Atomic Layer Deposition for Improved Electrochemical Stability for Lithium Ion Batteries

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Atomic Layer Deposition for Improved Electrochemical Stability for Lithium Ion Batteries

by

Leah Autumn Riley

B.A., Mount Holyoke College, 2003
M.S., University of Southern California, 2005

A thesis submitted to the
Faculty of the Graduate School of the
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This thesis entitled:
Atomic Layer Deposition for Improved Electrochemical Stability for Lithium Ion Batteries
written by Leah Autumn Riley
has been approved for the Department of Mechanical Engineering

Prof. Se-Hee Lee

Dr. Anne Dillon

Date ________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
The dwindling supply of fossil fuels and the harmful green house gases which they produce have driven research towards developing a reliable and safe solution. Alternative forms of transportation, such as hybrid electric, plug-in hybrid electric and all electric vehicles in turn have recently received vast consumer attention. Lithium ion batteries (LIBs) are seen as the most promising option in HEVs and PHEVs. However, while prevalent in watches, computers and phones, significant improvements in both energy density and rate capability need to be achieved before LIBs are suitable for vehicular applications. Decades of research has yielded a range of anode and cathode materials that exhibit higher capacity and better rate capability than the traditional graphite and LiCoO$_2$ found in commercial batteries. Unfortunately due to material pulverization and electrode/electrolyte interfacial reactions high performance materials are often plagued with poor capacity retention and material degradation.

Surprisingly, many of the issues accompanying high performance materials can be suppressed by the application of as little as 8 angstroms of Al$_2$O$_3$ on the surface. Ultra-thin, conformal, ceramic passivating layers are grown using a thin film technique called Atomic Layer Deposition (ALD). Self-limiting and easily tailored, ALD is a superior coating method compared to the more common wet-chemical methods such as sol-gel. Conformal ALD is applied to commercially common materials (graphite, LiCoO$_2$), as well as high energy density alternatives (MoO$_3$, Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$). It will be shown that the ALD coating protects high surface area state-of-the-art nanoparticles from decomposition and protects electrode surfaces from HF attack and dissolution even
up to 5.0 V. In addition to extending overall electrochemical cycling stability, ALD will be shown to minimize hazards and risks, such as thermal runaway, by preventing unwanted side reactions with the organic liquid electrolyte. ALD is a simple, non-toxic and effective method for the implementation of LIBs in high power applications.
Dedication

I would like to dedicate this work to the great Michael Faraday, whose works on ion mobility and the decomposition of current conducting bodies are the foundation for lithium batteries and lie at the core of this research.

The surfaces at which, according to common phraseology, the electric current enters and leaves a decomposing body are most important places of action.

Michael Faraday (On Electrochemical Decomposition, 1834)
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Chapter 1

Introduction

1.0.1 The Problem

A) Depleting Natural Resources

Our world runs on non-renewable fossil fuels and combustible materials (Figure 1.1). Oil, coal, natural gas, and combustibles make up over 80% of the world’s energy supply [1]. Renewable sources such as geothermal, solar, and wind supply less than 0.1%. While the absolute energy production is greater than world energy consumption, the most popular fuel, oil, is being consumed as fast if not faster than the rate of production. It is estimated that the reserve to production (R-P), the length of time until world reserves have been depleted, for oil is approximately 40 years [2]. As the inevitable supply of oil decreases, large-scaled uses, such as residential heating, can easily shift towards other well established sources for power. However, the most heavy user of oil, vehicles and transportation, has no viable alternative when the wells go dry.

B) Absence of Energy Storage

To release energy stored in raw materials, fossil fuels are typically burned. Large power plants act as a central location to distribute the energy to communities as electricity. Users who are on the grid are capable of tapping into this electrical deluge. When the user consumption exceeds the power plant production, issues such as blackouts can occur. On the other hand, when the power plant burns too much fuel and the
Figure 1.1: 2010 International Energy Agency (IEA) Key World Energy Statistics: (a) Total world consumption for fuel type; and (b) Total world supply for fuel type. Statistics based upon 28 participating countries [1].
electricity is not fully consumed, the energy is wasted.

One of the primary drawbacks to the implementation of renewable energy for mass electricity production is that it depends upon factors beyond our immediate control. For a coal plant, if the grid needs more energy, more coal can be burned. However, for a solar farm, if it happens to be a cloudy day, there is no method to increase the incident solar radiation. In addition, many renewable sources are out of phase with the load. Figure 1.2 depicts the calculated solar output and the typical average user load during a 48 hour summer period. While photovoltaics (PV) can immediately meet the daytime energy load, after 5 p.m., solar radiation dramatically decreases and is unable to meet consumer needs.

1.0.2 An Opportunity

The pending crisis facing the global energy sector is a double edged sword. First, transportation is absolutely dependent upon oil. Second, large-scaled alternative generation methods, like solar or wind, while abundant are unreliable and unable to meet a 24-hour consumer demand. However, these issues provide an excellent opportunity in a model called Vehicle to Grid (V2G). V2G utilizes a nation’s fleet of plug-in electric
vehicles (PEVs) as a large-scale network of individual portable storage units for excess energy generation [3]. Regional power grids would be setup to draw energy from EVs during times of minimal energy generation at renewable plants. A preliminary investigation by Kempton et al. found that a system which combines fleets of electric vehicles and renewable power generation is substantially less expensive and more reliable than the use of large-scale, stand-alone, excess energy storage [3].

1.0.3 The Focus

For EVs and V2G to be commercially viable batteries need to have high-energy density, supply high power (for both driving and grid operation), and maintain extended cycle life at high rates of charge and discharge [3]. Lithium-ion batteries (LIBs) have shown a strong potential for high performance applications such as in plug-in hybrid electric vehicles (PHEVs) and hybrid electric vehicles (HEVs). In 2003 the Department of Energy’s (DOE) Vehicle Technologies (VT) Program created the FreedomCAR and Fuel Partnership. More recently, in 2010, bill S.3442 or Electric Vehicle Deployment Act of 2010 was introduced to Congress and referred to committee. Both programs strive to free American consumers from dependence on oil and harmful emissions through joint R&D at major energy corporations and laboratories across the nation [4].

Lithium ion batteries are commonly used in low energy applications such as laptops and cellphones. For large scale vehicular needs, current LIB technology is inadequate in both energy storage and power output. FreedomCAR and Fuel Partnership benchmarks require the development of state-of-the-art materials and systems to fully meet the need of automotive consumers. Decades of LIB research has produced many attractive alternatives to commercially popular graphite and LiCoO$_2$. However, unforeseen issues such as destructive volume expansion and undesired reaction with liquid electrolytes have prevented their commercial use.

Under the FreedomCAR and Fuel Partnership, this thesis aims at improving the
performance of existing materials for LIBs through the use of protective surface films
grown by atomic layer deposition (ALD). This work is also a demonstration of strong
collaboration between universities, national laboratories, and industry.

