Structure and surface chemistry of Al₂O₃ coated LiMn₂O₄ nanostructured electrodes with improved lifetime

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ABSTRACT

Aluminum oxide coatings deposited on LiMn₂O₄/carbon fiber electrodes by atomic layer deposition (ALD) are shown to enhance cathode performance in lithium-ion batteries. With a thin Al₂O₃ coating derived from 10 ALD cycles, the electrodes exhibit 2.5 times greater capacity retention over 500 cycles at a rate of 1C as well as enhanced rate capability and decreased polarization resistance. Structural and surface studies of the electrodes before and after cycling reveal that a near-surface phenomenon is responsible for the improved electrochemical performance. The crystal structure and overall morphology of the LiMn₂O₄ electrode are found to be unaffected by electrochemical cycling, both for coated and uncoated samples. However, evidence of Mn diffusion into the ALD coatings is observed from both transmission electron microscopy/energy-dispersive X-ray spectroscopy (TEM-EDS) and X-ray Photoelectron Spectroscopy (XPS) after electrochemical cycling. Furthermore, XPS analysis of the Al 2p photoemission peak for the ALD coated electrodes reveal a significant shift in binding energy and peak shape, suggesting the presence of an Al–O–F compound formed by sequestering HF in the electrolyte. These observations provide new insight toward understanding the mechanism in which ultrathin coatings of amphoteric oxides can inhibit capacity loss for LiMn₂O₄ cathodes in lithium-ion batteries.

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1. Introduction

Applications for which maximizing energy density is less critical than cost and safety (e.g., for hybrid vehicles and stationary...
storage), lithium-ion batteries utilizing LiMn$_2$O$_4$ make an excellent choice. However, the rapid capacity fade upon cycling for LiMn$_2$O$_4$ cathodes has prevented more widespread usage of this material [1,2]. Most discussions of the LiMn$_2$O$_4$ capacity fade focus on two mechanisms: dissolution of Mn and the Jahn-Teller distortion. Both of these mechanisms are related to the cathode state of charge (and, thus, the Mn oxidation state) and are most prominent when the Mn$^{3+}$ content in the cathode is relatively high. While the Jahn-Teller distortion is possible for LiMn$_2$O$_4$ in the discharged state, it has been reported to have a relatively minor contribution to capacity fade for cathodes cycled above 3 V vs Li/Li$^+$ [3]. Mn dissolution is often associated with the reaction proposed by J.C. Hunter in the early 1980’s, in which LiMn$_2$O$_4$ spinel was exposed to acidic solutions to produce the isostructural $\lambda$-MnO$_2$ phase [4]. Since then, the “Hunter Reaction” has become synonymous with Mn dissolution, in particular for electrolytes containing the LiPF$_6$ salt, which decomposes through a reaction with water to form HF acid [5]. In fact, the mechanism is more complicated than dissolution due simply to the reaction of LiMn$_2$O$_4$ with HF and can also include reactions with species formed by decomposing the electrolyte solvent in the charged state. As Amatucci and Tarascon summarized, the combined electrolyte decomposition and Mn dissolution further accelerate capacity fade in LiMn$_2$O$_4$. As graphite full cells by destroying the solid electrolyte interphase layer formed on the anode [2]. Because of the influence of decomposed solvent species and other factors, Mn dissolution is also observed for non-LiPF$_6$ electrolyte salts, although the effect is not as severe [6,7]. Surface coatings have been widely employed to reduce capacity fade in LiMn$_2$O$_4$. In some cases, lithium-conducting phases, such as other cathode materials and lithium-conducting glasses (e.g. LiCoO$_2$ and lithium-boron oxide) with favorable surface properties, can be employed to act as a physical barrier between LiMn$_2$O$_4$ and the electrolyte [8,9]. LiMn$_2$O$_4$ itself has been reported as a coating material to improve the thermal stability of LiCoO$_2$ [10,11]. Other protective coatings for LiMn$_2$O$_4$ utilize oxides of Al, Zn, Mg, Si and Zr to sequester acidic species in the electrolyte and thus inhibit Mn dissolution [12–14]. Like with the cation substituted electrodes, capacity retention is improved and can be correlated with a decreased Mn content in the electrolyte after cycling. One work using this approach suggested that surface coatings play a role in structurally reinforcing the underlying spinel to prevent microstrain during cycling at elevated temperatures (elevated temperatures are used to accelerate the Mn dissolution process) [15]. The influence of the morphology of the protective coatings has also been investigated. Several groups have reported that high surface area coatings consisting of agglomerated nanoparticles provide superior protection compared to dense coatings [3,12,16]. Very recently a new technique has been pursued to achieve the goal of long-lived cathode materials. In 2010, Jung et al. (U.C. Boulder and the National Renewable Energy Laboratory) reported that coatings of Al$_2$O$_3$ of less than one nanometer in thickness provided a significant improvement in capacity retention for a LiCoO$_2$ cathode [17]. The work of the X. Sun and Y. Wang groups have been actively exploring this area and demonstrated similar results with ALD using a variety of coating and cathode materials [18–21]. Unlike previous sol-gel-based, colloidal solution-based, or conventional solid-state reaction processes, which produce porous electrode coatings consisting of nanoparticles, these ALD coatings of Al$_2$O$_3$ were assumed to be fully dense and to behave as both electronic and ionic insulators [22]. Thin oxide coatings produced by ALD have also been investigated for anode coatings and solid-state electrolyte materials [23]. In this report, we build on our previous work using LiMn$_2$O$_4$ coated carbon fiber electrodes [24]. These electrodes can be constructed with an uninterrupted contact to the current collector and contain no binder or other additives, which enables direct observation of the influence of protective coatings of Al$_2$O$_3$ applied by atomic layer deposition to create an electrode completely encased in the protective oxide. This is in contrast to previous approaches in which either discrete powders or tape-cast electrodes were coated by ALD, wherein maintaining an uninterrupted interface was found to be critical to good electrode performance [21,25]. Using conventional electrochemical testing techniques, along with ex situ structural and surface chemistry characterization, the influence of ALD coatings on the cathode morphology, rate capability, and capacity retention are reported in this paper.

