Conformal Surface Coatings to Enable High Volume Expansion Li-Ion Anode Materials

Leah A. Riley, Andrew S. Cavanagh, Steven M. George, Yoon Seok Jung, Yanfa Yan, Se-Hee Lee, and Anne C. Dillon

An alumina surface coating is demonstrated to improve electrochemical performance of MoO₃ nanoparticles as high capacity/high-volume expansion anodes for Li-ion batteries. Thin, conformal surface coatings were grown using atomic layer deposition (ALD) that relies on self-limiting surface reactions. ALD coatings were tested on both individual nanoparticles and prefabricated electrodes containing conductive additive and binder. The coated and non-coated materials were characterized using transmission electron microscopy, energy-dispersive X-ray spectroscopy, electrochemical impedance spectroscopy, and galvanostatic charge/discharge cycling. Importantly, increased stability and capacity retention was only observed when the fully fabricated electrode was coated. The alumina layer both improves the adhesion of the entire electrode, during volume expansion/contraction and protects the nanoparticle surfaces. Coating the entire electrode also allows for an important carbothermal reduction process that occurs during electrode pre-heat treatment. ALD is thus demonstrated as a novel and necessary method that may be employed to coat the tortuous network of a battery electrode.

1. Introduction

For several decades, lithium-ion battery technologies have evolved with significant advancements in both stability and efficiency achieved. However, the commercial graphitic anodes for lithium-ion batteries are limited to a specific capacity of ~350 mAh g⁻¹. Furthermore, graphitic anodes, which typically operate at a potential of ~0.1 V vs Li/Li⁺, also do not meet the suggested HEV battery operating potential of ~0.5 V vs Li/Li⁺ that will mitigate Li-plating and eliminate safety concerns.[1] Thus, current technology is not suitable for high-performance applications including hybrid electric vehicles and plug-in hybrid electric vehicles (HEVs and PHEVs) that require higher energy and power densities as well as longer lifetimes. Hence, modern battery research is committed to develop a high-capacity alternative to graphite. Recently silicon and metal oxides have been significantly studied as they offer the potential of highly increased capacity. In contrast to the well-studied lithium intercalation mechanism of graphite, lithiation of crystalline silicon leads to the formation of a metastable amorphous alloy, sustaining up to 4.4 Li⁺ per Si.[2] Transition metal oxides undergo a conversion reaction at lower voltages, yielding pure metal and Li₂O as shown in Equation (1).[3]

\[
\text{MO}_x + 2x\text{Li}^+ + 2xe^- \rightarrow x\text{Li}_2\text{O} + M
\]  

(1)

However, for materials, such as silicon and transition metal oxides, which can accommodate more than 4Li⁺/formula unit, extreme volume changes (> 100%) occur resulting in fracturing and loss of electrical conductivity and mechanical integrity with a subsequent rapid fade in capacity.

In order to mitigate capacity degradation, researchers have employed various nanostructures that may better accommodate volume strain. Many methods employ alternative binder-free and 3-D cell constructions, such as thin film,[4–6] nanowires,[7–9] and embedded composites and membranes.[10, 11] Although higher reversible capacities using alternative cell architectures have been achieved, most of these formats are not yet plausible for large scale, commercial, roll-to-roll processing.

High-volume expansion materials have also been demonstrated using conventional (more commercially applicable) slurries of active material, conductive additive, and binder spread onto a current collector. For example, Lui et al. used hydrothermally synthesized α-Fe₂O₃ nanorods in a conventional slurry to dramatically increase capacity, from 112 to 763 mAh g⁻¹ after 30 cycles, compared to that of commercially available material.[12] In addition, Beattie et al. maintained close to silicon’s theoretical capacity (4200 mAh g⁻¹) for 20 cycles.
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using commercial nanopowder in a conventional format. However, in each example, enhanced performance could only be obtained by adding large quantities of conductive additive and binder to maintain electrical conductivity, and cutting down the active material to ≤ 40 wt.% to allow for volume expansion. Li et al. demonstrated that binder choice and electrode pre-heat treatment could stabilize µ-sized particles of α-Fe2O3 with an active material loading of 80% but required cycling at a lower rate of C/5 (five hours each for charge and discharge).[13]