1.1 Goals

Generally speaking, the goal for this research is to help stabilize high energy
density materials for commercial use in LIBs. This dissertation has been narrowed
down to three primary objectives.

The initial objective is improving the electrochemical stability and rate capability
of MoO$_3$, a replacement anode material for graphite, by coating electrodes and particles
with Al$_2$O$_3$ using ALD. Nanoparticle MoO$_3$, in collaboration with the National Renewable
Energy Laboratory (NREL), was optimized for use in a thick composite electrode
(Chapt 6). Both prefabricated electrodes and nanoparticles were coated by ALD and
tested for changes in electrochemical performance (Chapt 7). Improvements in surface
protection and mechanical stability through adhesion were explored (Chapt 8).

The second objective is to utilize the high energy density MoO$_3$ anode in a lithium
metal-free full cell. This work includes collaboration with Argonne National Laboratory
(ANL). The stable material developed from the first objective was then paired with a
lithium excess cathode (ANL-NMC). The ALD-MoO$_3$/ANL-NMC was electrochemically
tested and compared to commercial C$_6$/LCO LIBs (Chapt 9).

The final objective is improving the capacity retention of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$,
a LiCoO$_2$ cathode replacement, up to 5.0 V through ALD surface passivation. The cath-
odde material was obtained through collaboration with HRL Laboratories. In additional
to electrochemical performance results, changes to the cathode surface structure during
deep cycling up to 4.6 V for pristine and ALD-coated samples were compared. The
effect of particle versus electrode coating at high voltages, 5.0 V, was also explored
(Chapt 10).
References


2.1 The Electrochemical Process

In general, a battery is a device which stores and releases energy through change in chemical structure or composition. To release the stored energy, batteries undergo an electrochemical reaction. In an electrochemical reaction the stored energy is converted directly into electric current through controlled oxidation and reduction.\(^1\)

Reduction is defined as the gain of an electron while oxidation is the loss of an electron. A redox\(^2\) reaction can be written either as individual steps (Eq. 2.1) or the sum of the parts (Eq. 2.2) [1]. While the single-step version in equation 2.2 provides a compact summary of the complete reaction, it is only when the chemical processes are written separately that it becomes clear that O\(_2\) undergoes reduction while H\(_2\) is undergoes oxidation.

\[
\begin{align*}
O_2 + 4e^- & \rightarrow 2O^{2-} \\
2H_2 & \rightarrow 4H^+ + 4e^- \\
O_2 + 2H_2 & \rightarrow 2H_2O
\end{align*}
\] (2.1)

The electrochemical process for lithium ion batteries is slightly more complex than for the formation of water since electron transfer is accompanied by the transfer of a positively charge lithium ion. Commonly, the oxidation couple is a metal oxide.

\(^1\) In the case of fossil fuels, the energy is first converted first to heat through combustion and then mechanically converted to electrical current. The two-step conversion process largely accounts for the poor efficiency of internal combustion engines.

\(^2\) reduction-oxidation reaction
(\(Li_{1-x}MO_2\), where M is a transition metal), while the reduction couple is lithium bearing carbon material (\(Li_xC_6\)). The individual half reactions can be written as,

\[
\begin{align*}
Li_{1-x}MO_2 + xLi^+ + xe^- & \leftrightarrow LiMO_2 \\
Li_xC_6 & \leftrightarrow C_6 + xLi^+ + xe^- 
\end{align*}
\] (2.3)

Lithium batteries take advantage of the two step nature of redox reactions by physically separating the couples. A schematic of a lithium ion battery is depicted in Figure 2.1. The physical gap between the couples is bridged by a unique medium called an electrolyte. The electrolyte is designed to be conductive to lithium ions but resistive to the flow of electrons. Since the chemical reactions (and release of energy) in Eqs. 2.3 require the transfer of both lithium ions and electrons, the electronically insulating electrolyte effectively stores the chemical energy within the couples. However, when an external metal wire is attached to each terminal, the couples become linked both ionically (through the electrolyte) electronically (through the wire), so the redox reaction will occur.

By combining the two half reactions shown in 2.3 the full reaction becomes,

\[
Li_{1-x}MO_2 + Li_xC_6 \leftrightarrow LiMO_2 + C_6 
\] (2.4)

Notice that Eq. 2.4 is written as a fully reversible reaction.

Thermodynamically, since the reaction is fully reversible, the energy can be quantified by Gibb’s Free Energy (\(\Delta G\)),

\[
\Delta G = G_{products} - G_{reactants}
\]
\[
dG = -SdT + VdP \tag{2.5}
\]

Gibb’s Free Energy represents the energy that can be extracted from a system of constant volume (\(\Delta V = 0\)) and no heat flux at the boundaries (\(\Delta S = 0\)) [2]. For electrochemical systems, the free energy (\(\Delta G\)) can be used to perform work (W) to move an
Figure 2.1: Schematic of the electrochemical process in a Li-ion cell [1]
electrical charge \((q)\). From electrostatics,

\[
w_{\text{elect}} = q_{\text{elect}} E
\]

\[
Q = \sum q = -nF
\]

\[
\Delta G = -nFE
\]

(2.6)

where \(n\) is the number of moles of electrons transferred, \(F\) is Faraday’s constant, and \(E\) is the electromotive force, \(\xi\), or as the open circuit voltage, \(OCV\). It is important to recognize that by combining Eq. 2.5 and Eq. 2.6 the open circuit voltage is not an absolute value, rather it is dependent upon the difference in free energy between the two couples.

The simplified equations for Gibb’s Free Energy (Eqs. 2.5) assumes a closed system where the concentration of all species is fixed \((n_i = \text{constant})\). For open systems, such as battery electrodes, the concentration of lithium within each couple, \(n_{Li}\), will vary during the redox reaction. Taking into account a free energy change as a function of composition, Gibb’s Free Energy can be rewritten as,

\[
dG = -SdT + VdP + \sum_{i=1}^{k} \frac{\partial G}{\partial n_i} dn_i
\]

(2.7)

Since lithium is the only species to undergo changes in concentration during the redox reaction, the equation can be further simplified to,

\[
dG_{\text{LIB}} = -SdT + VdP + \mu_{Li}dn_{Li}
\]

(2.8)

where

\[
\mu_{Li} = \left( \frac{\partial G}{\partial n_{Li}} \right)_{T,P} \equiv \bar{G}_{Li}
\]

(2.9)

In electrochemistry \(\mu\) is referred to as chemical potential [2]. In broad terms, the chemical potential measures the escaping tendency of a species. The greater the chemical potential, the more likely a species will move away from the system. When placed in a gradient species will spontaneously move from high to low chemical potential.
From the definition of chemical potential the reaction between $\text{Li}_{1-x}\text{MO}_2$ and $\text{Li}_x\text{C}$ can be rewritten as,

$$
\Delta \mu_{\text{Li}} = \mu_B - \mu_A 
$$  \hspace{1cm} (2.10) \\
$$
\mu_A = \mu_{\text{Li}_x\text{C}} + \mu_{\text{Li}_{1-x}\text{MO}_2} 
$$  \hspace{1cm} (2.11) \\
$$
\mu_B = \mu_{\text{C}} + \mu_{\text{LiMO}_2} 
$$  \hspace{1cm} (2.12)

At a concentration of $x=1$, all of the lithium sits within the carbon electrode and the battery is considered to be in a *fully charged* state. In this initial state, $\mu_A$ is greater than $\mu_B$. When placed into an external circuit, lithium will spontaneously move from the carbon to the metal oxide (*discharge*). The reaction will continue until $\mu_A = \mu_B$. At this point, the battery is *fully discharged*. After equilibrium, a potential gradient can be reestablished by driving the lithium using an external power supply (*charge*).

