

Amorphous Metal Fluoride Passivation Coatings Prepared by Atomic Layer Deposition on LiCoO₂ for Li-Ion Batteries

Joong Sun Park,[†] Anil U. Mane,[‡] Jeffrey W. Elam,[‡] and Jason R. Croy^{*,†}

[†]Chemical Sciences and Engineering Division and [‡]Energy Systems Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

S Supporting Information

The fabrication of robust interfaces between electrodes and electrolytes that satisfy the application-dependent, electrochemical demands of various systems is one of the great challenges of interfacial science.^{1–3} In particular, irreversible reactions between nonaqueous electrolytes and metal oxides are often considered to be a rate-limiting step adversely affecting the overall performance of lithium-ion (Li-ion) batteries.^{4–6} Li-ion batteries, in general, suffer irreversible capacity losses during high voltage operation due, in part, to corrosion of active materials in the acidic electrolyte as well as electrolyte decomposition. Small levels of moisture (~20–100 ppm) present in battery-grade electrolytes can react with lithium salts (e.g., LiPF₆) to generate hydrofluoric acid (HF). HF subsequently attacks the surfaces of electrode materials causing transition metal dissolution and migration to the negative electrode.^{5,7} Furthermore, surface layers can form as a result of electrolyte oxidation at high voltages which impede Li-ion diffusion.

Coating electrode surfaces with metal oxides such as Al₂O₃, MgO, ZnO, and TiO₂ has proven to be effective in mitigating irreversible side reactions.^{8–11} These metal oxide coatings, however, are also susceptible to HF attack and may not be stable over long-term cycling, converting partially to metal fluorides when scavenging HF as reported earlier.^{12,13} Furthermore, byproducts of these reactions generate additional water in the electrolyte, again making electrode/electrolyte interfaces unstable. With this limitation in mind, it stands to reason that metal fluoride coatings might provide better stability against the corrosive effects of HF. In addition, the high electronegativity of fluorine results in strongly bonded cations relative to oxygen and should be beneficial in limiting unwanted surface reactions. In particular, AlF₃-coated positive electrodes (LiCoO₂, LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, Li[Li_{0.19}Mn_{0.57}Ni_{0.16}Co_{0.08}]O₂, etc.) have demonstrated significant improvements in cycling stability and safety when AlF₃ is applied via solution-based routes.^{14–16} However, wet-chemical processes, as well as standard physical vapor deposition (PVD), have limitations. Nonuniform thicknesses and/or compositional variation of coating layers can arise from the directional nature of deposition (PVD) or by the secondary heating steps required for solution-based routes. Atomic layer deposition (ALD) is a modified form of chemical vapor deposition (CVD) that uses the self-limiting nature of specific precursors to deposit films in a layer-by-layer fashion. ALD is particularly well-suited for coating electrode surfaces in that a conformal coating can be applied with precise control of thickness and composition.¹⁷ Previous studies on ALD-coated electrodes have

primarily focused on metal oxides such as Al₂O₃, TiO₂, LiAlO₂, and LiTaO₃ because the ALD chemistry of these oxides is well-known.^{10,11,18–21} Metal fluoride growth by ALD is complex and challenging, mainly due to the lack of suitable fluorine precursors. For example, HF, a highly aggressive chemical etching agent, has been used to deposit CaF₂, ZnF₂, and SrF₂.²² More recently, alternative ALD chemistries have been developed such as MgF₂ and LiF ALD using either TaF₅ or TiF₄ as the fluorine precursor for optical applications.^{23–25} However, the substrate temperatures in these cases were 300–400 °C, high enough to degrade battery electrode laminates containing polymeric binders. Another potential limitation of AlF₃ for Li-ion batteries is that it is a wide-bandgap dielectric and hence electrically insulating. Although still promising as a coating, methods to enhance the material's conductivity while maintaining its superb resistance to chemical attack could be advantageous.

Herein we report the deposition of ultrathin, amorphous, composite aluminum–tungsten–fluoride (AlW_xF_y) films on LiCoO₂ electrodes via ALD using trimethylaluminum (TMA) and tungsten hexafluoride (WF₆) at 200 °C. These films are highly conducting but incorporate AlF₃ in the composite. Although LiCoO₂ is the most commercially successful cathode material for Li-ion batteries, the practical use of LiCoO₂ is limited, in part, to surface reactions involving cobalt dissolution and electrolyte oxidation, as well as structural transformations occurring at potentials higher than ~4.3 V (vs Li/Li⁺).^{26,27} As such, LiCoO₂ might be considered as a model system for surface studies on Li-ion cathodes. Ultrathin AlW_xF_y coatings (~1 nm) on LiCoO₂ are shown to significantly increase stability relative to bare LiCoO₂ when cycled up to 4.4 V. These results reveal new possibilities for designing ultrathin and electrochemically robust coatings of metal fluorides via ALD, and potentially other techniques, to enhance the stability of Li-ion electrodes.