2. Methods and materials

2.1. Assembly of Al$_2$O$_3$ coated LiMn$_2$O$_4$ electrodes

A schematic illustration revealing the electrode fabrication procedure (and a proposed mechanism by which ALD coatings of aluminum-oxide can enhance the capacity retention of LiMn$_2$O$_4$) is shown in Fig. 1. Electrodes were prepared by coating nanosized LiMn$_2$O$_4$ crystallites onto carbon fiber paper (LMO/CFP) via a hydrothermal method, as described in our previous work [24]. In brief, pieces of carbon fiber paper (Spectracarb TM 2050A-0850 GDL, Engineered Fibers Technology LLC) were pre-treated by thermal oxidation in air at 350 °C for 5 h to increase the wetting by a hydrothermal solution, which contained 20 mM K$_2$MnO$_4$, 20 mM NH$_4$Cl and 50 mM LiOH. The carbon fiber paper was submerged in the hydrothermal solution, sealed inside of a Teflon-lined autoclave, and then heated to 100 °C for a period of 12 h followed by 140 °C for a period of 24 h. The LMO/CFP was thoroughly rinsed with deionized water and then cut into 9/16" diameter circular (~1 cm$^2$) electrodes for ALD coating and electrochemical testing. Aluminum-oxide coatings were applied by a Savannah 100 (Ultra-tech, MA, USA) atomic layer deposition system. The chamber was
held under vacuum for a minimum of 10 min before deposition. Each ALD deposition cycle was then conducted at 175 °C using a pulse time of 0.1 s for the trimethylaluminum (TMA) precursor and 0.015 s for the water vapor. Pulsing of each solution was followed by 15 s of pause under vacuum to exhaust the prior precursor vapor. During deposition, the flow rate of the N2 (Ultra High Purity, AirGas, PA, USA) carrier gas was set at 20 SCCM.

2.2. Electrochemical testing

Half-cells of the ALD coated and uncoated LMO/CFP electrodes were constructed, dried overnight in a vacuum oven, and assembled in an Ar filled glove box using Swagelok-type cell hardware. The counter and pseudo-reference electrode was Li metal and the electrolyte was 1 M LiPF6 in 1:1 EC:DMC (Novolyte) soaked into a glass-fiber separator (Whatman GF/D). After assembly, cells were cycled using an Arbin BT2000 battery cyclic at room temperature with rates of C/10 to 10C (1C = 148 mAh g\textsuperscript{-1} LiMn\textsubscript{2}O\textsubscript{4}). Electrochemical Impedance Spectroscopy (EIS) was also measured after various numbers of total cycles using a Solartron SI 1287 Electrochemical Interface and Solartron SI 1255 Frequency Response Analyzer. Details of the fitting procedure for EIS are provided in the Supporting Information section.