From Eq. 2.6 the open circuit voltage of the system is,

$$
\text{OCV} = \frac{\Delta \mu}{F} 
$$  \hspace{1cm} (2.13)

and depends only on the chemical potential gradient and not on the lithium concentration gradient.

### 2.2 Material Selection

As previously described, a redox reaction occurs between two couples. The ideal electrochemical storage materials should:

1. react reversibly with lithium to allow for both insertion and extraction
2. be chemically inert to the electrolyte or electrical connections over all possible lithium concentrations
3. mechanically remain stable during lithium insertion and extraction
4. conduct both lithium ions and electrons
Even though the material selection criteria for both couples is identical, in reality, the practical issues vary greatly. The terms anode and cathode are assigned in order to differentiate between the spontaneous reduction and oxidation half reactions.

In the 1970’s, initial demonstrations of lithium batteries were comprised of a metal oxide or sulfide cathode \((\text{Li}_{x}\text{TiS}_2, \text{Li}_{x}\text{CoO}_2, \text{Li}_{x}\text{Mn}_2\text{O}_4)\) and a pure lithium metal anode \([3, 4, 5]\). Not too long after, graphite was chosen as a commercially superior anode due to safety and stability issues surrounding the high reactivity of lithium metal \([6, 7]\). Since the switch to graphite anodes, very little has changed within composition of commercial lithium batteries. The remainder of this chapter will briefly cover the electrochemical properties and issues facing graphite anodes and lithium metal oxides cathode.

### 2.3 Carboneous Anodes

#### 2.3.1 Electrochemical Performance

The most commercially popular and well-researched anode, graphite is stable in air, less reactive than metal oxides, non-toxic, abundant, and electronically conductive. Unlike in Li-metal, where the lithium reacts with the electrode surface in the form of plating, in graphitic intercalation materials provide active lattice sites to host lithium atoms. Graphite \((\text{C}_6)\) is a layered material comprised of hexagonal nets (Figure ??) \([8, 9]\). The carbon atoms lie in 2D planes, allowing for the intercalation of lithium cations as well as a host of anions.\([10, 11, 12, 9]\) Crystalline graphite comes in two forms: hexagonal, where every other sheet is transposed to form an \(ABAB\) stacking, and rhombohedral, which follows an \(ABCABC\) stacking order \([13]\). Stacking order is found to have a negligible effect on both capacity and operating voltage since the planes shift into an \(AA\) stacking order during lithium insertion \([13]\). Upon the complete lithiation of
graphite \((\text{LiC}_6)\) the graphene interplanar spacing increases by 10.5\% to accommodate for the lithium ion, from \(d=0.335\text{nm}\) to \(0.3706\text{nm}\) \cite{14}. The benefit of graphitic materials, is that any lithium inserted into the lattice can be subsequently and completely removed. The fully reversible electrochemical reaction can be written as:

\[
\text{C}_6 + x\text{Li}^+ + xe^- \leftrightarrow x\text{LiC}_6
\]  

where \(0 < x < 1\). Even after the insertion and extraction of lithium from the lattice, the hexagonal crystalline structure of graphite remains intact. The stability of the structure makes graphite the ideal electrode active material.

2.3.2 Issues

Graphite is easily marketable for use in low power, small scale electronics. Unfortunately, graphite suffers from a host of issues preventing it’s implementation into larger scale applications such as hybrid-electric (HEV) and plug-in hybrid-electric vehicles (PHEV).

2.3.2.1 Reactivity

Theoretically, the intercalation of lithium into graphite is completely reversible making it attractive as an anode material in lithium batteries. However, during the first electrochemical cycle graphite exhibits a Coulombic Efficiency of only 90\%. During the first insertion (formation) into graphite, the carbon electrode is covered with a passivat-
ing layer called the solid electrolyte interphase (SEI) [15]. Aurbach identified that the formation of the SEI is caused by the reduction reaction between the liquid electrolyte and the carbon surface. Dolle et al. found SEI growth to be self-limiting up to $x=0.5$ for $\text{Li}_x\text{C}_6$ [15]. After complete formation, the SEI prevents further electrochemical reduction on the graphite surface. The passive layer helps to protect the graphite surface from HF and water attack but is comprised of lithium bearing compounds ($\text{Li}_2\text{CO}_3$, $\text{Li}_2\text{O}$, $\text{LiOH}$, $\text{LiF}$, and $(\text{ROCO}_2\text{Li})_2$) [16]. Since lithium cannot be removed from the SEI, a the low Coulombic efficiency seen during the first cycle of graphite. The actually SEI composition depends upon the choice of electrolyte.

For the case of propylene carbonate (PC), the solvent can co-intercalate with lithium leading to graphite exfoliation [9, 17]. Upon entering the lattice the solvent decomposes into unstable and gaseous compounds [18]. The expansion of the d-spacing becomes so severe that individual sheets of graphene peel from the bulk material [19]. When used as an active material for lithium batteries, however, exfoliation removes available active material and sites for lithium storage. While exfoliation can be prevented by using different solvents, it limits the possible electrolyte choices.

### 2.3.2.2 Purification Cost

Natural graphite is attractive for commercial purposes because it is abundant and cheap. Graphite ore is mined, repeatedly ground and filtered, and finally milled and sieved for commercial sale. Unfortunately, mined ore is typically a mix of different carbon structures, impurities, and uniformity. Impurities and defects can lower the weaken the performance of graphite. While natural graphite is globally abundant, only a limited number of countries have direct access to usable graphite ore. Over 75% of the world’s supply is mined in either China and North Korea [20]. There are no graphite mining operations within the United States.