ALD of AlW_xF_y was accomplished using alternating exposures of WF₆ and TMA. Although a detailed manuscript describing this process is in preparation, a brief summary of the AlW_xF_y chemistry and properties will be provided herein. In situ quartz crystal microbalance (QCM) measurements recorded during alternating, 1 s WF₆ and TMA exposures at 200 °C showed a staircase pattern comprised of 160 ng/cm² steps consistent with layer-by-layer growth (Figure 1a).

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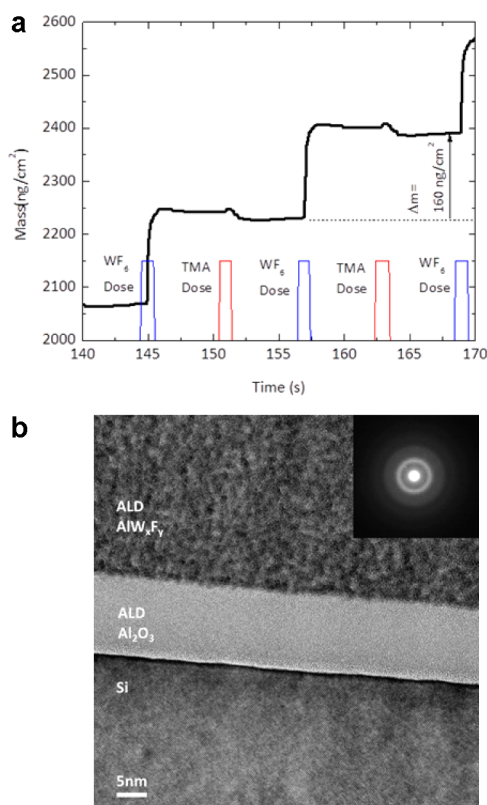


Figure 1. (a) In situ QCM mass uptake during two alternating cycles of WF_6 and TMA. (b) HRTEM image of the films deposited using alternating exposures to TMA- WF_6 on an ALD Al_2O_3 -coated Si wafer (inset: NBD of the AlW_xF_y film with beam size of ~ 50 nm).

Additional QCM measurements (not shown) verified that each of the precursor exposures was self-limiting under these conditions. Ellipsometric measurements indicated a growth rate of $2.56 \text{ \AA/cycle}$ and combined with the QCM data yield a film density of 6.5 g/cm^3 . The resulting films that appear amorphous by X-ray diffraction are highly conducting; four-point probe measurements give a resistivity of $3.5 \times 10^{-2} \Omega\cdot\text{cm}$. The growth rate of the film, deposited by alternating cycles of TMA- WF_6 , is relatively high compared to that of typical oxides ($\sim 1\text{--}1.5 \text{ \AA/cycle}$) and is due in part to tungsten and/or tungsten carbide byproducts that have growth rates of $2.5 \text{ \AA/cycle}$.²⁸

X-ray photoelectron spectroscopy (XPS) survey scans, performed during depth-profiling of these films deposited on silicon, revealed that they are comprised of W, C, Al, and F. Higher resolution XPS analysis demonstrated that the Al and F are bound as AlF_3 and that the W may be present as both metallic W and tungsten carbide (WC_x) (see Figure S1 in Supporting Information). For brevity, we refer to these films as AlW_xF_y . High resolution transmission electron microscopy (HRTEM) and nanobeam diffraction (NBD) measurements, taken from cross sections of an AlW_xF_y film deposited on Al_2O_3 -coated silicon (Figure 1b), confirmed the amorphous nature of the films. These measurements also revealed that the AlW_xF_y exists as a nanocomposite of ~ 1 nm particles in a matrix of lower density. In analogy with our previous studies, we hypothesize that the darker particles in Figure 1b are W and WC_x , while the surrounding matrix of lower density material is AlF_3 .^{29,30} It is interesting to note that these findings are similar

to our previous study of ALD films prepared using niobium pentafluoride and TMA.³¹

To evaluate the electrochemical properties of the AlW_xF_y coating, 5 ALD cycles of TMA- N_2 - WF_6 - N_2 (~ 1 nm) were applied on laminates of LiCoO_2 . An XPS survey scan of the coated LiCoO_2 confirmed that the AlW_xF_y films are deposited on the laminates (Supporting Information Figure S2). Figure 2a

