



Influence of Coating Protocols on Alumina-Coated Cathode Material: Atomic Layer Deposition versus Wet-Chemical Coating

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Surface alumina coating is an effective way to protect the cathode materials in lithium-ion batteries, particularly when operating under high voltages. However, the actual structures and functions of surface alumina coatings formed by different synthesis methods are still not clear. In this work, we systematically compared two different synthesis approaches, wet chemical (WC) coating and atomic layer deposition (ALD), for alumina coatings on $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532). Using nuclear magnetic resonance and electron microscope characterizations, we found that high-temperature annealing can significantly affect the atomic and chemical structures of alumina coating layers formed by WC method, leading to the formation of more α - LiAlO_2 buffer layer attached closely to the cathode particles and the improvement of electrochemical performance. Such strong interaction between cathode materials and alumina coatings during annealing is related to the Li extraction during the solution-based coating procedures. On the other hand, ALD-coated samples are less influenced by the high-temperature annealing, showing good electrochemical performance both before and after the heat-treatment. This work proves that different coating protocols have critical influences on the atomic and chemical structures of surface alumina coatings as well as the electrochemical performance of the coated cathodes.

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The development of portable electronic devices and electric vehicles leads to the high demand for next-generation lithium-ion batteries with higher capacities, longer lifetime, lower cost, and better safety.^{1,2} To reach these targets, Ni- and Mn-based layered cathode materials such as $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) has raised great research interests due to their high energy density, good thermal stability, and relatively low costs.³⁻⁸ However, NMC materials suffer from various surface degradation mechanisms during the operation cycles, such as transition metal dissolution, surface structure transformations (due to transition metal rearrangement and oxygen loss), and electrolyte decomposition at the surface of cathodes.⁴ Previous studies have shown that surface alumina coating is an effective way to protect the cathode materials including NMC during the charging-discharging process by suppressing the metal leaching and reducing the electrode surface interactions with electrolytes.⁹⁻¹⁴ Two widely applied alumina-coating methods are atomic layer deposition (ALD)¹²⁻¹⁴ and wet-chemical (WC)⁹⁻¹¹ methods. The ALD method is usually believed to have better control of the coating quality and uniformity with no need for high-temperature treatment, while the WC method is generally believed to be low-cost and can be more easily scaled up but requires post-coating heat-treatment.^{15,16} Despite these widely acknowledged advantages and disadvantages, the influences of different coating protocols on the atomic and chemical structures of the alumina coating layers are still unknown. Characterizing the real structure and chemistry of the alumina layers coated by different methods and investigating the corresponding influences on the interfacial reactions between coatings and cathode materials would be critical for the fundamental understanding of coating protocols and the optimization of surface coatings.

In this work, we performed a systematic comparison between ALD and WC coating protocols to demonstrate how the coating method could influence the chemistry and structure of surface alumina coating, and consequentially affect the electrochemical performance. Similar amounts of alumina were coated on $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532) cathode materials using ALD and WC coating methods, with and

without post-coating heat-treatment. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and solid state Nuclear Magnetic Resonance (NMR) characterization techniques were used to investigate the structures and chemistries of the coated cathode materials. After the initial coating process, the samples coated by the ALD method show less surface Li extraction and more uniform coating morphology than the WC coated sample. Before annealing, WC and ALD samples show similar morphology and crystallinity, but the ALD samples have much better electrochemical performance. After annealing at 800°C for 8h, ALD-coated samples show less change in coating morphology and chemistry. However, annealing leads to strong interactions between alumina coatings and NMC532 cores in WC-coated samples, forming more LiAlO_2 species as an interphase layer that attached more closely and more uniformly onto the NMC532 particles, accompanied by significant impedance reduction and capacity improvement. In general, we found different coating protocols have a great influence on the surface chemistry, coating morphology, and electrochemical performance of alumina-coated NMC532. These new findings can help us develop new design principles and coating protocols for the next-generation surface-coated cathode materials with improved stability and capacity.

