppressed detrimental side reactions even when the NCM811 cathode material was cycled in an extended voltage range up to 4.6 V. In addition to protecting the internal Ni-rich core material from the HF attack in electrolytes as reported in the literature [29,41], the conformational and uniform Al₂O₃ coating also reduced the electrolyte decomposition induced by high oxidation of Ni⁴⁺/Ni³⁺ redox, especially under the deeply-charged condition at a high cut-off voltage of 4.6 V. As shown in Figure 4a,b, the pristine NCM811 cathode material suffered from distinct capacity decay to 127.5 mAh/g after 100 electrochemical cycles, while the 20 Al₂O₃ ALD NCM811 retained a much higher capacity of 157.2 mAh/g in the 100th cycle. Furthermore, the NCM811 also encountered an obvious working voltage fading from 3.80 initially to 3.76 V in the 100th cycle. By contrast, electrochemical polarity was effectively inhibited in the 20 Al₂O₃ ALD NCM811 cathode material, resulting in a well-preserved working voltage from 3.84 V in the first cycle to 3.83 V after 100 cycles. The 10 Al₂O₃ ALD NCM811 delivered moderate cycling performance as shown in Figure 4a, between the NCM811 and 20 Al₂O₃ ALD NCM811, which was attributed to the thinner Al₂O₃ coating around 1 nm. On the other hand, the much thicker coating of Al₂O₃ layer (>5 nm) after 50 ALD cycles resulted in satisfactory cycling stability, but the lithium storage capacity had to be sacrificed (Figure 4a), owing to the inferior conductivity of insulating Al₂O₃ oxide [42,43]. According to reports in the literature [13,44], Ni-rich cathode materials undergo inevitable phase transitions among three hexagonal (H1, H2, and H3) and one monoclinic (M) phases in their layered structures during lithiation/delithiation, which further aggravate undesired capacity fading in long-term electrochemical cycles. In order to examine possible phase transitions, related differential capacity (dQ/dV) profiles are shown in Figure 4c, which were transferred from charge/discharge curves in Figure 4b. The initial anodic peak of pristine NCM811 showed the much higher intensity by contrast with 20 Al₂O₃ ALD NCM811, indicating severe parasitic side reactions that occurred during the first phase transformation from the hexagonal H1 to monoclinic M phases. Subsequent M to H2, and H2 to H3 took place around at 4.0 and 4.2 V as marked in Figure 4c, respectively, when the Ni-rich cathode materials were charged to a high cutoff voltage. In successive discharge processes, phase transitions from H3 to H2 to M were reduced, resulting in dominant cathodic peaks around 3.75 V both in NCM811 and 20 Al₂O₃ ALD NCM811 cathodes. However, two redox pairs at higher voltages around 4.0 and 4.2 V were detected in the 100th cycle of pristine NCM811 cathode (peak voltages of detected anodic and cathodic peaks are marked by underlines), while the 20 Al₂O₃ ALD NCM811 gave rise to the smoother dQ/dV curves above 3.9 V, revealing significantly suppressed phase transitions for its enhanced cycling stability after the optimal Al₂O₃ ALD coating. Furthermore, total resistance changes of these two cathodes after 100 cycles were determined by EIS spectra as shown in Figure 4d. These measurements were conducted on their fully-discharged states after prolonged electrochemical cycles. EIS spectra of fresh cells were also recorded at open circuit voltage states for the comparison. It is worth noting that two fresh cells of NCM811 and the 20 Al₂O₃ ALD NCM811 cathodes both showed small resistances around 25 Ω. However, two Nyquist circles with larger diameters were captured in both cathodes after 100 cycles. The selected equivalent circuit, as the inset, was used to calculate the associated resistances based on
fitting solid lines. For the pristine NCM811, one Nyquist circle in high frequency may be attributed to impure phases, such as spinel-like and/or rock-salt phases formed during prolonged cycles as reported in the literature [45,46], and others in low frequency were assigned to the solid electrolyte interphase (SEI) film. By contrast, two Nyquist circles in 20 Al₂O₃ ALD NCM811 resulted from the Al₂O₃ coating and SEI film at the surface of cycled cathode material, respectively. It is noticeable that introduction of 2 nm Al₂O₃ coating led to acceptable resistance at 29 Ω, which was smaller than the 35 Ω caused by the secondary impure structure that formed at the surface of NCM811 without surface modification. Moreover, the 20 Al₂O₃ ALD NCM811 resulted in considerable decrease (160 Ω) corresponding to SEI film resistance, while the pristine NCM811 brought about larger SEI resistance (250 Ω). Electrochemical performance demonstrated significant effects of the optimized Al₂O₃ ALD coating on reducing electrochemical polarity and improving reversibility of Ni-rich cathode materials for superior lithium ion batteries.

![Figure 4](image-url)

**Figure 4.** Electrochemical performance of different cathode materials in a broad voltage range of 2.7–4.6 V vs. Li⁺/Li: (a) cycling performance at 0.1 C for 100 cycles; (b) charge/discharge curves of bare NCM811 and 20 Al₂O₃ ALD NCM811 in the first and 100th cycles at 0.1 C; (c) dQ/dV profiles of bare NCM811 and 20 Al₂O₃ ALD NCM811 in the first and 100th cycles; and (d) EIS spectra captured on fresh cells (solid patterns) at open circuit voltage states and after 100 cycles at fully-discharged states (hollow patterns).

4. Conclusions

Enhanced cycling stability of Ni-rich LiNi₀.₈Co₀.₁Mn₀.₁O₂ cathode material in an extended voltage range has been realized by surface modification of ultrathin Al₂O₃ coating through atomic layer deposition. The oxide ALD growth leads to impressive conformity and uniformity of resultant Al₂O₃ layer, and the coating thickness can be precisely controlled at 1.12 Å per ALD cycle. The optimal thickness of the Al₂O₃ coating for LiNi₀.₈Co₀.₁Mn₀.₁O₂ cathode material is in 2 nm level through performing 20 ALD cycles. Either the thicker or thinner coating thickness leads to decreased lithium storage capacity together with inferior cycling performance of different Al₂O₃
coated LiNi0.8Co0.1Mn0.1O2 cathodes. The optimized 20 Al2O3 ALD modified LiNi0.8Co0.1Mn0.1O2 cathode material distinctly shows increased discharge capacity and columbic efficiency in the first cycle, as well as improved capacity retention after successive 100 cycles in comparison with the pristine material. Electrochemical features in the first and 100th cycle of cathode materials, with and without Al2O3 protection were compared, involving charge/discharge curves, differential capacity profiles, and electrochemical impedance spectra. The Al2O3 coating has been demonstrated to suppress parasitic side reactions and phase transitions during prolonged lithiation/delithiation of the LiNi0.8Co0.1Mn0.1O2 cathode, resulting in reduced electrochemical polarity and enhanced cycling stability for Ni-rich cathode materials cycled in broad voltage ranges.


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