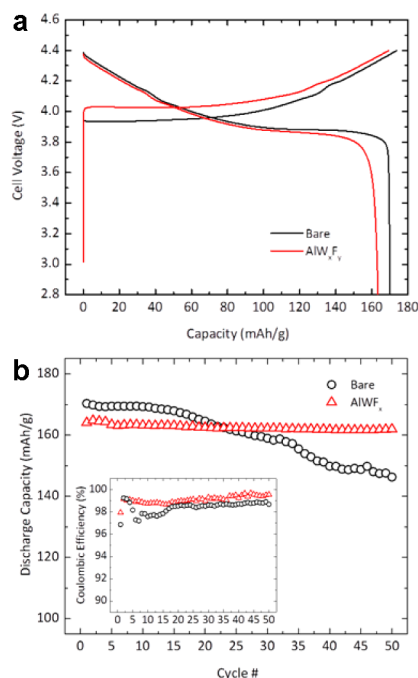


Figure 2. (a) First-cycle voltage profiles of bare (black) and AlW_xF_y -coated (red) LiCoO_2 between 4.4 and 2.5 V at 20 mA/g; the inset shows first- and second-charge voltage profiles of the coated LiCoO_2 . (b) Discharge capacities of bare (black) and coated (red) $\text{Li}^+/\text{LiCoO}_2$ cells at a current rate of 20 mA/g between 4.4 and 2.5 V; the inset shows Coulombic efficiencies of the samples.

shows first-cycle voltage profiles of two $\text{Li}^+/\text{LiCoO}_2$ cells, with and without AlW_xF_y coatings, between 4.4 and 2.5 V at 20 mA/g. Uncoated LiCoO_2 exhibited first-cycle capacities of ~ 170 mAh/g compared to ~ 165 mAh/g of the coated sample. This difference, though fairly negligible, might be attributed to the inactive nature of the coating layer resulting in slightly higher first-cycle impedance. The polarization on charging, however, disappeared after the first cycle, indicating possible changes, such as a lithiated phase in the film, allowing diffusion of lithium ions and similar lithium extraction/insertion voltages as the uncoated electrode (inset Figure 2a). Recent molecular dynamics (MD) calculations on Al_2O_3 coating suggests that the Al_2O_3 coating layer absorbs lithium until it reaches the thermodynamically stable composition during the lithiation process.³² The characteristic hexagonal to monoclinic transformation of LiCoO_2 occurring at ~ 4.1 V is observed for both cells, though slightly less pronounced for the coated electrode. This is an indication that the ALD coating process did not drastically alter the bulk characteristics of the material, similar to previous coating studies on LiCoO_2 .^{10,11,14–16} The discharge capacity of the uncoated LiCoO_2 continuously decreased while the coated electrode showed excellent capacity retention over the course of cycling between 4.4 and 2.5 V. The bare LiCoO_2 retained only 85% of its initial capacity, while the 1 nm AlW_xF_y coating enabled a 99% capacity retention after 50 charge–

discharge cycles as shown Figure 2b. The capacity loss of the bare material is attributed to parasitic, interfacial reactions as previously reported.^{14,33,34} It should be noted that thicker (~ 10 nm) AlW_xF_y coatings on LiCoO_2 showed discharge capacities of just ~ 10 mAh/g, revealing a limitation in practical thicknesses.

Figure 3a,b shows voltage profiles and corresponding differential capacity (dQ/dV) plots of bare and coated samples

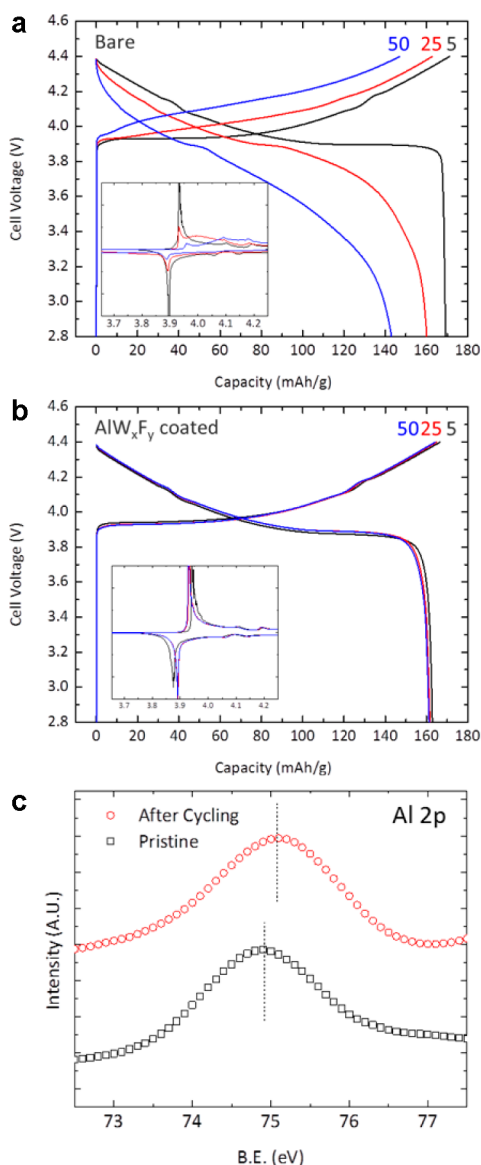


Figure 3. Voltage profiles of (a) bare and (b) AlW_xF_y coated LiCoO_2 on cycles 5, 25, and 50 and corresponding dQ/dV plots of bare and coated LiCoO_2 (inset). (c) Al 2p XPS spectra of AlW_xF_y -coated LiCoO_2 before and after the 50th cycle.