In order to accommodate for the high volume expansion of silicon, Kang et al. coated Si particles with Co–Co3O4 by sol-gel.[14] The coating improved the 12th cycle efficiency from 55% to 88% for micron-sized particles. While appropriate for larger particles, the coating was comprised of particulates ranging from 0.1 to 1 micron in diameter. Thus the coating itself is larger than most nanomaterials. For thin conformal coatings (Å-level control) Jung et al. demonstrated atomic layer deposition (ALD) as a promising alternative for surface passivation that maximizes active material loading.[15] ALD grown coatings have also been shown to grow deep within porous structures of prefabricated electrodes.[16]

The layered structure of α-MoO3 was first proposed as a material of interest for Li-ion batteries as a cathode in the 1970s,[17] but was not demonstrated as an anode material due to the volume expansion occurring for high Li-loading at lower potential. Using nanoparticle α-MoO3 for an anode, we previously demonstrated an anomalous reversible capacity as a thin film electrode and then achieved improved reversible capacity (~1000 mAhg⁻¹) in a traditional electrode architecture.[18,19] Our electrode composition contained only 10 wt.% conductive additive, 20 wt.% binder and 70 wt.% active material. We also established a necessary electrode heat treatment at 250°C, unique to MoO3, that enabled both carbothermal reduction, and electrode adhesion via binder melting without early onset of binder breakdown. Both the cycle life and capacity were then improved despite the volume change, with minimal additives. However, stable cycling was only observed at a lower rate of C/10 (10 h each for charge and discharge).

Our current work focuses on improving the durable high-rate capability of high volume expansion nanoparticle MoO3 conventional anodes by applying a thin coating of alumina on the electrode surface using atomic layer deposition (ALD). Unlike the sol-gel methods that have been previously employed, ALD is a “dry” process that can be easily applied to full electrodes and allows for very thin conformal films to be deposited. By coating the full electrode the ALD coating appears to “knit” the active material to the conductive additive thereby preserving mechanical integrity during volume expansion/contraction. The ALD coating also protects the high surface area of the nanoparticles from decomposition and reaction with the liquid electrolyte. Finally, full electrode coating allows for pre-heat treatments that enable important interactions between the active material and additives to be achieved. Ultimately improved durability at high rates is demonstrated. When ALD is performed directly on the particles rather than on the composite electrodes, superior performance is not achieved. Importantly, we note that it is not possible to employ sol gel techniques on composite electrodes.

2. Results and Discussion

As discussed previously in detail,[18–20] the crystalline MoO3 is grown using a unique hot-wire chemical vapor deposition (HWCVD) technique. In this study, self-limiting ALD is performed using trimethylaluminum (TMA) and H2O precursors. Unlike wet-chemical techniques, ALD precursors can easily traverse tortuous paths within porous structures, providing a uniform coating on all exposed surfaces. Likewise, by using a rotary reactor, uniform growth can also be achieved on individual particles. One ALD cycle consists of TMA exposure, a purge, and H2O exposure. Each complete deposition cycle of ALD grows ~1–2 Å of Al2O3 on porous surfaces and powders. Additional layers are grown by repeating the ALD cycle. Alumina grown by ALD has been shown to have 75% the density of bulk amorphous alumina.[20] A transmission electron microscope (TEM) image of a bare MoO3 nanoparticle (prior to the application of an ALD coating) is shown in Figure 1 a. The elemental composition of the circular area labeled P1 was examined using energy dispersive X-ray spectroscopy (EDS) to verify that no aluminum was present before ALD (Figure 1b). Figure 1 c is a TEM image of a MoO3 nanoparticle coated with 4-cycles of TMA/H2O, resulting in a thin coating of alumina. The crystalline structure for the MoO3 nanoparticles is apparent in both Figures 1 a and c. However for the coated particle (Figure 1c), a thin, bright white surface film, less than 1 nm in thickness, is visible that is absent from the bare powder. EDS of the ALD surface region in the identical location as on the

![Figure 1](image-url)
bare sample confirms that the bright film is a very thin layer of Al₂O₃ upon the surface of the nanoparticle (Figure 1 d). Note that the ALD coating also appears to improve the surface roughness of the particles.

