Atomic Layer Deposition of Stable LiAlF₄ Lithium Ion Conductive Interfacial Layer for Stable Cathode Cycling

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ABSTRACT: Modern lithium ion batteries are often desired to operate at a wide electrochemical window to maximize energy densities. While pushing the limit of cutoff potentials allows batteries to provide greater energy densities with enhanced specific capacities and higher voltage outputs, it raises key challenges with thermodynamic and kinetic stability in the battery. This is especially true for layered lithium transition-metal oxides, where capacities can improve but stabilities are compromised as wider electrochemical windows are applied. To overcome the above-mentioned challenges, we used atomic layer deposition to develop a LiAlF₄ solid thin film with robust stability and satisfactory ion conductivity, which is superior to commonly used LiF and AlF₃. With a predicted stable electrochemical window of approximately 2.0 ± 0.9 to 5.7 ± 0.7 V vs Li⁺/Li for LiAlF₄, excellent stability was achieved for high Ni content LiNi₀.₈Mn₀.₁Co₀.₁O₂ electrodes with LiAlF₄ interfacial layer at a wide electrochemical window of 2.75−4.50 V vs Li⁺/Li.

KEYWORDS: lithium ion batteries, layered lithium transition-metal oxide, atomic layer deposition, lithium aluminum fluoride, lithium ion conductive interfacial layer, surface coating

Driven by increasing energy storage demands in consumer electronics, electrical vehicles, and even grid scale power, modern lithium ion batteries are often desired to operate at wide electrochemical windows for enhanced specific capacities and higher voltage outputs. Operating at extreme voltages posts grand challenges in the field of materials research, as issues with instability plague the electrodes, electrolytes, and their interfaces. To maintain a long cycle life, developing a stable interfacial layer is critical, as degradation typically starts to propagate where the electrode and electrolyte meet. The accumulation of byproducts at the interface leads to high internal resistance, which can eventually cause battery failure. In the past few decades, great efforts have been devoted to achieve a stable interfacial layer. A great example of such is the solid-electrolyte interphase (SEI) formation on the graphite anode, which enabled the commercialization of lithium ion batteries in the 1990s. On the cathode side, the need to develop a stable interfacial layer is more and more important nowadays as its instability has become a limiting factor for batteries to operate safely for tens of years, especially when the cutoff potentials have been aggressively pushed to more positive for greater energy output.

To solve the challenge, various methods including, but not limited to, surface coating, surface modification by doping, and electrolyte additive formulation have been studied. To date, thin films including Al₂O₃, AlF₃ and lithium containing compounds (e.g., LiNi₀.₅Mn₀.₅O₂, LiFePO₄, Li₂MnO₃, and Li₂ZrO₃ for improved capacity and lithium ion conductivity) have been successfully deposited using different coating methods with varying levels of successes. However, a superior film which satisfies all major requirements simultaneously including electrochemically inert, chemically stable, lithium ion conductive, and highly uniform is still missing. In this study, we report a LiAlF₄ thin film prepared by atomic layer deposition (ALD) which satisfies all four requirements mentioned above for cathode to operate at wide electrochemical windows. We studied the effect of coating...
on high Ni content LiNi0.8Mn0.1Co0.1O2 (NMC-811) cycled at 2.75−4.50 V vs Li+/Li. The high Ni content layered lithium transition-metal oxides have attracted great interest, owing to their high capacity and low cost. However, the replacement of Co with Ni reduces the structural stability, especially at high applied potentials and on the interface. The film we developed served as a stable and lithium permeable interfacial layer for NMC-811. Good cycling stability can be obtained for 300 cycles with capacity retention higher than 99.9% per cycle at a wide electrochemical window of 2.75−4.50 V vs Li+/Li.

RESULTS/DISCUSSION

The interface between electrode and electrolyte is one of the most important components of the battery. It must be stable enough to withstand years of battery operation without degradation while retaining low resistance for lithium ions to diffuse through. Therefore, in order for the interfacial layer to work properly to enhance the stability of the cathode rather than to limit its performance, a few requirements need to be met simultaneously.

First, the interfacial layer has to be electrochemically and chemically stable to withstand the harsh battery operation conditions. To avoid the risk of decomposition by reduction or oxidation during cycling, the electrochemical stability window of the interfacial layer has to be wide enough so that it does not participate in the redox reactions. In Figure 1a, we provided the stability windows of a few candidate lithium containing compounds for this purpose, as reported by Richards et al.