Experimental

Material preparation.—The pristine NMC532 cathode materials used in this work were commercial powders from TODA America Inc. During the WC coating process, the cathode powders were first added into the aqueous solution made of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich) and DI water. The ratios between Al and pristine cathode powders were determined to produce a final Al_2O_3 ratio of 0.2, 0.5, 2, or 5 wt%, which were noted as 02-WC, 05-WC, 2-WC, and 5-WC, respectively. The mixture was stirred at room temperature for 6 h. Then the temperature was raised to 80°C and the stirring was continued overnight to evaporate the water. The remaining mixture was further dried in the vacuum for 4 h, to get the as-coated particles. The ALD coating in this paper was done by Forge Nano Inc. The coating was applied at 180°C using Strem 93–1360 Trimethylaluminum (min. 98%) and deionized water. A mass spectrum was used to indicate break-through to know when to stop-start precursor dosing. Two ALD-coated NMC532 particles with

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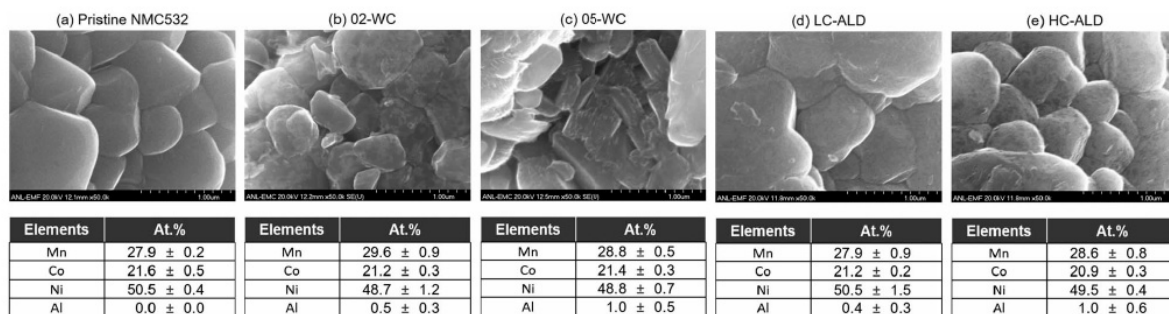


Figure 1. SEM and EDS results of the pristine and alumina-coated NMC532 particles. (a) Pristine NMC532, (b) 0.2%-Al₂O₃ WC coated NMC532 (02-WC), (c) 0.5%-Al₂O₃ WC coated NMC532 (05-WC), (d) low-cycled-number ALD coated NMC532 (LC-ALD), and (e) high-cycled-number ALD coated NMC532 (HC-ALD). The error bars of the EDS results represent the standard deviation of the atomic percentages measured at least seven different spots, demonstrating the uniformity of the elemental distribution.

different ALD cycles were prepared, which are noted as LC-ALD (low-cycle) and HC-ALD (high-cycle) for 2-cycle and 8-cycle ALD coated samples, respectively. Some of the as-coated powders by WC or ALD method were heat-treated in air at 800°C for 8 h, which were noted as 02-WC-HT, 05-WC-HT, 2-WC-HT, 5-WC-HT, LC-ALD-HT, and HC-ALD-HT, respectively. Some WC-coated powders with the 2 wt% alumina loading were also annealed in air at some intermediate temperatures including 450 and 500°C for 8 h, which were noted as 2-WC-450C and 2-WC-500C, respectively, to further study the temperature effects on interfacial reactions between surface alumina coatings and bulk NMC532 cores in WC-coated samples during heat treatments.

Electrochemical testing.—Electrochemical tests were performed using 2032-type coin cells. The cathodes were prepared by laminating Al foil current collectors with a slurry containing 90 wt% cathode oxide powder, 5 wt% C45 carbon, and 5 wt% polyvinylidene difluoride (PVDF) binder in N-Methyl 2-Pyrrolidone (NMP). The anodes were Li metal plates. The electrolyte was a 1.2 M solution of LiPF₆ in a 3:7 mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC). Celgard-2325 was used as the separator and the lithium metal plate was used as the anode. The cells were cycled between 3 and 4.5 V, first at the rate of C/10 for 4 cycles, then at C/3 for 80 cycles. Hybrid pulse-power capability (HPPC) cycles with discharge/charge pulses at the rate of 2C/1.5C for 10 s were used to investigate the impedance change. HPPC cycles were inserted after the C/10 cycles and between every 20 C/3 cycles in some half-cell tests and all full-cell tests. The discharge area specific impedance (ASI) are calculated as $ASI = \Delta V / \Delta I$, where ΔV and ΔI are the voltage and current change during the discharge pulse, respectively. For each sample in half-cell tests, at least three coin cells were made to check the reproducibility.