A locally operated alternative to natural graphite is synthetic graphite. Coal-
based carbons, such as coke and ash, undergo graphitization through high temperature scintering for a lengthy 2-3 weeks (Figure 2.3). Temperature and time can be tailored to create well-ordered, battery grade graphite. Similar heating processes applied to natural graphite may improve the structure but will not remove elemental impurities. The primary benefits of choosing synthetic graphite are the purity (carbon ≥99.9%), the ability for local synthesis, and the crystallinity desired for reversible intercalation. The major drawback, is that scintering increases the production cost of synthetic graphite to nearly 20 times that of natural graphite [21]. Trends also indicate that the price of graphite will continue to rise with the proliferation of lithium ion batteries [21].

2.3.2.3 Limited Capacity

The most important and the most detrimental property of graphite for vehicular technology is the limited gravimetric and volumetric energy storage capacity. Even though a carbon atom is light compared to metal atoms, it requires at least six carbons to store a single lithium (corresponding to a gravimetric capacity of 372 mAh g$^{-1}$ and a volumetric capacity around 800 mAh cm$^{-3}$). Heavier metal oxides, as depicted in Figure 2.4, are advantageous as one mole can accommodate between 2 and 5 moles of lithium.
Figure 2.4: Operating voltages and capacities for a variety of possible anode materials (Courtesy of Dr. Yoon Seok Jung)
It is important to note that while capacity \( (Q) \) is a measurement for the number of lithium stored, the energy capacity is defined by,

\[
E = nqV = QV
\]  \hspace{1cm} (2.15)

\( q \) represents the charge associated with a single electron \( (1.602 \times 10^{-19} \text{ C}) \) while \( n \) is the number of electrons stored. Each electron is accompanied by a single lithium ion, so for all intensive purposes, \( n \) is also equal to the absolute number of lithium. Therefore, changes in operating voltage become equally as important as lithium storage capacity.

### 2.3.3 Graphite Alternatives

#### 2.3.3.1 Silicon Nanostructures

Silicon and silicon-containing alloys are one of the most popular graphite substitutes for anode active material in lithium ion batteries. Lithium-alloy anodes have been long explored due to the high packing density \([22]\). The benefit of silicon is that it undergoes an alloying process (Eq. 2.16 \([23]\)) during lithium insertion, allowing it to attain over 10x the gravimetric capacity of graphite \( (Q_{\text{silicon}}=4200 \text{ mAh g}^{-1}) \).

\[
xSi + yLi^+ + ye^- \rightarrow Li_ySi_x
\]  \hspace{1cm} (2.16)

Table 2.3.3.1 displays compositional alloys of silicon and lithium and volume of the formed unit cell. Notice that in a fully lithiated state of \( \text{Li}_{22}\text{Si}_5 \), the volume of the unit cell increases by nearly 400% (strain = 45%). This large and destructive volume change causes silicon pulverization, a loss of electronic contact and pathways, and large irreversible capacities \([24]\). The structural changes are recorded by J.R. Dahn using both in situ atomic force microscopy (AFM) and time-lapse optical microscopy \([25]\). With a state-of-the-art experimental setup, Dahn observed the first cycle crack formation on a silicon thin film, noting that the film was impervious to fracture up to a 100% change volume. Different methods have been proposed to accommodate for the large changes in volume while maintaining the high theoretical capacity of silicon.
Table 2.1: Cell structure and volume of Li-Si Alloys [26]

<table>
<thead>
<tr>
<th>Compound and crystal structure</th>
<th>Unit cell volume ($\text{Å}^3$)</th>
<th>Volume per silicon atom ($\text{Å}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon cubic</td>
<td>160.2</td>
<td>20.0</td>
</tr>
<tr>
<td>$\text{Li}_{12}\text{Si}<em>7$, ((\text{Li}</em>{1.71}\text{Si})) orthorhombic</td>
<td>243.6</td>
<td>58.0</td>
</tr>
<tr>
<td>$\text{Li}_{14}\text{Si}<em>6$, ((\text{Li}</em>{1.71}\text{Si})) rhombohedral</td>
<td>308.9</td>
<td>51.5</td>
</tr>
<tr>
<td>$\text{Li}_{13}\text{Si}<em>4$, ((\text{Li}</em>{3.25}\text{Si})) orthorhombic</td>
<td>538.4</td>
<td>67.3</td>
</tr>
<tr>
<td>$\text{Li}_{22}\text{Si}<em>5$, ((\text{Li}</em>{4.4}\text{Si})) cubic</td>
<td>659.2</td>
<td>82.4</td>
</tr>
</tbody>
</table>

2.3.3.2 Conversion Reaction Metal Oxides

While not as high in capacity as fully lithiated silicon, transition metal oxides which store lithium by undergoing a conversion reaction are extremely promising anode materials. Most transition-metal have been extensively explored as an anode, where lithium simply intercalates into crystal vacancies [27, 28]. These 3D structures would typically operate above 1.5 V and are considered low voltage cathodes [28, 29]. As an intercalation compound, metal oxides generally held no advantage over graphite or $\text{LiCoO}_2$. However, in 2000, Poizot et al. reported on the electrochemical advantages of nano-sized transition metal oxides when discharged down to 0 V [30]. Unlike traditional insertion and alloying mechanisms as described for Si and graphite, below 1.0 V select metal oxides undergo a conversion reaction where lithium is stored in the reversible form of $\text{Li}_2\text{O}$ while the metal oxide, $\text{MO}$, becomes elemental metal, $\text{M}$. The reaction is written as the following equation [30]:

$$2\text{Li} \rightleftharpoons 2\text{Li}^+ + 2e^-$$

$$\text{MO} + 2\text{Li}^+ + 2e^- \rightleftharpoons \text{Li}_2\text{O} + \text{M}$$

$$\text{MO} + 2\text{Li} \rightleftharpoons \text{Li}_2\text{O} + \text{M}$$

Common transition metal oxides which adhere to Eq. 2.17 are $\text{Fe}_2\text{O}_3$ [31], $\text{Fe}_3\text{O}_4$ [31], $\text{Co}_3\text{O}_4$ [32], $\text{CoO}$ [33], $\text{MoO}_3$, and $\text{Cr}_2\text{O}_3$ [34]. Tarascon discovered through electrochemical and XRD data that an intermediate lithium-metal oxide phase forms prior
to the complete conversion to Li$_2$O [32]. Since a significant portion of the volume expansion occurs during the phase change to Li$_2$O, Tarascon surmises that the material synthesis and electrochemical testing parameters can be optimized to help improve the overall performance and stability of the anode. Upon the completion of the conversion reaction, transition metal oxides exhibit capacities greater than that of graphite making it an attractive replacement.

However, as explained by Malini et al, there exists significant issues, when compared with graphite, which need to be fully addressed before conversion reaction transition metal oxides enter commercial battery applications [35].