Electrochemical capacity and stability comparisons for bare MoO₃ electrodes, ALD coated MoO₃ nanoparticles (CP) electrodes, and ALD coated nano-MoO₃ electrodes (CE) are depicted in Figure 2 a. All electrodes were of a 70:10:20 composition active material (AM): acetylene black (AB): binder (PVDF) and subjected to 250 °C heat treatment. For electrodes comprised of CP, an alumina surface layer was grown on MoO₃ particles prior to coin cell fabrication, leaving the carbon additive and binder uncoated. Conversely, ALD was also applied after electrode fabrication, coating all exposed electrode surfaces and pores, to make the CE. The dotted horizontal line at C/2 (following two cycles at C/10), b) Coulombic efficiency, c) rate capability and d) voltage profile for ALD coated electrode of nMoO₃.

Electrode coating provides beneficial protection against capacity degradation while the individual particle coating appears detrimental to overall performance. The voltage profiles depicted in Figure 2 d compare the 1st cycle (C/10) to the 40th cycle (C/2) for the very stable ALD coated electrode sample. Despite the increase in current density, the extraction profiles are nearly identical after 40 cycles (although an irreversible capacity loss is observed in the first insertion cycle). The 4th cycle is also shown to demonstrate consistency in the voltage profiles when cycling at the same rate.

In a recent study, Miller et al. found that a 5 nm ALD alumina surface coating deforms elastically up to −2% strain and that the critical strain for steady state crack propagation occurs at −5.1%.[22]

Using these findings as a guide, the theoretical strain of alumina surface coatings when applied to various active materials is calculated in Table 1. Alumina coatings on materials which experience small changes in volume, such as LiCoO₂, remain in the elastic region of deformation and are obviously relevant to the work of Jung et al.[18] In this report the LiCoO₂ was cycled up to 4.5 V vs Li/Li⁺ where cobalt dissolution and oxidative decomposition of the electrolyte are known to occur. Thus the Al₂O₃ definitely served as a protective coating.[16] However, for high volume expansion materials, such as MoO₃, at least a 100% volume change during lithiation occurs corresponding to a strain of 26%, that must induce cracking and fracturing along the protective surface layer. It is thus somewhat surprising that the ALD coatings improve the cycling performance of the high volume expansion materials, when mechanical integrity is usually lost upon cycling. A schematic of the expansion effects for bare, CP, and CE is depicted in Figures 3 a–c. The white circles represent MoO₃ nanoparticles, the black smaller circles indicate the AB conductive additive, and the gray surfaces signify ALD coatings. For simplicity, the schematic follows the evolution of a

Figure 2. Comparison between bare, 4-cycle ALD coated MoO₃ nanoparticles and 4-cycle ALD coated electrodes in a composition of 70:10:20 (MoO₃: AB: PVDF) for a) cycling stability at C/2 (following two cycles at C/10), b) Coulombic efficiency, c) rate capability and d) voltage profile for ALD coated electrode of nMoO₃.
A single nanoparticle, partially surrounded by conductive additive. Although cracking must occur, the alumina is still able to “knit” the electrode together and retain electric conductivity/mechanical integrity that is otherwise lost upon the extreme volume expansion/contraction. Unlike the active material, the conductive additive undergoes no change in volume during cycling. Since MoO$_3$ is an electrical insulator ($\sim 10^{-11}$–$10^{-8}$ S cm$^{-1}$), the AB:MoO$_3$ interface is extremely important to the overall conductivity and electrical resistance of the electrode facilitating electron transport along the active material surfaces.$^{[23]}$ By growing an ALD surface coating on the pre-fabricated electrodes, the carbon additive may be effectively attached to the active material in spite of ALD cracking as depicted in Figure 3c. This maintains electrical contact with the MoO$_3$ surface and also delays mechanical degradation. Using similar logic, failure of pristine and CP cells can be attributed to the disintegration of electron and ion transport pathways due to volume expansion.$^{[24]}$ The enhanced CE stability may also be partially attributed to the physical insulation of the MoO$_3$ from direct contact with the liquid electrolyte due to the partial surface coating even after cracking.