Structural characterizations.—²⁷Al MAS NMR experiments were performed at 11.7 T (500 MHz) on Bruker Avance III spectrometer at a Larmor frequency of 130.25 MHz. A rotor-synchronized echo pulse sequence with the pulse width of 1.5 μs and pulse delay of 15 s was used to acquire the spectra with a 2.5 mm probe at spinning speed of 30 kHz. The spectra were referenced to 1 M Al(NO₃)₃ at 0 ppm. ⁷Li MAS-NMR experiments were also performed at 11.7 T on a Bruker Avance III HD spectrometer, operating at a Larmor frequency of 194.32 MHz, using a 2.5 mm MAS probe. All spectra were acquired at 30 kHz with a rotor synchronized echo pulse sequence. A $\pi/2$ pulse width of 2.5 μs was used with sufficiently long pulse recycle delays of 15 s. The spectra were referenced to 1 M LiCl at 0 ppm.

²⁷Al MAS NMR experiments were also performed using the high field solid-state NMR at the Environmental Molecular Science Laboratory at Pacific Northwest National Laboratory (PNNL). The measurement was done at 20.5 T (850 MHz for proton) utilizing an Agilent VNMRs spectrometer using a 1.6 mm MAS probe (double tuned for ¹H and ²⁷Al). Chemical shifts were referenced to 1 M AlCl₃ (aq)

(0.0 ppm) for ²⁷Al. The MAS NMR spectra of ²⁷Al were collected at 26.5 kHz (125 ppm) sample spinning using a rotor synchronized Hahn echo sequence every 5 or 20 s using a 2.1 μs selective $\pi/2$.

SEM images were taken using a Hitachi S-4700-II microscope in the Center for Nanoscale Materials of Argonne National Laboratory, equipped with Energy Dispersive Spectrometry (EDS). The dry powders were directly sprayed onto the conductive carbon tape before imaging. Images were taken at 20 kV operating voltage. EDS were measured at more than 7 different spots for each sample to examine the uniformity of the coating.

TEM studies were performed at 200 kV on a JEOL 2100F in the Center for Nanoscale Materials of Argonne National Laboratory. The images were taken using Gatan Digital Micrograph v2.01 (Gatan Inc.). This TEM is equipped with energy dispersive spectrometry, which was used to confirm the TEM images of the particle surfaces shown in this paper were all covered by the aluminum-containing coating.

Results and Discussion

To determine the morphology and effective Al loading of alumina-coated NMC532 particles synthesized in this work, SEM and EDS were performed on samples prepared by different coating methods, as shown in Figure 1. The SEM images demonstrate that after the ALD coating, the originally smooth NMC532 surface is covered by a thin layer of alumina. Darker spots and segregated small plateaus can be observed in both LC-ALD and HC-ALD samples. Compared with LC-ALD, the HC-ALD sample with higher numbers of ALD cycles shows higher Al loading in EDS as well as more surface features in SEM image. On the other hand, for the WC coated samples, similar spots and plateaus are observed on the surface, which again implies a successful surface alumina coating. The surface of 02-WC and 05-WC samples look rougher than the LC-ALD and HC-ALD samples, respectively, despite the similar Al loadings between 02-WC and LC-ALD, as well as between 05-WC and HC-ALD, indicating the ALD method forms more uniform surface coating than the WC method under the same Al loading. Additionally, the atomic structure and morphology of the surface coating layers were also characterized by TEM. As shown in Figure 2, before high-temperature heat-treatment, both ALD and WC methods lead to amorphous coating layers on top of the crystalline NMC532. The coating layers are several nanometers thick and are unevenly distributed on the surface of all the coated samples. The surface of the WC coated samples is slightly less uniform in thickness than the ALD coated samples, which is consistent with the SEM observations in Figure 1.