on cycles 5, 25, and 50. Voltage profiles of the uncoated LiCoO_2 clearly showed increased polarization on charge and discharge with continued cycling accompanied by a broadening and shifting of the dQ/dV peaks, typical of increasing impedance and structural degradation. On the other hand, voltage profiles and dQ/dV plots of the AlW_xF_y -coated material showed little change upon cycling. This data reveals that the phase transition associated with lithium ordering at ~ 4.1 V is a relatively “soft” transition, and a significant fraction of the

lithium can be repeatedly, and reversibly, extracted without significant damage to the bulk of the structure. Furthermore, it is clear that surface damage, mitigated here by the AlW_xF_y film, is a much greater factor in the degradation of LiCoO_2 under these cycling conditions. XPS studies were employed on AlW_xF_y -coated materials to probe the chemical composition of the surface before/after the electrochemical cycling. Figure 3c shows Al 2p_{3/2} spectra of pristine, coated LiCoO_2 and after 50 cycles. The binding energy of the pristine and cycled samples was fitted to 74.9 and 75.0 eV, respectively, indicating only marginal change in the binding energy after electrochemical cycling and a stable AlW_xF_y coating under insertion/extraction of lithium. The fitted value is higher than those of Al_2O_3 (74.2 eV)³⁵ and LiAlO_2 (73.4 eV)³⁶ and is closer to O–Al–F (75.3 eV) bonding as reported earlier.³⁷

Figure 4 compares the rate capability up to 400 mA/g for the coated and uncoated LiCoO_2 . AlW_xF_y -coated LiCoO_2 exhibited

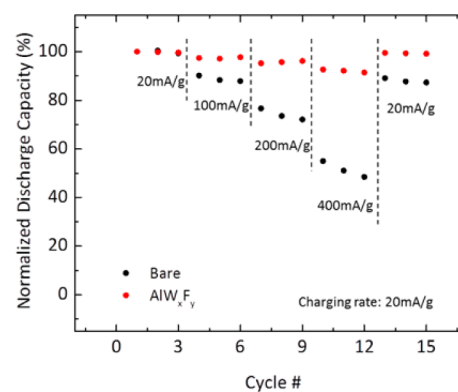


Figure 4. Rate capabilities of bare (black) and AlW_xF_y -coated (red) LiCoO_2 electrodes.

superior rate capability at all current rates compared to the uncoated material, but the most dramatic improvements occurred at the highest rates (200–400 mA/g). Discharge capacities at a current of 400 mA/g were 51% and 92% of the first-cycle capacities for bare and AlW_xF_y materials, respectively. It is well-known that reactions at electrode/electrolyte interfaces result in surface films that greatly increase cathode electrode impedances, thereby causing capacity fade and poor power performance.³⁸ Furthermore, it has been shown, in agreement with our results in Figure 3b, that mitigating reactions at the surface of LiCoO_2 results in more stable bulk processes.³⁹ As such, the data herein clearly demonstrate the improved surface stability of AlW_xF_y -coated LiCoO_2 , resulting in excellent electrochemical performance.

In summary, a novel ALD process allowing the deposition of metal fluoride materials has been developed for surface protection of Li-ion battery electrodes. An ~ 1 nm AlW_xF_y film deposited on LiCoO_2 electrodes has been shown to dramatically enhance cycle life and rate capability of $\text{Li}^+/\text{LiCoO}_2$ cells. These AlW_xF_y thin film composites appear to combine the chemical inertness of AlF_3 with the high electrical conductivity of a metal. This study suggests new opportunities for ALD and the design of advanced surface structures enabling high capacity lithium ion batteries. Studies are now underway to better understand the structure and composition of these films on Li-ion electrodes and their effect on electrochemical performance. For example, full-cell studies will be important in understanding long-term cycling stability, transition metal

dissolution, and impedance growth. Moreover, adjusting the composition of the ALD composites may yield further improvements in performance.

■ ASSOCIATED CONTENT

■ Supporting Information

A detailed description of the experimental procedure including atomic layer deposition, material synthesis, and characterization methods used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: croy@anl.gov.

Notes

The authors declare no competing financial interest.

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