![Image](https://example.com/image1)

Figure 1. (a) Calculated electrochemical stability windows of Li3N, Li2O, LiF, LiAlO2, Li3PO4, and LiAlF4. The windows of the first five candidates have been reported (please see the Methods section and Supporting Information for detailed calculation of the decomposition potentials and reactions); we use DFT to calculate the window of LiAlF4. The operating electrochemical window of NMC-811 in this study and typical operation electrochemical window of LiCoO2 are included for comparison. (b) Selection criteria (chemical stability, electrochemical stability, and Li ion conductivity) of a few interfacial materials.

using the formation energy reported in the Materials Project database. Among them, nitrides (e.g., Li2N, 0.0−0.6 V vs Li+/Li), oxides (e.g., Li2O, 0−3.1 V vs Li+/Li LiAlO2, 0.2−3.7 V vs Li+/Li), and phosphate (e.g., Li3PO4, 0.7−4.2 V vs Li+/Li) are thermodynamically unstable (see Supporting Information for detailed calculation) in the range where lithiation/delithiation of layered lithium transition-metal oxides take place and therefore are prone to be decomposed by oxidation with years of battery operation. For comparison, fluorides are promising thanks to their superior stability. The stability window is as wide as 0−6.4 V vs Li+/Li for LiF, a binary fluoride compound. Using these same methods, we find that the stability window of the fluorides remains wide even with the addition of second metal ions. We perform density functional theory (DFT) calculations on LiAlF4 and find a formation energy of −3.547 eV/atom or −2053.4 kJ/mol for LiAlF4 and predict an electrochemical window of 2.0 ± 0.9 to 5.7 ± 0.7 V vs Li+/Li (see Methods section and Supporting Information for detailed calculation and error estimate). As seen in the far right bar in Figure 1a, our calculations indicate LiAlF4 is thermodynamically stable in the entire operation window of the layered lithium transition-metal oxides, unlike most other candidates. Experimentally, cyclic voltammetry scans and XPS characterization were performed for LiAlF4 films. The results also show that LiAlF4 is stable in the electrochemical window of 2.75−4.50 V vs Li+/Li (see Supporting Information for more details). In addition to its wide electrochemical window, fluoride compounds have superior chemical stability at the interface when compared with other chemical compositions. For example, oxides and nitrides would be attacked by trace amounts of H2O and HF in the electrolyte. Even in the ambient air, fluorides are considered to be more resistant against moisture and CO2 than oxides and nitrides, which makes the handling and processing of coated electrodes easier.

Second, the interfacial layers have to be lithium ion conductive to maintain the power density of the battery. A uniform coating of poor lithium ion conductors such as metal oxides (Al2O3,11,12 and AlF3,24) often induces an increased overpotential and a reduced capacity. In order to minimize the ion resistance, lithium containing thin films (Li2N,15 LiF,16,20,27 LiAlO2,28 LiPON,29 and LiFePO430) have been studied. Among them, fluorides are particularly promising due to the above-mentioned stability. While LiF is a poor lithium ion conductor, mixing LiF with divalent fluoride or trivalent fluoride has shown improved lithium ion conductivity. Before this work, LiAlF4 has not been used in lithium ion batteries experimentally, although LiAlF4 has shown success in electrochromic devices using evaporation methods.

Last but not the least, the interfacial layer needs to be uniform across the large high surface area of the electrode. While solution-phase coating methods on individual particles of cathode materials hold the advantages of being cost-effective and easy integration for large scale production, the non-uniformity is inherent upon postgrowth annealing, and film cracking may take place during slurry making and/or calendaring processes. Due to the complexity and compatibility of synthesis, there is no report of LiAlF4 synthesis other than physical evaporation, to the best of our knowledge. However, evaporation methods limit the application of LiAlF4 to devices with a planar geometry.32,33 Compared to the above-mentioned methods, ALD could achieve uniform coating on high surface area electrodes directly.
ALD LiF deposition was first reported by Mantymaki et al. using lithium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (Lithd) and TiF$_4$ as precursors. The deposition is challenging as the growth is temperature gradient dependent, requires a large Lithd dose, and has a poor adhesion to the substrate. Although these drawbacks can be partially overcome by introducing Mg(thd)$_2$ subcycles, the process is unnecessarily complicated. In this study, we propose a different LiF ALD
chemistry based on lithium tert-butoxide as the lithium source. Lithium tert-butoxide has a relatively high vapor pressure and good thermal stability among different lithium organometallic compounds. LiF thin films can be acquired at growth temperatures ranging from 200 to 300 °C (see Supporting Information for more detailed characterizations). The highest growth rate achieved was 0.5 Å per ALD cycle at 250 °C. At 250 °C, the coverage of LiF deposition is uniform and featured small grains (Figure 2d). The AlF3 deposition was done following literature reports. Unlike LiF which shows individual grains, an AlF3 film prepared by ALD is uniform and featureless (Figure 2e). ALD provides great flexibility to prepare complex films by integrating different recipes. In this study, LiAlF4 film was prepared by introducing alternative subcycles of LiF (LiOtBu and TiF4) and AlF3 (AlCl3 and TiF4). The LiAlF4 prepared by this method is uniform (Figure 2f) as well and its thicknesses increased linearly with total ALD cycles (Figure 2c). Among three ALD films, LiF thin film prepared by ALD is crystalline, while AlF3 and LiAlF4 thin films prepared by ALD are amorphous (see Supporting Information for grazing incidence X-ray diffraction (GIXRD) characterization).