In previous studies, we have shown that the annealing after WC coating process can help to crystallize the surface alumina coating, make it more closely attached to the cathode particles, and form an interphase layer with higher Li conductivity, which lead to better electrochemical performance after the high-temperature treatment.^{17,18} In this work, to study the influence of high-temperature annealing on

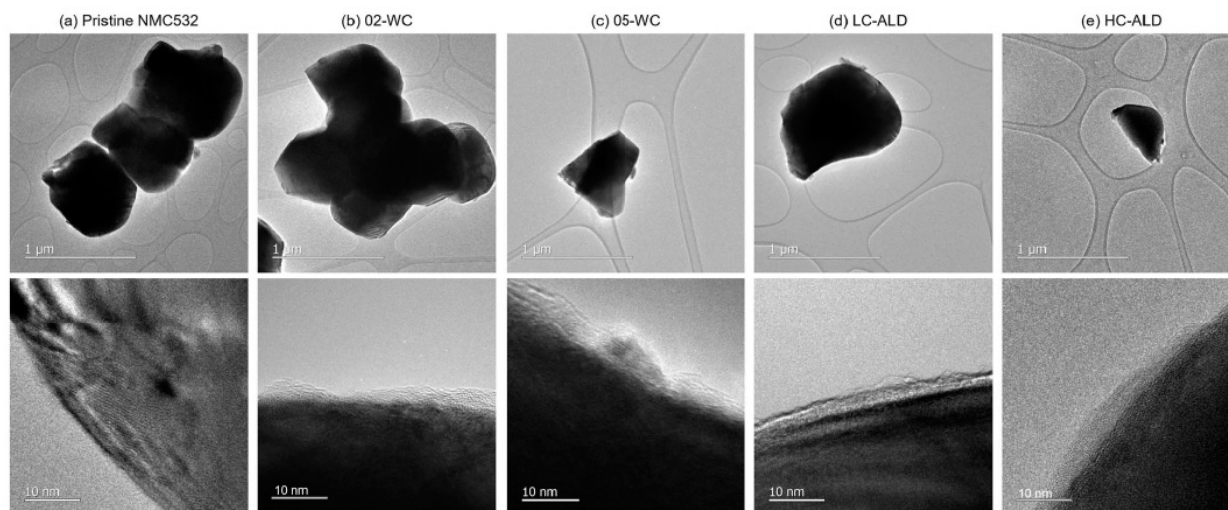


Figure 2. TEM images of the pristine and alumina-coated NMC532 particles. (a) Pristine NMC532, (b) 0.2%- Al_2O_3 WC coated NMC532 (02-WC), (c) 0.5%- Al_2O_3 WC coated NMC532 (05-WC), (d) low-cycle-number ALD coated NMC532 (LC-ALD), and (e) high-cycle-number ALD coated NMC532 (HC-ALD).

samples coated by different methods, we heat-treated both ALD and WC coated samples at 800°C in air for 8h. The TEM images in Figure 3 show that after the annealing, the surface alumina coating layers become crystalline in both WC- and ALD-coated samples. The SEM images in Figures 3a–3b show that for the WC-coated samples, high-temperature treatment leads to a smoother coating layer attached more closely and more evenly on top of NMC532. In comparison, the high-temperature treatment does not smoothen the surface coatings of the ALD samples (see Figures 3c–3d). Actually, more aggregated small dots were formed on ALD samples after the annealing. This implies that the coating layers formed by different methods may have very different morphology evolution behavior in response to high-temperature treatment.

The different morphology evolution behavior of the WC and ALD samples after annealing indicate the different interaction mechanisms between alumina coatings and NMC532 cores. To explore the potential structural and chemical evolutions of surface alumina coatings, we measured the ^{27}Al and ^7Li NMR spectra of different samples before and after annealing, as shown in Figure 4. The ^{27}Al MAS NMR spectra in Figure 4a demonstrates that after the high-temperature treatments, the envelope of the spinning sidebands of 05-WC is significantly