(1) Slower kinetics and larger polarization

(2) Low capacity retention compared

(3) High operating voltage

(4) Irreversible first-cycle capacity loss

(5) Poor rate capability

(6) Large hysteresis

(7) Low Coulombic efficiency

It is important to note that the enumerated list is a comparison between metal oxides and graphite anodes. Metal oxides actually perform significantly better than the popular silicon anodes. When compared to silicon, transition metal oxides have a greater capacity retention, lower irreversible capacity losses, better rate capability, and higher Coulombic efficiency. Chapters 6 and 7 will discuss methods to address many of the issues of metal oxide anodes.
2.4 Metal-Oxide Cathodes

2.4.1 Crystalline Structures

Lithium-bearing, metal oxide cathodes can be grouped as supporting 1D, 2D, or 3D motion of lithium within the structure (Fig. 2.5). Table 2.4.1 provides some examples of structures and materials for each framework. In a 1D structure, such as $\alpha$-MnO$_2$, lithium ions diffuse linearly through channels [36]. 1D channels are undesirable since the passageways are easily blocked by crystal defects, preventing the reversible storage of lithium. 2D-layered structures, such as LiCoO$_2$, allow for the diffusion of lithium within a plane, while lithium ions in 3D spinel-type structures are free to move in all directions.

Table 2.2: Examples of common cathode materials for a given structural framework for lithium diffusion.

<table>
<thead>
<tr>
<th>Framework</th>
<th>Structure</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>Channel</td>
<td>$\alpha$-MnO$_2$</td>
</tr>
<tr>
<td>2D</td>
<td>Layered</td>
<td>LiMO$_2$ ($M=V, Cr, Co, Ni$)</td>
</tr>
<tr>
<td>3D</td>
<td>Spinel</td>
<td>LiFePO$_4$, LiMn$_2$O$_4$</td>
</tr>
</tbody>
</table>
2.4.2 Electrochemical Properties

The most commercially common and historically popular cathode is layered LiCoO$_2$. The unit cell of LiCoO$_2$ is hexagonal ($R3m$) with alternating layers of lithium and cobalt between layers of oxygen as seen in Figure 2.6 [37, 38]. This form of LiCoO$_2$ is also called HT-LiCoO$_2$ as it is synthesized at high temperatures (800 °C). The structure is 2D where both the lithium and the cobalt sit in interstitial octahedral sites. Even though graphite and LiCoO$_2$ are both considered to be layered, their electrochemical properties differ significantly. Lithium within LiCoO$_2$ is not as strongly held to the oxygen layers as the cobalt. The removal of the lithium results in the formation of stronger Co-O covalent bonding. After half of the lithium is removed, the structure of LiCoO$_2$ destabilizes from hexagonal to monoclinic [39]. The structural change prevents the reversible reinsertion of lithium into the cathode. Therefore, while the theoretical capacity of LiCoO$_2$ is 273 mAh g$^{-1}$, only half of that capacity is reversible [39].

A 3D form of LiCoO$_2$ is possible through low temperature synthesis and is commonly referred to as LT-LiCoO$_2$ [39]. Below a solid state reaction synthesis temperature of around 400 °C, LiCoO$_2$ displays a cubic ($Fd\bar{3}m$) spinel-type structure as depicted in Figure 2.5-c [38]. Due to the structural differences between LT and HT-LiCoO$_2$, the voltage plateaus are 3.6 V and above 4.0 V, respectively [40]. However, the spinel-type LT-LiCoO$_2$ also suffers from irreversible lithium extraction below Li$_{0.5}$CoO$_2$.

2.4.3 Issues

2.4.3.1 Toxicity and Availability

Largest concerns in widely using LiCoO$_2$ as a cathode material are the high cost and the extreme toxicity of cobalt compounds [41]. Cobalt is an “essential” element that is found in the human body in the form of vitamin B$_{12}$ [42]. Radioactive isotopes (Co-58 and Co-60) are also used in nuclear power plants [43]. While non-radioactive
Figure 2.6: Crystal structure of the layered form of LiCoO$_2$ [37].
metal cobalt is not a cumulative toxin, increased health risks due to inhalation and skin absorption have been shown in laboratory tests and factory workers [42]. Prolonged exposure yielded lesions in both the respiratory and the gastrointestinal tract, with suggested connections to cancer. Figure 2.7 depicts the mass fraction of common elements within the Earth. In addition to being toxic, cobalt is one of the least common transition metal elements available for mining. Between 2001 and 2005, over 50% of the world’s cobalt was produced by the war-torn Congo (Kinshasa) and Zambia [44]. Alternatives such as nickel, manganese, iron, or aluminum reduce health risks, are more abundant than cobalt, and are primarily mined in politically and economically stable countries such as Brazil and Australia.

2.4.3.2 Crystal Stability and Cobalt Dissolution

Dissolution of electrodes occurs when active material is lost to the electrolyte in the form of ions. As lithium is extracted and inserted, small defects and localized oxygen deficiencies can arise [18]. These defects weaken the M-O bondings force. A large polarization at a high potential is able to break the weaken bond, causing the loss of metal ions in the non-aqueous, liquid electrolyte [18]. In LiCoO$_2$, there is a direct correlation between Co-dissolution and capacity fade [45]. As the active material leaches into the electrolyte, fewer interstitial sites will be available for the lithium ions.

Cobalt dissolution can also be expedited by the presence of water in the electrolyte. In solution, water will react with the lithium salt,

$$H_2O + LiPF_6 \rightarrow POF_3 + 2HF + LiF$$

(2.17)

to form hydrofluoric acid (HF) [18]. The excess H$^+$ accelerates the loss of metal ions and the formation of trace water. Like most chemical reactions, dissolution can also be promoted with increased temperature.
Figure 2.7: Elemental content of the Earth’s available resources.
2.4.4 LiMO$_2$ Alternatives

Figure 2.8 shows the capacity and operating voltage for a variety of cathode materials. LiCoO$_2$ exhibits average capacity when compared with other possible materials. Most common alternatives, such as LiFePO$_4$ and LiMn$_2$O$_4$, sacrifice energy density for stability and cost. The ideal LiCoO$_2$ replacement cathode will be cheap and environmentally friendly while improving the total capacity.

Recent investigations for LiCoO$_2$ alternatives are led by transition metal substitution of cobalt. A variety of metals such as nickel, manganese, zinc, aluminum, chromium, and titanium have been extensively studied as a doping agent to form LiCo$_{1-y}$M$_y$O$_2$ [46, 47, 48]. Other studies have implemented a double metal replacement forming compounds such as Li-Ni-Mn-Co-O and Li-Ni-Co-Al-O [49]. It is believed that metal doping improves the structural integrity of the metal-oxide layered and has a stabilizing effect on the overall electrochemical performance [46]. As previously mentioned, LiCoO$_2$ undergoes a highly destructive phase change from hexagonal to monoclinic above 4.2 V. Kim and Chung found that through doping, layered Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ could be charged up to 4.7 V with a first cycle capacity of 250 mAh g$^{-1}$ while maintaining the hexagonal structure [50]. Doped transition-metal oxide materials have also been shown to prevent Li-M interplanar mixing, leading to higher ion kinetics [49].