XPS characterizations were carried out to analyze chemical compositions of ALD grown films (Figure 3). The ALD LiF film showed a distinct Li 1s peak and F 1s peak at 55.3 and 684.8 eV, both agreeing well with literature reports for bulk LiF. The ALD AlF3 film showed a clear Al 2p peak at 76.2 eV, also in agreement with reported values for bulk AlF3. Due to the higher electronegativity of Al compared to Li, the F 1s peak in AlF3 shifted to higher binding energy compared to the F 1s peak in LiF. The observed peak position of 686.5 eV was close to the F 1s peak in α-AlF3. ALD LiAlF4 film had all three elements with Li 1s, Al 2p, and F 1s peaks sitting at 55.6, 75.3, and 685.5 eV. Compared to ALD LiF and AlF3 films, the Li 1s peak in the LiAlF4 film shifted to higher binding energy, and the Al 2p peak in the LiAlF4 film shifted to lower binding energy as expected. The F 1s peak in LiAlF4 film also shifted to higher binding energy compared to the F 1s peak in LiF, but lower binding energy compared to the F 1s peak in AlF3. The peak position analysis demonstrated that the LiAlF4 film forms one single chemical composition rather than a physical mixture of LiF and AlF3.

The depth profile of LiAlF4 film was also investigated (Figure 3b). The C and O impurities on the surface were low and quickly disappeared after the first sputtering cycle, indicating the nature of surface absorbed impurities. Ti, C, and O impurities remained low throughout the entire film. The Li:Al:F atomic ratio was consistent across different film depths with an average being 1.2:1.0:4.5 according to XPS. For comparison, the F/Li atomic ratio in ALD LiF film and F/Al atomic ratio in ALD AlF3 film were 0.97 and 3.45, respectively (see Supporting Information). Previous reports of AlF3 ALD also show an excess of fluorine compared to metal ions using a different cauterization method (time-of-flight elastic recoil detection analysis). The excess of fluorine may create metal vacancies in ALD grown films for enhanced lithium ion conductivity.

The lithium ion conductivity of ALD LiAlF4 film was tested by depositing films with different thicknesses onto stainless steel substrates, which were then assembled into coin cells (the
Figure 5. (a) Rate performance of pristine, 20c ALD LiAlF4 coated, 20c ALD LiF coated, and 20c ALD AlF3 coated NMC-811 electrodes at room temperature with an electrochemical window of 2.75–4.50 V vs Li+/Li. (b, c) Voltage vs capacity plots of pristine, 20c ALD LiAlF4 coated, 20c ALD LiF coated, and 20c ALD AlF3 coated NMC-811 electrodes at 5th and 35th cycles, respectively.