2.3. Post cycling characterization of structure and surface chemistry

Electrodes were further characterized \textit{ex situ} before and after cycling via powder X-ray diffraction (XRD), scanning electron microscopy (SEM, LEO 1530 thermally-assisted field emission SEM), energy dispersive X-ray spectroscopy (EDS, Oxford Instruments thin window silicon drift detector), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha), and transmission electron microscopy (TEM, FEI Technai F30). TEM samples were prepared by scraping a small amount of particulates from the CFP supported electrodes onto a carbon-film coated Cu grid. Powder X-ray diffraction was conducted using Beamline X7B at the National Synchrotron Light Source at Brookhaven National Lab with an X-ray wavelength of 0.3196 Å. XPS analysis utilized a low-energy electron flood gun to reduce charging effects, and binding energies were corrected using the C 1s peak position at 284.8 eV. Details of the peak fitting procedure used for XPS analyses are provided in the Supporting Information section.

3. Results and discussion

The morphologies of as-prepared LMO/CFP and ALD coated LMO/CFP are quite similar as shown in Fig. 2. All samples consist of discrete crystallites in the size range of 100–500 nm and no changes in surface features are apparent (at the indicated scale in Fig. 2) as a function of the Al\textsubscript{2}O\textsubscript{3} coating thickness. When analyzed using EDS during SEM analysis, as-prepared Al\textsubscript{2}O\textsubscript{3} coated electrodes exhibit an increase in Al and O content with an increase in the number of ALD cycles. Likewise, the average areal mass of the electrodes (mg cm\textsuperscript{-2}) increases slightly with increasing ALD cycles (Figs. S1 and S2). Analysis by TEM reveals a clear delineation between the crystalline LiMn\textsubscript{2}O\textsubscript{4} particle and the amorphous ALD coating. A 50 ALD layer coating of approximately 5.1 nm thickness (shown in Fig. 2F) is consistent with a assumed ALD growth rate of 0.9–1.1 Å per layer for Al\textsubscript{2}O\textsubscript{3} on Si using a TMA precursor. An EDS line-scan conducted during TEM analysis shows that the signal intensity for Al begins to increase slightly before the Mn signal, and then remains relatively constant. The Mn signal continues to increase along the distance of the line scan as the LiMn\textsubscript{2}O\textsubscript{4} particle becomes thicker. A TEM image of the 10 ALD layer coated sample is shown in Fig. S3 (note: the 10 ALD layer Al\textsubscript{2}O\textsubscript{3} coating is too thin for chemical analyses by EDS). SEM images of the LiMn\textsubscript{2}O\textsubscript{4} particles in ALD coated and uncoated electrodes are shown in Fig. S4, and appear to have a slightly rougher morphology than the uncycled electrodes while no obvious pitting is observed.

The observed capacities of the LMO/CFP electrodes were normalized by the mass of the LiMn\textsubscript{2}O\textsubscript{4} content in each electrode, which was about 30 wt% of the total electrode mass (Fig. S2) [24]. For the 50 ALD layer coated electrodes, the mass contribution from the ALD coatings is removed when calculating the normalized capacity, while the mass difference for the 10 ALD layer electrodes is negligible compared to the uncoated electrode. Despite these corrections, it is apparent in Fig. 3 that the discharge capacity of the 50 ALD layer coated electrodes is significantly lower than for the 10 ALD layer coated and uncoated electrodes, even when cycled at a rate of C/10. At the lowest rate tested, the uncoated and 10 ALD layer coated electrodes exhibit similar capacities, whereas for rates up to 1C, the 10 ALD layer coated electrode exhibits higher capacity compared to the uncoated electrode. This is similar to the observation reported by Walz et al. who found that an LiMn\textsubscript{2}O\textsubscript{4} electrode coated with TiO\textsubscript{2} nanoparticles had a higher rate capability than an uncoated electrode, which was attributed to the coating resulting in a more uniform current density [3]. While the total capacity of the 50 ALD layer coated electrode is severely reduced, the relative rate capability (i.e., the percentage of original capacity maintained at increasing current density) is not similarly influenced. The capacity of the 50 ALD layer electrode actually increases very slightly between the C/10 and C/5 rate regions and exhibits the smallest drop between the 1C and 5C regions, which was consistent with the assumption that the ALD coating can improve the homogeneity of near-surface current density on the coated electrodes. At rates of 5C and 10C the uncoated and 10 ALD layer coated electrodes show roughly comparable capacities.