One of the more promising cathodes is lithium excess materials, or Li[Li-Mn-Ni-Co]O$_2$ (Fig. 2.8). Lithium rich cathodes can reversibly retain up to 75% more lithium than standard commercial LiCoO$_2$. Often refered to as Li$_2$MnO$_3$-stabilized LiMO$_2$ or Li[M$_2$]O$_4$, these higher capacity materials have either a layered-spinel or layered-layered structure. Excess lithium is stored within the metal-oxide layers in the form of Li$_2$MnO$_3$. Up to 4.4 V, the excess lithium layers are normally electrochemically inactive. However, as lithium is extracted from the typical octahedra sites, like in LiCoO$_2$, lithium from the excess layers diffuse into the vacancies, stabilizing the hexagonal layered structure.
Figure 2.8: Operating voltages and capacities for a variety of possible anode materials
(Courtesy of Dr. Yoon Seok Jung)
Furthermore, at potentials above 4.4 V, the excess lithium layers become electrochemical active and the capacity can exceed 280 mAh g\(^{-1}\). A detailed discussion of the structure of lithium excess cathodes can be found in Chapter 9.

Elemental sulfur and sulfur-based compounds theoretically have the highest capacity of known cathode composites. Sulfur is substantially less expensive due to it’s increased availability (Fig. 2.7) than cobalt ($0.12 versus $35 per lbs) and is primarily exported from countries such as Canada and Venezuela [51]. The elemental form of sulfur poses no health risks, though gaseous sulfur bi-products such as SO\(_2\) can lead to pulmonary diseases and asthma [52]. Electrochemically, elemental sulfur is not reversible. Sulfur is a highly reactive substance with poor electronic conductivity. The low order sulfide (Li\(_2\)S\(_2\), Li\(_2\)S) formed during lithium insertion are both highly insulating in nature and soluble in the liquid organic electrolyte [53]. Sulfur has shown the most success when implemented into polymer gel and solid state electrolytes [53, 54].
References


Chapter 3

Recent Developments on Surface Coatings for Lithium Batteries

3.1 Designing Against Failure

Important material properties when designing a lithium ion battery can be split into three categories (Table 3.1): Kinetics, Reactivity, and Structure. Kinetics determine the rate at which processes occur. Reactivity is a measure of the degree of chemical reactions that occur within the battery. Structure defines the operating voltage and capacity but also the phase and volume changes a material may undergo during lithium insertion and extraction. All the design parameters are highly interconnected. For example, the reactivity of the electrolyte can be lowered by using a gel polymer or solid state form, which in turn slow the kinetics of lithium ions. A high capacity material can be chosen for its structure but which may promote thermal runaway with the liquid electrolyte. The take home message is that there is no silver bullet that can address all failure issues found in lithium ion batteries. Each solution will come at a performance cost. The key is minimizing the costs while maximizing the benefits.

A majority of the issues that occur within a lithium battery occur at material interfaces. Referred to as the “electrode-electrolyte interface”, the electrochemical breakdown of the organic electrolyte and the dissolution and decomposition of the active material at the surface is primarily responsible for battery failure. This work focuses on utilizing surface coatings in order to mitigate electrode-electrolyte interaction. Surface coatings have long been used to protect materials from unwanted corrosion or degrada-
Table 3.1: Design parameters for material selection and operating conditions of lithium ion batteries

<table>
<thead>
<tr>
<th>Modes</th>
<th>Factors Affecting Stability</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetics</td>
<td>Viscosity of Electrolyte</td>
<td>$(\eta)$</td>
</tr>
<tr>
<td></td>
<td>Electronic Conductivity</td>
<td>$(\sigma = 1/\rho)$</td>
</tr>
<tr>
<td></td>
<td>Charge-Transfer Reaction</td>
<td>$(R_{ct})$</td>
</tr>
<tr>
<td></td>
<td>Solid State Diffusion</td>
<td>$(t_D = L^2/D)$</td>
</tr>
<tr>
<td>Reactivity</td>
<td>Dissolution</td>
<td>$(k \propto e^{-E/RT})$</td>
</tr>
<tr>
<td></td>
<td>Decomposition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymerization</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exfoliation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thermal Runaway</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Phase and Volume Changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Capacity</td>
<td></td>
</tr>
</tbody>
</table>
tion with the environment. Vehicles are painted to prevent a metal chassis from rusting in the rain. A thin application of Teflon eliminates any high temperature reaction that may occur between the food we cook and the pans we use. Even a coating of sunblock reduces skin exposure to cancer causing solar radiation. It is important that the coating not only protects the surface from a predetermined hazard but allow for the regular use of the object. For example, a garage is an excellent alternative against rust, but the car can no longer be driven when inside the garage. Likewise, non-stick Teflon alternatives are only viable as a coating if they are also non-toxic. A toxic-coating would prevent high temperature pan-food interactions while rendering the food completely inedible. Therefore, a successful lithium battery coating will prevent surface degradation while allowing for continued, regular electrochemical reactions to occur.

3.2 Wet Chemical Coatings

Surface coatings are frequently used to prevent electrode-electrolyte interfacial reactions. Typically, the coatings are grown on powders using a sol-gel method. Sol-gel is considered a wet-chemical technique as it uses a solvent to promote material growth. The process is frequently used in industry for the growth of thin films. The processing flowchart for the synthesis of $\text{Al}_2\text{O}_3$ on $\text{LiCoO}_2$ developed by Park is shown in Figure 3.1 [1]. The metal-organic precursor is dissolved and heated in a basic solution during which evaporation causes the mixture to gel. Active material particles are interdispersed within the gel which is further dried and annealed to remove excess organics. After coating, Park found that the bulk structure of the $\text{LiCoO}_2$ remained intact while the localized surface formed a $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$ solid solution [1].

The sol-gel coating had no adverse effect on the initial capacity or voltage profile, as seen in Figure 3.2. The electrochemical performance results and cycle stability of the sol-gel coated particles were found to be superior to the uncoated particles when cycled up to 4.4 V. Using XRD, Park determined that the coated particles remained in the
Figure 3.1: Schematic flow chart of the fabrication steps used for the sol-gel preparation on LiCoO$_2$ powders
preferred hexagonal phase throughout cycling while the uncoated particles underwent the destructive transition to monoclinic around 4.15 V. The modified LiCoO$_2$ surface also limits the dissolution of cobalt up to 4.5 V due to the Al-doped solid solution [2, 3]. The effects of surface doping are found to occur only during high temperature calcination [2]. A few studies have also looked at surface modifications on natural graphite anode particles [4, 5]. The modified anodes showed electrochemical performance improvements, the studies were unable to verify the thickness, conformity, or role of the modified surface.