The ALD LiAlF4 thin film coating was performed directly on the NMC-811 electrodes instead of NMC-811 particles. The surface coating mechanism of the ALD technique ensures the coating occurs on the surface, generating an uniform thin film covering the entire electrode while maintaining the interconnectivity of the NMC-811 particles (see Supporting Information for SEM characterization of NMC-811 electrodes before and after ALD LiAlF4 coating). In Figure 5, we tested the rate performance of pristine and ALD coated NMC-811 electrodes with an electrochemical window of 2.75–4.50 V vs Li+/Li. At the lowest rate of 20 mA/g, the discharge capacity of pristine NMC-811 electrode quickly dropped from 206.0 mAh/g to 195.9 mAh/g within the first 10 cycles. While cathodes with 20 cycles of ALD LiF coating, AlF3 coating, and LiAlF4 coating all showed improved stability, their specific capacities were different. With the highest lithium ion conductivity among the three, LiAlF4 coated electrode delivered an average capacity of 197.7 mAh/g at 20 mA/g during 1–10 cycles and 147.6 mAh/g at 200 mA/g during 31–41st cycles, both of which were close to or even higher than pristine NMC-811 (200.8 mAh/g at 20 mA/g and 142.0 mAh/g at 200 mA/g). However, owing to the poor conductivity of LiF, a dense and uniform LiF coating on the surface of cathode materials would hinder the lithium ion transport and cause polarization. The average capacities of LiF coated electrodes were only 170.8 mAh/g at 20 mA/g during 1–10 cycles and 94.5 mAh/g at 200 mA/g during 31–41st cycles. While AlF3 has been reported as a coating layer to stabilize both anodes and cathodes in lithium batteries, the mechanism of how lithium ion conducts through the coating layer is not clear. For instance, AlF3 would convert to Li3AlF6, LiF, Al, and various Li alloys on the anode depending on how low an equilibrium potential is applied (see Supporting Information for detailed calculation). In addition to the lithium ion conductivity provided by some of these products, the phase transformation itself may leads to a poor film, which allows lithium ions to pass through as well. However, the porosity of the film may lead to battery degradation by allowing interfacial reactions between electrode and electrolyte. On the cathode part, owing to the high...
operation voltage, it is unlikely for lithiation to take place in AlF3 thermodynamically according to our thermodynamic calculation. As a result, a thicker coating has led to higher overpotential and reduced capacity in the past.24 This phenomenon becomes more substantial when metal fluoride is applied using ALD, which is known for its conformity of coverage. The average capacities of AlF3 coated electrodes were only 183.7 mAh/g at 20 mA/g and 106.0 mAh/g at 200 mA/g. A similar phenomenon has also been observed for other fluoride coating with only five ALD cycles.43 The uniform ALD coating provides enhanced stability, but comes at the cost of serving as an additional lithium ion diffusion barrier. When the lithium ion conductivity of the film is low (such as LiF and AlF3), such barriers lead to a high overpotential during cycling (Figure 5b,c) and thus a poor rate performance. Our results show that having a stable and lithium ion conductive interfacial layer is important.

The long-term stability of pristine and ALD LiAlF4 coated NMC-811 electrodes was further analyzed using galvanostatic cycling at both room temperature and an elevated temperature (Figure 6) at a wide electrochemical window of 2.75–4.50 V vs Li+/Li. At room temperature, the electrode with LiAlF4 coating maintained a capacity higher than 140 mAh/g after 300 cycles (24% decay over 300 cycles or 0.08% per cycle). For pristine NMC-811, the capacity dropped quickly to <140 mAh/g after 113 cycles (29% decay over 113 cycles or 0.26% per cycle). The poor cycle stability at elevated temperatures is the most considerable drawback for high Ni content layered lithium metal oxides.19,20,44 Therefore, testing the long-term cycle stability at elevated temperatures presents a rigorous, meaningful, and real-world relevant test for NMC-811. Thanks to the enhanced lithium ion conductivity of both the coating layer and NMC-811 itself at 50 °C, batteries were cycled at a higher rate of 200 mAh/g (Figure 6e). The capacities of both pristine NMC-811 electrodes decayed fast to <100 mAh/g within 100 cycles. In contrast, both ALD LiAlF4 coated samples showed excellent capacity retention within 100 cycles.