The effect of the coating on improving capacity retention is apparent even during rate capability testing. After returning to a C/5 rate, the 10 and 50 ALD layer electrodes recover 98.5% and 99.1% of their original C/5 discharge capacity, respectively, compared to 93.5% for the uncoated electrode. Extended cycling at room temperature for the uncoated and 10 ALD layer electrodes reveals that, after 500 cycles (Fig. 3C) at a 1C rate, the 10 ALD layer coated electrode retains over 2.5 times the roughly identical starting capacity compared to the uncoated electrode. For the 50 ALD layer coated electrodes, only 300 cycles were conducted at a rate of 1C, whereupon a capacity retention comparable to that of the 10 ALD layer coated electrodes is observed. A small discrepancy was apparent when comparing the 1C rate capacity for the uncoated electrodes in Fig. 3B and C. For the extended cycling tests, electrodes are cycled first for one C/10 formation cycle followed by extended cycling at 1C. During this testing, both the 10 ALD layer coated and uncoated electrodes have starting 1C capacities above 130 mAh g\textsuperscript{-1}. Meanwhile, the 1C capacity for both electrodes during the rate capability tests is about 128 mAh g\textsuperscript{-1} for the 10 ALD layer coated electrode and only 117 mAh g\textsuperscript{-1} for the uncoated electrode. However, when considering the 30th cycle capacity for the extended cycling test, which should be equivalent to the first 1C cycle observed for the multi rate tests, the capacities of the uncoated and 10 ALD layer coated electrodes are 121 mAh g\textsuperscript{-1} and 127 mAh g\textsuperscript{-1}, respectively, which are consistent with the observed 1C capacities in Fig. 3B.

Differential capacity plots for the first and tenth cycles at a C/10 rate (Fig. 3D and E respectively) show the typical pair of redox peaks expected for LiMn\textsubscript{2}O\textsubscript{4} during charging and discharging. For the ALD coated electrodes, an increased differential capacity is observed above about 4.2 V vs. Li/Li\textsuperscript{+} on the first cycle, which is greatly reduced by the 10th cycle. While all of the electrodes exhibit a larger charge capacity than discharge capacity during the first
Fig. 2. SEM images of LiMn$_2$O$_4$ as grown on CFP (A) and Al$_2$O$_3$-coated LiMn$_2$O$_4$ derived from 10 (B) and 50 (C) ALD cycles. A representative area of collection for EDS is shown in (D). EDS spectrum collected at 10 kV accelerating voltage shows higher Al and O content with increased ALD cycles (E). A high-resolution TEM image of a 50 ALD cycle coated LiMn$_2$O$_4$ particle is shown in (F) with an arrow indicating the direction of the EDS line-scan shown in (G). In Figure G, EDS signal collected for the first ~10 nm is expected to come exclusively from the carbon film of the TEM sample grid. SEM images of the electrodes after electrochemical cycling are shown in Figure S3.

Fig. 3. First cycle charge (dashed lines) and discharge (solid lines) profile at a C/10 rate (A), rate capability testing (B) and extended cycling at a rate of 1C (C). The 1C rate is defined as 148 mA/g. Differential capacity plots for the first (D) and tenth (E) cycle are shown for both ALD coated and uncoated electrodes.
cycle (Fig. 3A), it was not clear why only the ALD coated electrodes show a slight increase of differential capacity in the 4.2–4.4 V vs. Li/Li+ region during the first charge. One explanation could be that ALD coatings increased the over potential for the initial delithiation of the underlying LiMn₂O₄, which is consistent with the slightly higher oxidation potentials and slightly lower reduction potentials for the ALD coated electrodes on the first cycle compared to the uncoated electrode. By the 10th cycle, all of the electrodes exhibited redox peaks at 4.01 V and 4.13 V during charging and 4.11 V and 3.99 V during discharging.  