The electronic conductivity of each electrode was studied with electrochemical impedance spectroscopy (EIS). Figures 4a–c depict Bode plots for bare, CE, and CP at different voltages during the first complete discharge/charge cycle. The voltage of each electrode was held constant for one hour prior to EIS tests in order to allow for complete lithium diffusion and volume change. Both the bare and CE displayed similar resistances during initial lithiation to 1.5 V and 0.001 V (volume expansion). However, after subsequent lithium removal to 1.5 V (volume contraction), the bare electrode resistance measured twice that of the ALD coated electrode. This further confirms that the ALD coating helps to maintain an electrical path and good physical contact between the AB and the MoO$_3$ surface after volume expansion and contraction. Bode plots of the CP show similar resistances in the mid-frequency region at 1.5 V during lithiation, though also includes an additional low-frequency resistive interface. The low-frequency feature, unique

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Table 1. Strain on the ALD alumina surface coating and corresponding deformation for different active materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume expansion</th>
<th>Experimental capacity (mAh g$^{-1}$)</th>
<th>Calculated strain</th>
<th>Deformation region</th>
</tr>
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<tr>
<td>Graphite flakes</td>
<td>10%$^{[22]}$</td>
<td>372</td>
<td>3.19%</td>
<td>Elastic/Plastic</td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>1.5%$^{[33]}$</td>
<td>170</td>
<td>0.45%</td>
<td>Elastic</td>
</tr>
<tr>
<td>Silicon</td>
<td>400%$^{[27]}$</td>
<td>3200</td>
<td>70.9%</td>
<td>Fracture</td>
</tr>
<tr>
<td>Metal oxides</td>
<td>100–250%</td>
<td>800–1300</td>
<td>26–52%</td>
<td>Fracture</td>
</tr>
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Figure 3. Schematic representation of the effects of volume expansion upon a) bare particles, b) an ALD coated nano-MoO$_3$ particle and c) a particle from an ALD coated porous electrode.

Figure 4. First cycle discharge/charge Bode plots for a) bare b) ALD coated electrode, and c) ALD coated particles.
to the CP, is indicative of the physical interface caused by the Al2O3 insulation of the individually coated nanoparticles. The extra resistive layer indicated in Figure 4b decreases ion mobility and limits conductive electron pathways.

Physical contact between MoO3 nanoparticles and the conductive additive/binder ensures proper electron conduction and is necessary to achieve good cycling stability. If carbothermal reduction to MoO3y during the electrode pre-heat treatment is observed, it suggests that good conductivity is maintained. This is consistent with previous studies indicating that slightly reduced MoO3y that occurs upon ball milling, exhibits enhanced cycling stability.[25] Here the carbothermal reduction occurs upon heat treatment at 250 °C in Ar prior to coin cell assembly.[18] When heated, the surface oxygen of MoO3 reacts with both the melted polymer binder chains (T_melt ~ 170 °C), as well as the carbon additive to form CO and CO2, transforming the active material to a partially oxygen deficient state. The desorbing species that indicate this reaction were previously observed using temperature programmed desorption (TPD).[18]