Figure 6. (a) Cycle performance of pristine and 20c ALD LiAlF4 coated NMC-811 electrodes at room temperature with an electrochemical window of 2.75–4.50 V vs Li+/Li. (b, c) EIS characterizations of pristine and 20c ALD LiAlF4 coated NMC-811 electrodes after 1st, 10th, 25th, and 50th cycles. (d) Voltage vs capacity plots of pristine and 20c ALD LiAlF4 coated NMC-811 electrodes at 2nd and 50th cycles. (e) Cycle performance of pristine and 20c ALD LiAlF4 coated NMC-811 electrodes at elevated temperature (50 °C) with an electrochemical window of 2.75–4.50 V vs Li+/Li.
important to develop an uniformly, chemically inert, electrochemically stable, and lithium ion conductive interface to achieve long-term stability for high Ni content layered lithium metal oxides. Such a stable and uniform interface in principle could minimize the parasitic reactions between the electrode (such as NiOx) and the electrolyte. In order to prove this hypothesis, the magnitude of parasitic reactions was monitored by measuring the Coulombic efficiency (CE) of the battery. The CE is defined as CE = capacity of discharge/capacity of charge. The cycle life of lithium ion battery is not infinite because small amounts of active materials (electrode and/or electrolyte) are consumed by parasitic reactions during each cycle. As Li is excess in the counter electrode in the NMC-811/Li half-cells, the detected CE lower than unity (100.0%) can be explained by the parasitic reactions on the cathode. When tested at room temperature, the average CE of pristine NMC-811 was 99.3%, indicating a high degree of parasitic reactions, such as electrolyte oxidation by highly reactive Ni4+ at high-applied potentials, took place. In contrast, the average CE of LiAlF4/NMC-811 was 99.8%. The average CE dropped from 99.3% at room temperature to 97.4% at elevated temperature for pristine NMC-811. The decrease of CE suggests the magnitude of parasitic reactions increased at elevated temperature. With a stable and uniform ALD LiAlF4 coating, the average CE improved significantly from 97.4% to 99.7% at elevated temperature. The difference we observed in our CE measurement strongly supports our hypothesis that the improvement of cycle stability by LiAlF4 coating is through reduced parasitic reactions.

The parasitic reactions at the interface of electrode and electrolyte also cause the accumulation of side products on the surface of the cathode, and its accumulation can be detected using impedance spectroscopy.45 As shown in Figure 6b,c, the impedance spectra of the battery at different cycle numbers were recorded. The impedance spectra of NMC-811 electrodes with and without LiAlF4 coating comprised two semicircles and a straight line angled close to 45°. The small semicircle at high frequency was attributed to the solid–electrolyte interface (RSEI and CPESEI), while the one at medium frequency corresponded to the charge transfer process at the cathode–electrolyte interface (Rct and CPEct). The 45° inclined line at low frequency was related to the Warburg impedance (Zw), which was related to the diffusion of lithium ions within the cathode. Upon cycling, the semicircle at medium frequency increased significantly for the pristine NMC-811, indicating the slowdown of charge transport across the cathode–electrolyte interface. The charge transfer resistance at the electrode–electrolyte interface for both pristine NMC-811 and ALD LiAlF4 coated NMC-811 after different numbers of cycles can be calculated (see Supporting Information for more details). Although the initial charge-transfer resistance was similar for both pristine NMC-811 and ALD LiAlF4 coated NMC-811 after the first cycle, it increased much faster for pristine NMC-811 compared to ALD LiAlF4 coated NMC-811 upon cycling. We also noticed that the voltage hysteresis increased slower for coated sample when compared to pristine NMC-811 (Figure 6d). The fact that the LiAlF4 coating layer suppressed the fast impedance growth supports that LiAlF4 film could minimize the magnitude of parasitic reactions at the electrode–electrolyte interface. While there may be other factors that could also contribute to the improved stability when LiAlF4 is applied, the reduced parasitic reaction at the electrode–electrolyte interface is an important one as suggested by our CE analysis and impedance spectra analysis (see Supporting Information for a brief discussion of failure mechanisms and additional characterizations).

CONCLUSIONS

To summarize, we designed and synthesized a stable and lithium ion conductive LiAlF4 interfacial layer on lithium ion battery cathodes using atomic layer deposition. Our calculations show that the fluoride-based interfacial layer is thermodynamically stable within a wide electrochemical window. The stable and lithium ion conductive interfacial layer improved the stability of high Ni content NMC-811 electrodes without sacrificing rate performance. If a stable interface between electrode and electrolyte can be achieved by rational materials design, lithium ion batteries with higher energy density and longer cycle life may find more applications including portable electronic, vehicle electrification, and grid-scale energy storage and beyond.