To better understand the mechanism by which the ALD Al₂O₃ coating improved the capacity retention of LiMn₂O₄ electrodes, synchrotron X-ray diffraction analysis is used to characterize the structure of coated and uncoated electrodes before and after cycling. Rietveld refinements of the XRD patterns (Fig. 4) yielded a virtually identical lattice constant for uncycled electrodes with and without ALD coating. For the uncycled electrodes, the lattice constant is slightly less than the 8.247 Å value reported for stoichiometric, bulk LiMn₂O₄ (JCPDS No. 35–0782), which is consistent with a Li-rich composition reported for other hydrothermally produced lithium-manganese spinel oxides [26]. Three small impurity peaks (Fig. S5) are also apparent in the pre-cycled electrodes, which appear at the same 2θ locations for both the ALD coated and uncoated electrodes, suggesting that these peaks are not related to the ALD process or the Al₂O₃ coating. After cycling, these impurity peaks disappear while the peaks associated with the spinel phase remain essentially unchanged in both position and relative peak intensity. The phase associated with the impurity peaks could possibly be another manganese oxide which is either chemically or electrochemically consumed during cycling, which is consistent with the observation of an increased charge capacity and slightly shifted potentials for the first charge and discharge cycle shown in Fig. 3. Only a small change in lattice parameter in the main spinel phase is observed after cycling. For the uncoated electrode, a slight dilation towards the standard lattice parameter was observed, while for the 10 ALD cycle coated electrode, the lattice parameter is constricted by a similar amount. In both cases, the change in lattice parameter is less than 0.5% of the starting value. An amorphous (broad hump) region between 4 and 6° 2θ observed for all electrodes can be attributed to the carbon fiber current collector.  

EIS analysis is conducted for cells in the discharged state (3.1 V vs. Li/Li+) after various numbers of cycles conducted at a rate of 1C. However, before each impedance spectrum is collected, a single cycle at a C/10 rate is conducted to create a uniform reaction rate and open-cell potential. The equivalent circuit used and fitting results are shown in Fig. 5.  

The fitting results are summarized in Table S1 with values presented as an average of three identical electrodes of each type. Two semi-circles offset from the origin along the X-axis, and a sloped linear region, were observed for each impedance spectrum. The highest frequency semi-circle can be fit using a circuit model consisting of a resistor and capacitor in parallel (R₂ and C₁), while the lower frequency semi-circle is depressed and fit with a model of a resistor and constant-phase element in parallel (R₃ and CPE₃). As has often been previously reported, the x-axis offset can be treated as the solution resistance (Rₛ), which contained contributions from both the electrolyte conductivity and the contact resistance between the electrode and current-collector. For the semi-circle regions, the higher-frequency R₂ and C₁ are attributed to the SEI or sometimes “surface film”, the lower-frequency R₃ and CPE₃ were attributed to the charge-transfer resistance and double-layer capacitance, respectively, and the sloped linear region was associated with solid-state lithium diffusion [27–30]. Our analyses indicated that the two semi-circles have distinct time constants, which are identified by the positions of the marked frequencies in Fig. 5. However, our half-cell measurements did not provide enough information to unambiguously confirm each of the proposed circuit elements suggested in the literature. Instead, further discussion will only consider the solution resistance (Rₛ) and polarization resistance (Rₚ) defined as the sum of the R₃ and R₄ values.  

The general trend shows that the ALD coating has minimal influence on the solution resistance Rₛ for all samples and for all of the number of cycles. A large drop in Rₛ was observed between the first and 50th cycles, which is perhaps due to the removal of the unidentified phase observed in the pre-cycled electrode by XRD analysis or due to the influence of a native passivation layer on the Li anode. Comparatively small changes in Rₚ are observed between the 50th and 100th cycles. After 50 cycles, the 10 ALD layer coated electrodes exhibited the smallest value in Rₛ, which is slightly below the value observed for the uncoated electrode. The average Rₛ value for the 50 ALD layer coated electrodes is more than twice the average value for the 10 ALD layer coated electrodes, which is consistent with the lower capacity observed in Fig. 3.  