While effective, sol-gel and most other chemical deposition processes are limited to coatings on complete particles. Prefabricated composite electrodes consist of active material, conductive additive, and a polymer binder. Due to the low binder melting temperature ($T_m = 250$ C), the electrodes are unable to withstand the high calcination temperatures required in sol-gel. Alternative coating methods such as evaporation or radio frequency (r.f.) magnetron sputtering operate at lower temperatures, but are limited by line-of-sight [6, 7].

3.3 Atomic Layer Deposition

The most promising surface coating technique, and the focus of this study, for lithium ion batteries is atomic layer deposition (ALD). Originally named atomic layer epitaxy in 1977, ALD has only recently been explored as a possible method for battery surface coatings. ALD is a multi-step, self-limiting, chemical vapor deposition (CVD) process. Coatings are grown through the chemical reaction between two or more vapor precursors. ALD allows for the growth of materials not easily synthesized using single step sputtering or evaporation. For example, ZnS films are formed first by the CVD of ZnCl$_2$ followed by H$_2$S [8].

Figure 3.3 depicts a representational schematic of the deposition of Al$_2$O$_3$ on a LiCoO$_2$ particle using a binary reaction sequence [9]. The binary reaction can also be
Figure 3.2: (a) Initial capacities and (b) cycle-life performances of bare and coated LiCoO$_2$ cathodes by sol-gel measured at the rate of 0.5C between 4.4 and 2.75 V in Li/LiCoO$_2$ [1].
written as,

$$\text{AlOH}^* + \text{Al(CH}_3\text{)}_3 \rightarrow (\text{AlO} - \text{Al(CH}_3\text{)}_2)^* + \text{CH}_4 \quad (3.1)$$

$$\text{(AlO} - \text{Al(CH}_3\text{)}_2)^* + H_2\text{O} \rightarrow (\text{AlO} - \text{Al} - \text{OH})^* + \text{CH}_4 \quad (3.2)$$

where (*) denotes surface species. The materials surface is first exposed to a dose of trimethyl alumina (TMA). The methyl groups react with the surface hydroxyls, producing excess CH$_4$ waste. TMA is non-reactive with itself, so the chemical reaction will stop once the surface is fully coated by TMA. After the excess gas is pumped from the system, a water dose is added. The water strips away the remaining methyl groups, leaving behind a stable, hydroxyl terminated Al surface. The TMA-H$_2$O cycle can be repeated until the desired coating thickness is reached. ALD-Al$_2$O$_3$ thin films are amorphous, thermally stable, and generally free of pinholes and other defects [9]. Since ALD reacts directly with the surface, the coating also is inherently conformal by nature. In addition, simple chemistries such as Al$_2$O$_2$ run at low temperatures below 200 C and can be grown onto polymers and polymer-based electrode composites [9, 10].

3.4 Recent Literature Survey of ALD-coating Electrodes

ALD-coatings for lithium ion batteries is still in it’s infancy. Outside of works covered by this dissertation, only two papers have been published on the use of ALD on cathodes and electrodes.

3.4.1 Alumina on LiCoO$_2$

Initial studies of ALD coated battery materials were performed on LiCoO$_2$ micron-sized powders. Alumina was grown on the particle surfaces using a rotary reactor as described in §5 following the 2-step process shown in equation 3.2. Electrodes were cycled between 3.3 and 4.5 V (vs Li/Li$^+$) with a composition of 83.0:7.5:9.5
Figure 3.3: Schematic representation of single ALD cycle [9]
(LiCoO$_2$:AB:PVDF).

Results from 2-, 6-, and 10-layers of Al$_2$O$_3$ are shown in Figure 3.4. Bare LiCoO$_2$ (open circles) samples display a rapid capacity fade which can be attributed to cobalt dissolution and material degradation due to HF attack. It is important to note that the results were obtained without a high temperature anneal. A dramatic increase to the overall capacity retention and cycling stability are visible after only 2 layers of ALD. XPS verified that the 2-Al$_2$O$_3$ has a thickness of 3-4 angstroms.

The most striking improvement with the growth of ALD on the particle surfaces is seen in electrochemical impedance spectroscopy (EIS). Shown in Figure 3.5, each plot consists of two semi-circles. The first semi-circle, labeled with (#), represents the solid electrolyte interphase formed during cycling. The second, labeled with (*), represents the charge-transfer resistance ($\Omega_{ct}$) across the electrolyte/electrode interface. By the 10th cycle, the bare $\Omega_{ct}$ increased ten-fold while the ALD-coated particles exhibited little to no changes in the interfacial stability. These results are impressive given the ultrathin coating thickness and lack of high temperature heat treatment normally required for wet-chemical methods.

3.4.2 Alumina on Graphite

Given the success of ALD-Al$_2$O$_3$ on LiCoO$_2$, Jung made similar attempts using natural graphite [12]. As mentioned earlier, synthetic commercial-grade graphite is extremely pure and extremely expensive. The high temperature synthesis makes it unattractive compared to the cheaper, more abundant natural graphite. By applying a thin, 5-layer coating of amorphous alumina to the surface of the electrodes, Jung et al. achieved synthetic-like performance from cheap, natural graphite (3.6-a). ALD coatings applied directly to the graphite powders were unsuccessful and yielded degraded

\[1\] This author contributed towards the ALD-graphite work published in *Advanced Materials*. A copy of the published paper is included in Appendix B.
Figure 3.4: Charge-discharge cycle performance of electrodes fabricated using the bare LiCoO$_2$ powders of the Al$_2$O$_3$ ALD-coated LiCoO$_2$ powders using 2, 6, and 10 ALD cycles [11].
Figure 3.5: Series of mass-normalized impedance spectra for electrodes fabricated with bare and Al₂O₃ ALD-coated LiCoO₂ powders for various charge-discharge cycle numbers. [11].
performance results.

Graphite composite electrodes contain no additional carbon conductive additives. Therefore, when each individual particle is coated with an insulating layer of alumina, the graphite flakes becomes electrically isolated (Figure 3.6b). Direct ALD on prefabricated electrodes ensures proper physical contact and electrical pathways are established prior to coating. Evidence of ALD coverage throughout the porous electrode was confirmed using a focused ion beam (FIB) and energy dispersive X-ray spectroscopy (EDS).

The key to the ALD process is the reaction between the first vapor precursor and the hydroxyl-terminated surface. However, graphite lacks the OH-terminated surfaces along the basal planes (Fig. 2.2). Lacking OH-terminations the ALD precursors are chemically inert with the graphite surface. To counter the issue a group at Harvard exposed chemically inert carbon nanotubes (CNTs) with nitrogen dioxide (NO₂) where the NO₂ binds to the surface through physical adsorption [13]. The NO₂ coated carbon is then exposed to the typical Al₂O₃ binary reaction sequence. Since NO₂ readily reacts with TMA, the physical adsorption gas layer acts as nucleation sites for the alumina coating [13, 14]. The high conformal nature of the NO₂-functionalized alumina prevents the formation of an SEI (Fig. 3.6c) and increases the Coulombic efficiency (Fig. 3.6).