METHODS

DFT Calculations. To calculate the electrochemical window, we first calculated the formation energy of a crystalline form of LiAlF4 and then used the phase diagram building tool in the Materials Project (MP) database.47,48 To generate the LiAlF4 structure, we substituted in F for Cl in the stable LiAlCl4 structure in the MP database (MPID mp-22983) and fully relaxed the lattice vectors and the positions of the ions. The resulting formation energy is −3.35 eV/atom. This value is calculated at 0 K and 0 atm and uses a reference energy of zero for the pure elements. According to the MP phase diagram for the Li–Al–F ternary system, LiAlF4 is predicted to oxidize at a potential of 5.72 V vs Li/Li+ according to the following reaction:

\[
\text{LiAlF}_4 + \text{Li} + 0.5\text{F}^{-} + \text{AlF}_3
\]

The reducing reaction is predicted to occur at a potential of 2.05 V vs Li/Li+ according to the following reaction:

\[
\text{LiAlF}_4 + \text{Li} \rightarrow 2/3\text{Li}_2\text{AlF}_6 + 1/3\text{Al}
\]

For the DFT calculations we use the Vienna ab initio Simulation Package (VASP)49 with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)50 and the projector augmented wave (PAW)51 method. We use the following pseudopotentials: PAW_PBE Li sv, PAW_PBE Cl, and PAW_PBE F. We employ a plane wave cutoff energy of 520 eV and k-mesh with a density of at least 1500/atom.

We confirm experimentally the LiAlF4 thin film is amorphous (see Supporting Information for GIXRD characterization), but perform the DFT formation energy calculation on a representative crystalline phase for computational tractability. Work on Si52,53 Ge54 and SiO255 has been reported to indicate small and consistent energy differences between the crystalline and amorphous phases (~0.1 eV for Si) over compositional space during lithiation (i.e., Li2Si, Li4Ge, and Li2SiO2, respectively), suggesting that the electrochemical window of the crystalline phase may not be an unreasonable approximation of the amorphous phase. To estimate the uncertainty in this approximation, we introduce an error of ±0.1 eV/atom to all crystalline phases considered here. Propagating this error yields an uncertainty in the oxidation potential of ±0.7 V and an uncertainty in the reduction potential of ±0.9 V.

Materials Synthesis and Preparation. LiF deposition was performed using a Savannah S100 ALD system (Ultratech/Cambridge Nanotech). The LiF deposition consists of alternating pulse and purge of lithium tert-butoxide (99%, Alfa Aesar) and TiF4 (Sigma-Aldrich) as precursors. TiF4 was gently ground prior to use. A typical pulse and purge durations for lithium tert-butoxide subcycle are 1 s and 15 s, respectively. A typical pulse and purge durations for TiF4 subcycle are 0.1 s and 15 s, respectively. Lithium tert-butoxide was heated to 160–170 °C, and TiF4 was kept at 120–130 °C. LiF thin films can be
obtained at deposition temperatures ranging from 200 to 300 °C. ALF₃ ALD deposition was performed following literature reported recipes. The ALF₃ deposition consists of alternating pulse and purge of AlCl₃ (>99%, Sigma-Aldrich) and TiF₄ as precursors. Typical pulse and purge durations for AlCl₃ subcycle are 0.1 s and 15 s, respectively. Typical pulse and purge durations for TiF₄ subcycle are 0.1 s and 15 s, respectively. Both AlCl₃ and TiF₄ precursors were kept at 120–130 °C. ALF₃ thin film was deposited at a deposition temperature of 250 °C. LiAlF₄ ALD deposition was performed by alternating LiF and AlF₃ subcycles with a 1:1 ratio. LiAlF₄ thin film was obtained at 250 °C. High-purity argon gas was used as the carrier gas and purging gas for all the ALD processes mentioned above.

**Materials Characterizations.** SEM images were captured in a FEI XL30 Sirion SEM. XPS was performed on PHI 5000 VersaProbe, using an Al Kα (λ = 0.83 nm, hν = 1486.7 eV) X-ray source operated at 2 kV and 20 mA. A Woollam M2000 spectroscopic ellipsometer was used for measuring and fitting optical properties of ALD thin films on silicon substrates with native oxides.

**Electrochemical Measurements.** Electrochemical impedance spectroscopic (EIS) measurements were conducted using a Biologic VSP potentiostat over the frequency range from 0.1 Hz to 1 MHz in a spectroscopic (EIS) measurements were conducted using a Biologic silicon substrates with native oxides.

Battery cycling data were collected using a LAND 8-channel battery tester. LiPF₆ in 1:1 EC and DEC (BASF) was added as the electrolyte. Synthesis and Characterization of Li-β-Mn₂O₃ Cathode Materials by ALD Coating to Improve High Voltage Cycling Performance of Li-Ion Batteries. **J. Electrochem. Soc.** 2010, 157, A75–A81.

The authors declare no competing financial interest.

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