X-ray photoelectron spectroscopy are used to determine the binding energies of the Mn 2p photoelectron line on all electrodes and the Al 2p photoelectron line for ALD coated electrodes, both before cycling and after 300 charge and discharge cycles at a rate of 1C. Peak fitting is used to quantify the relative positions and areas of any sub-peaks within each photoelectron line. Binding energies for all Mn 2p peaks, as well as the doublet separations (ΔB.E.) and calculated Mn oxidation state (Mn Ox.), are summarized in Table S2. The Mn 2p peak is commonly used to characterize the near-surface oxidation state of LiMn₂O₄ and other manganese oxides [27,28,31–34]. Prior XPS studies of LiMn₂O₄ report values between 641.4 eV and 642.1 eV for the Mn 2p₃/2 sub-peak assigned to Mn³⁺ and 642.4 eV–643.6 eV for the Mn 2p₅/2 sub-peak assigned to Mn⁴⁺. Furthermore, the doublet separation between the Mn 2p₃/2 and Mn 2p₅/2 is listed in the NIST database as ranging from 11.6 eV to 11.9 eV for Mn oxide with a value of 11.6 eV reported for LiMn₂O₄ [34]. Interpretation of the Mn 2p can be particularly challenging because of the possibility for multiple oxidation states, which vary as a function of state of charge as well as cycling history.
but also due to the intrinsically asymmetric Mn 2p peak shape. To minimize any cognitive bias introduced during the fitting procedure, a cold-pressed LiMn$_2$O$_4$ pellet is used as a reference sample. Values for an asymmetrical Voight-type peak shape are derived from the reference sample and fixed for all other electrodes. The full width-at-half-maximum (FWHM) values are allowed to vary within a narrow range. Details of the fitting procedure, as well as the fitting results for the reference peak (Fig. S6), are described in the Supporting Information section.

As shown in Fig. 6, all electrodes before cycling exhibit Mn 2p binding energies slightly lower than previously reported literature values, but are internally consistent regardless of the presence of an ALD coating. However, an obvious decrease in the Mn 2p signal for the 50 ALD layer coated electrode is apparent before cycling. While this observation is reasonable given the increased thickness of the ALD layer compared to the 10 ALD layer coated electrode, it introduced some uncertainty into the analysis of the uncycled 50 ALD layer electrode. With the exception of the 50 ALD layer electrode, the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ doublet separation for each set of sub-peaks is near 11.6 eV, suggesting that the peak fitting routine was reasonable. The near-surface Mn oxidation state is calculated using the relative area for peaks associated with Mn$^{4+}$ and Mn$^{3+}$ in the Mn 2p$_{3/2}$ region. For the uncoated, uncycled electrode, an average oxidation state of Mn$_{3.5}^{3+}$ can be obtained, which is expected for stoichiometric LiMn$_2$O$_4$.

Meanwhile, the relative peak area associated with Mn$^{3+}$ increased with increasing ALD layer thickness, and as a result both of the 10 ALD layer and 50 ALD layer electrodes show a decreased Mn oxidation state relative to the LiMn$_2$O$_4$ surface without any ALD coating. It is unclear whether this reduction was due to a reaction occurring during the ALD process or due to the decreasing signal-to-noise ratio for the Mn 2p peak. At the temperature used for the ALD process (175°C), no reaction is expected between the carbon fiber substrate and LiMn$_2$O$_4$ coating (Fig. S2). However, the Al precursor TMA is in fact a strong reducing agent which suggests the possibility that this decreased oxidation state is due to a reaction of the substrate with the ALD precursors [35]. The typical depiction of the ALD process using TMA and H$_2$O reactants is the two-step methyl transfer reaction described by George et al. with surface species indicated by asterisks,

\[
\text{AlOH}^+ + \text{Al(CH$_3$)$_3$} \rightarrow \text{AlOAl(CH$_3$)$_2$ + CH}_4
\]

\[
\text{AlCH}_3^+ + \text{H}_2\text{O} \rightarrow \text{AlO} - \text{AlOH}^+ + \text{CH}_4
\]

assumes a reaction between incoming TMA molecules and omnipresent hydroxyl groups on the surface of an oxide substrate [36,37]. However, these reactions do not explicitly involve reduction of the substrate, and in fact ALD coatings using TMA have been demonstrated for relatively inert surfaces including carbon and gold [37,38]. Furthermore, according to the Hunter reaction a decreased oxidation state of Mn should lead to an accelerated
capacity fade due to Mn dissolution, which is not observed for the ALD coated samples. Thus, while TMA may be the reducing agent responsible for the observed Mn oxidation state change in the ALD alumina coated electrodes, this effect does not override the benefits of the alumina coating.