broadened, while that of HC-ALD is only slightly broadened. The broadening of the spinning sidebands observed in ^{27}Al NMR spectra is due to the reducing of the average distance between the Al atoms in the coating layers and the paramagnetic transition metal atoms in the cathode bulk, which has been reported in the previous WC coating papers.^{17,18} This means the annealing process leads to more pronounced morphological and structural changes in surface alumina coated by the WC method, making the coating layer more closely and more evenly attached to the NMC532. In comparison, the surface alumina coated by ALD method is less influenced by the annealing. This is consistent with the morphological changes observed in Figure 3, where the heat treatments make the coating layers of WC-coated samples smoother and more evenly distributed, while the coating layers of ALD-coated samples remain rough after the annealing. Such different coating evolution behaviors in response to heat-treatment can also be observed in the chemical changes of surface Al species. As shown in Figure 4b, for both 05-WC and HC-ALD samples without heat treatments, the Al atoms have a single chemical environment around 0 ppm, which comes from the 6-coordinate $\text{Al}(\text{OH})_3$ or Al_2O_3 configurations. The 05-WC sample showed a narrower peak than the HC-ALD sample, implying that the WC-coated alumina layers have more ordered

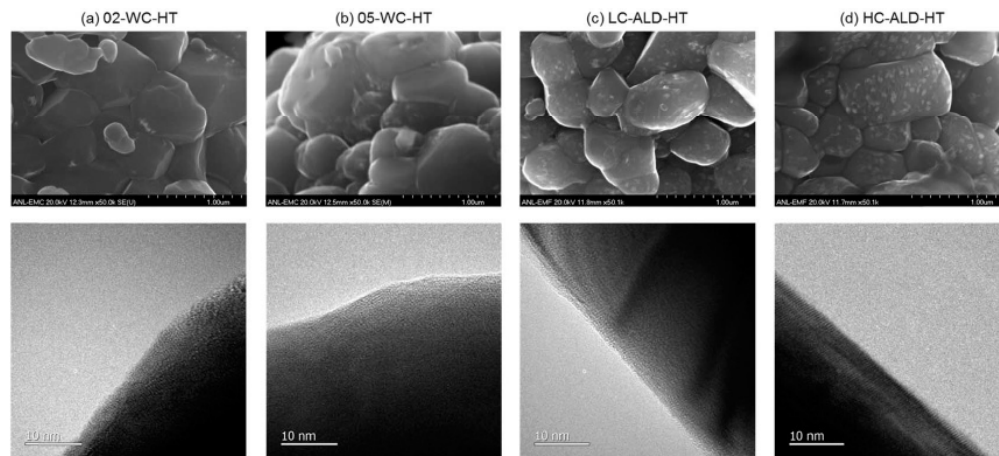


Figure 3. SEM and TEM results of alumina coated NMC532 particles after high-temperature annealing in air at 800°C for 8h. (a) 02-WC-HT, (b) 05-WC-HT, (c) LC-ALD-HT, and (d) HC-ALD-HT.