Differential capacity plots may be employed to determine lithium insertion potentials, and in general, negative peak shifts can be attributed to two factors: kinetics or change in oxidation state. Figure 5 compares the differential capacity plots of heat-treated and non-heat treated electrodes. (For this comparison, identical particle sizes and testing conditions were used in order to eliminate kinetics as a possible cause for the voltage shifts.) The initial insertion of lithium into pure MoO3, represented by the non-heat treated electrode, exists in two distinct phases. The first phase is the intercalation of lithium into Mo–O interplanar octahedral sites that can accommodate approximately 1.5 Li+. [26–28] The second phase, common to transition metal oxides, is the conversion stage described in Equation (1), where MoO3 undergoes a displacement reaction to form Mo metal and Li2O creating a highly disordered and amorphous structure at low voltages (<1.0 V). [26–28] Peaks at potentials greater than 2.0 V are associated with the first phase, lithium intercalation, while the large features below 0.5 V represent the second phase, the conversion reaction. The dashed line in Figure 5, observed for the non-heat treated electrode, is typical of pure MoO3. The peak attributed to the conversion reaction is found at 0.4 V. For the heat-treated electrode, the low voltage peak is significantly shifted towards a negative potential indicating MoO3 reduction. This heat treatment that, enables effective interactions with the conductive additive, was previously shown necessary to achieve stable cycling.[18]

Similar analysis was used to examine the CE and CP. The first cycle differential discharge capacity plots are shown in Figure 6. Again both the CE and CP were subjected to heat treatment at 250 °C prior to coin cell assembly. The CE lithium uptake looks similar to that of the bare sample. Importantly, by coating over the surface of the electrode, the MoO3 remains capable of undergoing reduction due to the direct contact with AB or binder. The comparable peak positions and heights between bare and CE signify that the active material undergoes no significant chemical change after the coating is applied. The very small difference in peak position of −0.08 V seen between the pristine and CE is most likely due to slightly slower kinetics through the alumina.[30] Alternately, the CP lithiation potentials show similar characteristics to that of non-reduced, non-heat treated MoO3 in Figure 5. Unlike the bare heat-treated MoO3 and CE, the multi-pronged, peak remains close to 0.5 V. This suggests that the ALD coating inhibits the carbothermal reduction by preventing physical contact between the MoO3 and AB/binder. Thus ALD coatings to the entire electrode are necessary to enable favorable reactions that occur during electrode pre-heat treatment.

ALD coatings were also applied on commercial MoO3 electrodes. Figure 7 displays results from coating the electrodes of commercially available micron sized MoO3 with 4 cycles of Al2O3 using ALD. Despite the tremendous improvements reported above for coating high surface area nanoparticle electrodes, a similar benefit is not observed for micron-sized parti-
C/2 is observed and changed after an overnight 250°C heat treatment of the micron-sized MoO₃ electrodes. This suggests that high surface areas and extensive contact with the conductive additive are required to most importantly maintain electrical conductivity and achieve reduction to an MoO₃₋ₓ state.

Finally, it is important to note that all specific capacities are calculated using both the weight of the active material and the weight of the alumina coatings. The viability of passive surface coatings in commercial applications greatly depends upon the total volumetric and gravimetric capacities of the system (active material, conductive additive, binder, coating, etc.). The surface coating mass was included in the calculations in order to present an accurate change in total gravimetric capacities. From Figure 2a, 4-layers of alumina on electrodes show that the stable capacity is reduced by ~10% compared to the bare. This is consistent with the fact that the calculated weight of an Al₂O₃ coating that is 4–8 Å thick on an MoO₃ nanoparticle with a diameter of ~40 nm is 7~14 wt %.

Thus, at the nanoscale a thin coating is necessary both to achieve high gravimetric capacities and fast ionic conduction.

3. Conclusions

Molybdenum trioxide nanoparticles and electrodes have been coated with Al₂O₃ by ALD and electrochemically tested versus lithium metal from 0.001–3 V. Unlike sol-gel, ALD allows for a uniform coating on both particles and electrodes as well as tailored uniformity for monolayer deposition. Electrodes coated with only 4-monolayers of Al₂O₃ outperform electrodes fabricated from bare nanoparticles as well as particles coated with ALD prior to electrode fabrication. For the coated electrodes a stable capacity of 900 mAh g⁻¹ for 50 cycles at a rate of C/2 is observed and ~600 mAh g⁻¹ is observed at a rate of 5C. The bare sample showed early cycling degradation beginning after only 20 cycles and the particles coated with ALD prior to electrode fabrication deteriorated even more rapidly. When the ALD coating is applied to the entire electrode it creates some adhesion to the conductive additive allowing for less mechanical degradation from the extreme volume expansion/contraction that occurs upon cycling. Some surface protection against electrolyte reaction may also be achieved even though cracking in the ALD layer must occur. Importantly the ALD coating on the entire electrode allows for carbothermal reduction of the MoO₃ to occur indicating intimate contact between the active material and conductive additive. In addition, the thin ALD coatings do not represent a significant volume or weight fraction of the nanoscale materials. Thus even a brittle Al₂O₃ coating directly on the surface of MoO₃ has been demonstrated to stabilize high volume expansion nanoparticles. Future investigations will be on ALD coatings of more elastic materials.