After cycling, all of the Mn 2p peaks shift to slightly higher binding energies, suggesting an increased oxidation state for Mn. However, only the uncoated electrode exhibits a change in relative Mn\(^{3+/4+}\) peak areas and, thus, a change in the average Mn oxidation state. Previous works have also reported reduction of manganese and other transition metals during electrochemical cycling of lithium-ion battery positive electrodes, and that this reduction can be inhibited with appropriate surface coatings [19,39]. Two important changes were observed when comparing the Mn 2p peaks for the coated and uncoated electrodes before and after cycling. First, the apparent Mn 2p signal-to-noise ratio for the cycled 50 ALD layer electrode improves dramatically compared with the uncycled electrode using identical XPS analysis conditions. This could imply that the ALD layer experienced a significant change in morphology or thickness, resulting in an improved yield of Mn 2p photoelectrons. An alternative explanation is that Mn ions can migrate into the coating and nearer to the surface during the Mn dissolution process or form a new phase on the surface of the electrodes. A recent study of spinel LixNi0.5Mn1.5O4/C0 revealed the formation of Ni\(^{2+/3+}\) complexes with β-diketonate ligands produced by oxidation of the electrolyte during electrochemical cycling [40]. These phases or others like it may also be present at the surface of the ALD coated electrodes after electrochemical cycling, leading to an enhanced Mn 2p signal in XPS, though from our analysis these complexes cannot be specifically identified. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images (Fig. S7) comparing the 50 ALD layer coated electrode before and after cycling reveal a brighter edge on the cycled electrode. The increased contrast in the cycled sample could be attributed to the presence of higher atomic number Mn, indicating diffusion of Mn from the LiMn2O4 particle onto the surface of the Al2O3 coating. This is consistent with both the EDS data collected in TEM (Fig. S7C), which indicates an increase in Mn and Al signal at roughly the same lateral position, as well as the increased signal to noise ratio for the 50 ALD layer electrode shown in Fig. 6A compared to Fig. 6B.

The second observation is that while the cycled ALD coated electrodes show qualitatively reasonable fits under the same conditions used for the uncycled electrodes, the uncoated electrode after cycling does not. This is observed as a slight under-estimation of the total peak intensity for the Mn 2p\(^{3/2}\) peak and a slight over-estimation for the Mn 2p\(^{1/2}\) peak when comparing the raw experimental data with the calculated fit. Furthermore, while the Mn 2p signal-to-noise ratio for the uncoated electrodes remains high, the doublet separation between the Mn 2p\(^{1/2}\) and Mn 2p\(^{3/2}\) peaks increases relative to the uncycled electrode. This implies that the peak parameters derived from the LiMn2O4 reference material no longer adequately represent the uncoated sample after electrochemical cycling. These observations likely result from the formation of a new phase on the surface of the uncoated electrode.

Compared to the Mn 2p spectra, analysis of the Al 2p photoelectron peaks shown in Fig. 7 and summarized in Table S3 reveal a much more dramatic change as a result of electrochemical cycling. Regardless of ALD coating thickness, a single well defined peak is identified in the Al 2p region before electrochemical cycling. The binding energies of these peaks are approximately 74.5 eV, which is consistent with previous reports of aluminum oxide deposited onto LiMn2O4 by ALD [41]. After cycling, the peak maximum shifts to higher binding energies and developed a broader, slightly asymmetrical peak shape. Al was assumed to exist with a single oxidation state, Al\(^{3+}\), and thus the observed binding energy shift is likely due to a change in chemical bonding. An increased binding energy could be caused by increased electronegativity in the bonding character. Among the available and likely bond forming anions that are more electronegative than oxygen, only fluorine can be
responsible for the large change in binding energy observed after cycling. The peak associated with residual aluminum oxide is also found to shift slightly to lower binding energies for both the 10 ALD layer and 50 ALD layer electrodes. Thus, the data suggests that, after electrochemical cycling, the original, pure alumina coating consists of a mixture of aluminum fluoride, aluminum oxy-fluoride, or fluorine-doped alumina and unreacted alumina. This conclusion is further supported by observing the relative intensity of the assumed Al-O and Al-F peaks. For the thinner 10 ALD layer electrode, only a small shoulder region can be attributed to residual unreacted aluminum-oxide, while for the 50 ALD layer electrode, the residual peak is distinctly stronger.