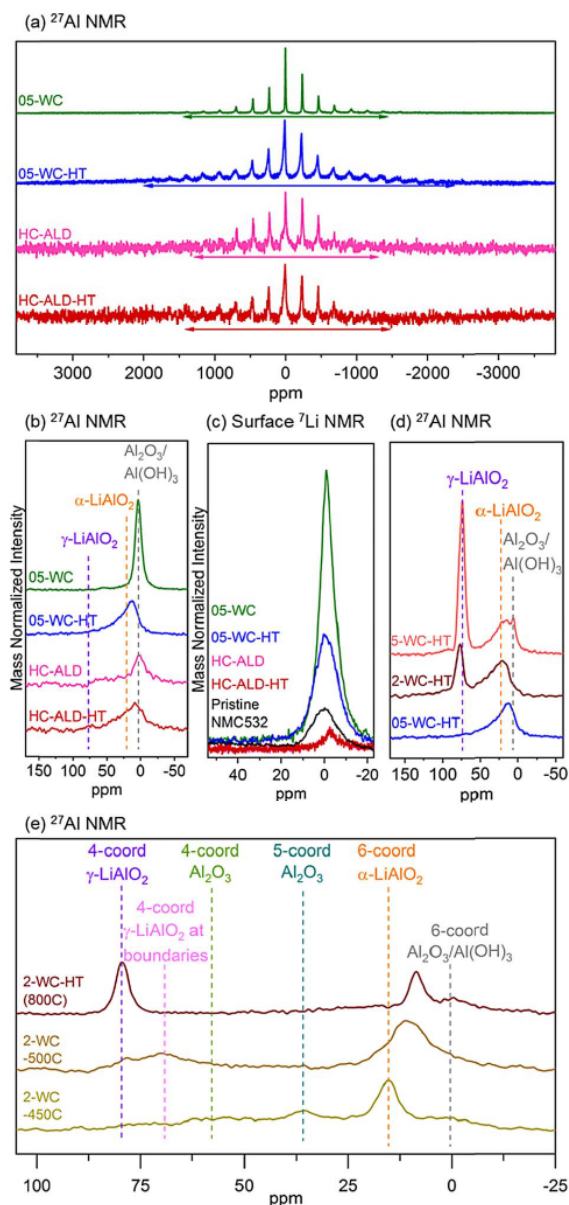


Figure 4. (a) ^{27}Al MAS NMR, (b) zoom-in of ^{27}Al MAS NMR, and (c) surface ^7Li MAS NMR results of 0.5% Al_2O_3 -coated NMC532 particles coated by WC and ALD methods, before and after annealing. (d) and (e) are the zoom-in of ^{27}Al MAS NMR results of WC-coated NMC532 with different alumina loadings and different annealing temperatures, respectively. Spectra in (e) are measured at higher magnetic field. Spectra in (a), (d) and (e) are normalized by the height of main peak near 0 ppm, while the spectra in (b) and (c) are normalized by the mass of measured samples.

short-range structures. Both samples showed similar area under the main peak in Figure 4b after the mass-normalization, implying they have the similar amount of Al in the surface coating layers. After the high-temperature annealing at 800°C, the main ^{27}Al peak of 05-WC-HT shifted to ~ 14 ppm, representing the formation of 6-coordinate α - LiAlO_2 phase coming from the interfacial reaction between the surface alumina coatings and the Li species on top of NMC532. The chemical evolution of surface Al species implied that after the high-temperature treatment, the surface coating layer is no longer a loose coverage on

top of cathode materials, but a new interphase layer attached closely to the primary NMC532 particles. Such interaction between surface alumina coating and NMC bulk to form LiAlO_2 species has been reported in previous works,^{17–19} but in previous studies with much higher alumina loading (2 or 5 wt%), the high-temperature annealing leads to the formation of mainly 4-coordinate γ - LiAlO_2 , with a smaller amount of α - LiAlO_2 existing as a buffer layer between the NMC532 and the γ - LiAlO_2 to release the strain caused by lattice mismatching.¹⁷ As shown in Figure 4d, the higher Al loading on the surface, the more coordinate γ - LiAlO_2 will form after high-temperature annealing. In this work, with only 0.5 wt% alumina loading in 05-WC, there is almost no γ - LiAlO_2 phase formation, and only the lattice-matching α - LiAlO_2 is formed on top of NMC532, which is beneficial to the electrochemical performance since the α - LiAlO_2 is a much better Li conductor than the γ - LiAlO_2 . To further investigate the formation of LiAlO_2 interphases during heat treatments, we also measured the Al chemical environments of WC-coated 2wt%-alumina-loaded samples annealed at some intermediate temperatures using high field NMR, as shown in Figure 4e. From Figure 4e, we can find that after annealing at a relatively low temperature of 450°C, α - LiAlO_2 is almost the only interphase formed on top of NMC532. Then when increasing the annealing temperature from 500 to 800°C, more and more γ - LiAlO_2 formed after heat treatments, indicating that the α - LiAlO_2 is firstly formed directly on top of NMC532 as a buffer layer while the γ - LiAlO_2 is formed later on top of the α - LiAlO_2 layer (with enough Al loadings). On the other hand, for the HC-ALD-HT sample, annealing also caused the shift of Al chemical environment, but only to ~ 8 ppm, indicating a mixture of α - LiAlO_2 and Al_2O_3 is formed. The less α - LiAlO_2 formation and more Al_2O_3 retention in ALD samples after annealing demonstrate again that the coating layers formed by ALD method have less interfacial reaction with NMC532 during the annealing. For both ALD- and WC-coated samples, high temperature does not obviously change the total area under the mass-normalized ^{27}Al main and sideband peaks, implying there is almost no Al intercalation or Al loss during the annealing process.