Experimental Section

Electrode Fabrication: Active material, nano-MoO₃, was obtained using a hot-wire chemical vapor deposition method as described by Riley et al. The deposition chamber was held at 300°C in a 75 Torr argon atmosphere with a partial pressure of ~7% oxygen. The collected powder was then annealed in air at 300°C for 2.5 h to obtain a fully oxidized α-MoO₃ sample. Electrodes were made using a 70:10:20 composition of AM:AB:PVDVF dissolved in N-methyl-2-pyrrolidone. Upon spreading on 20 nm thick Cu foil, the NMP was evaporated at 120°C for 1 h in air and then again for 8 h under vacuum. All electrodes were then heat treated at 250°C on a hot plate in an Ar glove box overnight.

ALD Growth: Al₂O₃ ALD was grown on MoO₃ nanoparticles and on composite electrodes containing MoO₃ nanoparticles, AB and PVDVF. ALD on MoO₃ nanoparticles prior to electrode fabrication was performed using a rotary ALD reactor. To perform ALD on powders, the powders were placed in a porous stainless steel cylinder in the reaction chamber. The cylinder was positioned on a magnetically coupled shaft via a load lock door. A rotor turns the cylinder to agitate the powder. A capacitance manometer was used to measure the pressure in the reaction chamber. The introduction of precursor and purge gases was controlled via a series of pneumatic and needle valves. To evacuate the chamber, a gate valve was opened to connect the chamber to a vacuum pump. Once coated, electrodes were constructed using the method described above with the ALD-nano-MoO₃ particles. For electrode coatings, first the electrode was made as described above and subsequently ALD films were deposited. Although the composite electrodes are porous, the internal surfaces are accessible to the ALD precursors.

The Al₂O₃ ALD reaction sequence was: 1) Trimethylaluminum dose to 1.0 Torr; 2) TMA reaction time; 3) evacuation of reaction products and excess TMA; 4) N₂ dose to 20.0 Torr; 5) N₂ static time; 6) evacuation of N₂ and any entrained gases; 7) H₂O dose to 1.0 Torr; 8) H₂O reaction time; 9) evacuation of reaction products and excess H₂O; 10) dose N₂; 11) N₂ static time; and 12) evacuation of N₂ and any entrained gases. This sequence constitutes one cycle of Al₂O₃ ALD. The reactor temperature was 180°C.

Material Characterization: The Al₂O₃ ALD coated and bare MoO₃ nanoparticles were examined by transmission electron microscopy using a FEI Tecnai F20 UT microscope operated at 200 kV. The presence of Al₂O₃ layer on the surface of MoO₃ nanoparticles was confirmed by nano-probe energy dispersive X-ray spectroscopy.
Electrochemical Testing: All electrodes were electrochemically tested in coin cells (CR2023) using LiPF₆ in 1:1 ethylene carbonate: dimethyl carbonate liquid electrolyte and lithium foil as a counter electrode. Coin cells were symmetrically charged and discharged from 0.001 V to 3.0 V with constant current first at a charge/discharge rate of C/10 for 2 cycles, followed by a rate of C/2. For rate study tests, the current was increased after 3 cycles at each pre-designed C-rate. AC impedance was taken for the first cycle when the current, during a voltage hold, dropped below 15 μA, indicating near-charge equilibrium and limited lithium movement across electrodes.

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