Several authors have suggested that Al₂O₃ can sequester HF by the following reaction [42,43],

$$ \text{Al}_2\text{O}_3(s) + 6\text{HF}(l) \rightarrow 2\text{AlF}_3(s) + 3\text{H}_2\text{O}(l) $$

Thermodynamic data for Reaction 3 yielded a value for the standard Gibbs free energy of Reaction 3 of ~356.1 kJ mol⁻¹ at 298 K [44,45]. Myung et al. reached a similar conclusion for higher temperature (400 °C) solution-deposited Al₂O₃ coatings on Li [Li₀.05Ni₀.4Co₀.15 Mn₀.4]O₂, and observed various aluminum-oxy-fluoride compounds including Al₂O₂F₂ and Al₂OF₄ using time-of-flight secondary ion mass spectroscopy (TOF-SIMS), accompanied by a decreased HF content in the electrolyte, with eventual formation of AlF₃ [42].

However, the byproduct of water formed along with AlF₃ according to Reaction 3 would enable further HF production and thus increase the rate of Mn dissolution, which seems counterintuitive based on the large amount of empirical evidence showing that aluminum-oxides and other compound do indeed improve capacity retention for LiMn₂O₄ and reduce HF content in the electrolyte. In light of this contradiction, Oh et al. utilized TOF-SIMS to observe Al₂O₃ coated LiCoO₂ cathodes after electrochemical cycling and suggested that Al₂O₃ coatings instead form a final compound of AlF₃•H₂O in the presence of HF [46]. The residual Al—O bonding shown in our XPS analysis may indicate that HF molecules are not completely disassociated by contact with Al₂O₃ and that a compound with both Al—O and Al—F bonding remains. This is shown schematically in Fig. 1D.

### 4. Conclusions

ALD was used to deposit coatings of Al₂O₃ onto LiMn₂O₄ grown on carbon fiber electrodes via hydrothermal synthesis. Among the samples studied, the 10 ALD layer coated electrodes exhibited the best performance, with significantly enhanced capacity retention and improved rate capability. However, the structure of the electrodes remained virtually unchanged when examined using synchrotron X-ray diffraction and electron microscopy. No cracking or electrode pulverization was observed for either the coated or uncoated electrodes. These observations suggest that the capacity loss observed in the uncoated electrodes is due primarily to Mn dissolution. XPS analysis of the Mn 2p photoelectron line showed that the oxidation state of Mn decreased slightly for the uncoated sample after electrochemical cycling, while for the ALD coated samples the Mn oxidation state was unchanged. Meanwhile, XPS analysis of the Al 2p photoelectron line revealed a large shift in the binding energy and change in the Al 2p peak shape, implying that aluminum oxide is capable of scavenging HF from the electrolyte through the formation of an aluminum-oxy-fluoride compound. Finally, redistribution of Mn was observed both with TEM and XPS analysis in the 50 ALD layer coated electrode, suggesting that Mn migration, possibly due to the HF activated dissolution process, is not completely arrested by the coatings. This important observation suggests that the ALD coatings do not simply act as a mechanical barrier between the electrolyte and cathode surface.

![Fig. 7. Al 2p XPS peak comparing 10 ALD layer coated (A) and 50 ALD layer coated (B) electrode before and after 300 cycles at a 1C rate.](image-url)
Rather, the spontaneous formation of a new phase of good ionic conductivity on the electrode surface prevents the dramatic increase in polarization resistance or decrease in discharge capacity reported for other coating morphologies and techniques. Our results can inform future rational design of electrodes utilizing protective coatings, and in particular enable the use of low cost and high safety LiMn$_2$O$_4$ cathodes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.11.114.

References