In addition to the surface Al chemical environments, the coating methods also have a great influence on the surface Li species. The mass-normalized surface ^7Li NMR results in Figure 4c show that the WC coating method leads to a significant increase in surface Li species compared with pristine NMC532, which is due to the Li extraction process caused by Li-proton exchange in chemical solutions. Changing the solvents from water to organic solvents can reduce such Li extraction and therefore gain better electrochemical performance.¹⁹ In comparison, for ALD-coated samples, only a small amount of surface Li species can be observed, since there is no solution-based Li extraction issue during the ALD coating. Actually, the lack of surface Li species on the top of ALD-coated NMC532 particles may play important role in the surface Al chemical changes during annealing, which can suppress the interactions between surface alumina coating and the Li species on top of NMC532 to form LiAlO_2 species. This is consistent with our observations in Figure 4b.

To study the influence of the significant difference in the structure and chemistry of the surface alumina coatings caused by different coating methods, half-cell electrochemical tests were performed on the alumina-coated samples with and without annealing, as shown in Figure 5. In general, for both ALD- and WC-coated samples, the capacity retention rates are higher than the pristine NMC532, and thinner coating always leads to higher capacities. Before annealing, the ALD samples with different alumina loadings show similar performance. Increasing the number of ALD cycles slightly decreases the capacity, which might be due to higher Li transportation impedance with thicker coatings. In comparison, the unannealed WC-coated samples demonstrate much lower capacity, which might be due to the amorphous $\text{Al}(\text{OH})_3$ coatings with very low Li conductivity, as well as the corrosive nitrates left on the surface.^{18,19} After the heat treatments, the difference between WC and ALD samples as well as between high-loading and low-loading samples becomes smaller, as shown in Figure 5b. All the alumina-coated and high-temperature annealed samples outperformed the pristine NMC532 after 84 cycles. Particularly,

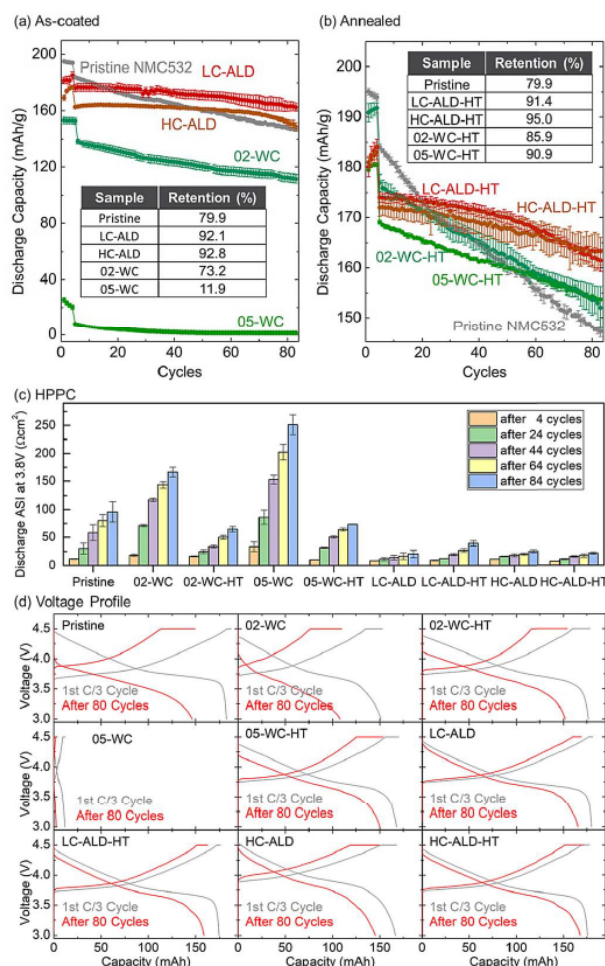


Figure 5. Half-cell test results of alumina-coated NMC532 particles, WC- or ALD-coated with different alumina loadings with and without heat-treatment. (a) Discharge capacity of as-coated samples. (b) Discharge capacity of 800°C-annealed samples. The discharge capacity of the pristine NMC532 particles was also shown in (a) and (b). The inserted tables show the discharge capacity retention rates over the 80 C/3 cycles. (c) The discharge ASI of the coated and pristine NMC532, measured by the HPPC cycles at the starting discharge voltage of 3.8 V. The error bars represent the standard deviation of three coin cell measurements for each sample. The cells were cycled between 3 and 4.5 V, first at the rate of C/10 for 4 cycles, then at C/3 for 80 cycles. HPPC cycles were inserted after the C/10 cycles and between every 20 C/3 cycles. The capacities of the HPPC cycles were not shown in (a) and (b). (d) The voltage profiles during the first and last C/3 cycle shown in (a) and (b).

the annealing process has only a limited influence on the electrochemical performance of ALD samples, but can significantly improve the performance of WC samples to be only slightly lower than the ALD samples. This is consistent with the more obvious morphological and chemical evolutions of WC samples compared with ALD samples after the heat treatments. The elevated electrochemical performance after annealing, particularly on WC-coated samples, indicates that the crystallization of surface coatings, the formation of LiAlO_2 species, and the removing of corrosive nitrates left from the WC coating process can effectively improve the quality and uniformity of surface coatings, leading to similar electrochemical performance among different samples. In addition, 02-WC-HT shows lower capacity retention rate over cycles than 05-WC-HT, probably because the lower loading leads to worse coating coverage after heat-treatment in the WC samples. On the

other hand, ALD is known to have better uniformity and better coverage even under very low loadings, therefore LC-ALD-HT shows similar capacity retention to HC-ALD-HT, despite the loading difference. Different coating protocols and heat treatments also lead to different impedance during the cycling, which matches the capacity trends mentioned above. As shown in Figure 5c, ALD-coated samples show the lowest impedance over the cycles. The heat-treatment only slightly increases the impedance of LC-ALD sample and slightly decreases the impedance of HC-ALD sample, which is similar to the annealing influence on the capacity changes of these ALD-coated samples. On the other hand, the unannealed WC-coated samples demonstrate much higher impedance rising over the cycles, which is consistent with their poor capacity performance. Heat treatments can effectively reduce the impedance of WC-coated samples, making their impedance even lower than the pristine NMC532, which matches the observation of significant performance improvement of those WC-coated samples after annealing. Figure 5d exhibits the voltage profile of the first and last aging cycles of different samples. After 80 cycles, the charging capacity gained during the 4.5V-holding increased, indicating the rising of cell impedance, which is consistent with the HPPC data shown in Figure 5c.

Conclusions

In this work, we systematically studied the influence of ALD vs. WC coating methods on alumina-coated NMC532 cathodes. Without heat-treatment, both methods show similar morphology and crystallinity for the surface alumina coating. Annealing at 800°C for 8h has a more significant influence on the structure and chemistry of the coating layers of WC-coated samples than of ALD-coated samples. Stronger interactions between surface alumina coatings and Li species on top of NMC532 can be observed on WC-coated samples after annealing, leading to the formation of more LiAlO_2 species attached more closely and more evenly to the NMC532 particles, which is attributed to the Li extraction process during the WC coating. In half-cell electrochemical tests, before annealing, ALD-coated samples demonstrate much higher capacities and much lower impedance than the WC-coated samples. After the high-temperature annealing, similar capacity and cyclability can be observed on ALD- and WC-coated cathodes with the high alumina loading (~0.5 wt%). When further decreasing the alumina loading to ~0.2 wt%, the capacity retention of the WC sample decreased, which might be related to low coverage; while no cyclability loss was observed on low-loading ALD-coated sample with better coating uniformity. This work proved that different coating protocols can greatly affect the atomic and chemical structures of surface alumina coating on cathode materials. ALD method leads to a better initial quality of the coating layers and is less influenced by the post-coating annealing process. While for WC method the high-temperature treatment is highly needed to optimize the coating structures and improve the performance accompanied by much stronger interfacial reactions between alumina coatings and cathode cores.

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