To verify the conformal nature of ALD-Al₂O₃ on graphite, Jung cycled a natural graphite electrodes in propylene carbonate\(^2\). The voltage profile in Figure 3.6e for bare natural graphite in PC exhibits signs of exfoliation and solvent cointercalation. The NO₂ functionalization protects the graphite surface from the electrolyte-electrode interaction, allowing graphite to reversibly cycle in PC.

### 3.5 Selection of Coating Material

Selection of a surface coating directly depends on the role of the coating. For materials with poor electronic conductivity, carbon coatings and matrices are commonly

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\(^2\) Graphite in propylene carbonate will lead to exfoliation, as described in §2.3.2.1
Figure 3.6: Electrochemical performance for ALD coated NG composite electrodes. a) Cycle performance. b) Schematic representation transport in NG composite electrodes prepared by ALD on powder and ALD directly on the electrodes. c) Differential first charge voltage profiles at room temperature. d) Coulombic efficiency at the first charge-discharge cycle. e) Voltage profiles at RT in PC electrolyte.
chosen to promote electron transport [15, 16, 17]. By improving electron kinetics within the electrode, the rate capability of active materials such as LiFePO₄ significantly improve while adding minimal cost and weight to the system.

Surface coatings are also chosen to protect from unwanted electrolyte/electrode surface interactions. Material loss such as dissolution and breakdown such as decomposition are commonly prevented using inert metal oxides. Using a wet-chemical method, LiCoO₂ was coated with ZrO₂, Al₂O₃, MgO, ZnO, and Li₂O-2B₂O₃ and electrochemically compared to bare, uncoated LiCoO₂ [18]. The authors found that the surface modified samples outperformed the bare in the order of ZnO = Al₂O₃ > Li₂O-2B₂O₃ > ZrO₂ > MgO for capacity increase. Studies of ultrathin ALD-ZnO surface films on LiCoO₂ were shown to be ineffective at preventing capacity fade, however [11]. This result seemed to be in direct contradiction with earlier work by Cho et al. who surmised that a higher fracture toughness would improve material stability [19]. In decreasing order of fracture toughness, the surface coatings can be written as ZrO₂ > Al₂O₃ > TiO₂ > B₂O₃ > SiO₂ [19].

This work focuses on coating two materials. The first is high energy density, high volume expansion MoO₃. The second is a high operating voltage commercial quality Li-Mn-Ni-Co-O. Based upon the previous literature studies of various metal oxide coatings, and the questionable electrochemical stability of ALD-ZnO thin films, Al₂O₃ is used as the coating choice throughout this dissertation.
References


Chapter 4

Discrepancies Regarding Electrochemical Diction

There exists no standardized method for reporting electrochemical capacities. For example, storage capacity can be normalized to mass (mAh g$^{-1}$), electrode area (mAh cm$^{-2}$), or electrode volume (mAh cm$^{-3}$). Commercial, large scale results on the other hand tend to report the absolute capacity (Ah) while others will only publish $x_{Li}$, making values difficult for comparison. As an additional variable, batteries are also comprised of an array of inactive, supporting materials, such as binder, conductive agents, wiring and housing, etc. Reported capacities may include or exclude the non-active material. For uniformity, this work will report specific capacities as a function of mass (mAh g$^{-1}$) normalized to the active material mass, unless otherwise stated. While the exclusion of supporting agents yields an inaccurate measurement of the actual capacity of the battery, the purpose of this research is to focus on the fundamental science to analyze and improve materials for energy storage, not for the commercial production and sale of lithium batteries.

As described, the fundamental electrochemical processes are oxidation and reduction which occur at surfaces of opposing electrodes. However, since the oxidation at one electrode infers a reduction at the counter electrode, it becomes convenient to refer to the electrochemical relative to a counter electrode. While the commonly used terms in the field of electrochemistry are charge and discharge, few consistencies within the literature can be found as to their proper use. Electrochemists may assign the labels
anode and cathode to electrodes based on desired use, rather than the electrochemical reactions. This becomes particularly confusing since the a single electrode will, by definition, undergo both a *cathodic* reaction when lithium is inserted and an *anodic* reaction when lithium is extracted.

In order to mitigate any confusion when discussing half cells, the following definitions will be used:

- **Lithiation** - Electrochemical insertion or intercalation of lithium into a crystal structure
- **Delithiation** - Electrochemical extraction or deintercalation of lithium from a crystal structure
- **Anode** - Electrode for which oxidation is spontaneous in a full cell
- **Cathode** - Electrode for which reduction is spontaneous in a full cell
- **Discharge** - Spontaneous electrochemical processes ($\Delta G < 0$)
- **Charge** - Nonspontaneous electrochemical processes ($\Delta G > 0$)

An often misunderstood and equally as confusing concept is the direction of current flow. Historically, the direction of *electric current* was defined to be from cathode to anode, following the flow of protons. In reality, the electrons are what actually flow through electric circuits, not protons, and do so in the *opposite* direction of electric circuit. For all intensive purposes, the historical and outdated definition for the direction of current flow is cumbersome and ineffective at clearly describing the battery kinetics. Therefore, for this work, *discussions* of current will follow the flow of electrons. Any calculations or mathematical analysis will adhere to the historical convention.

A commercially popular, and regularly misused, electrochemical terminology is current rate or *C-rate*. Broadly, C-rate is defined as the current necessary to charge (or discharge) an electrode to its theoretical capacity within a given period of time. For

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1. In 1834, following the previous designation of Benjamin Franklin, Michael Faraday published *On Electrochemical Decomposition* where he wrote, “The cathode is that surface at which the current leaves the decomposing body, and is its positive extremity.”

2. The use of the historical, and backwards, definition for current is unavoidable in calculations since all physics and mathematical theorems on the electrochemical process for the last 150 years are based upon the flow of protons.
example, a C-rate of C/10 indicates that, theoretically, the complete electrochemical process will take 10 hours, while 10C indicates 6 minutes. C-rate is not a measure of the actual time for the cell to charge and discharge, though it can be. There are a number of fundamental issues with the use of C-rate. First, for a given material with a capacity $Q_{\text{max}}$, determination of C-rate is based only upon the desired charge/discharge time. C-rate cannot account for the diffusion of lithium, the charge-transfer resistance, or the possible alteration of the electrode surface. While C-rate is a close approximation for well-known materials such as graphite, it becomes extremely inaccurate when compared to the actual reaction time for electrochemically volatile materials such as silicon. Second, $Q_{\text{max}}$ is a function of the reversible capacity of the material. In the case of LiCoO$_2$, not all of the lithium can be reversibly extracted and inserted, so the C-rate is calculated with a $Q$ of 170 mAh g$^{-1}$ which is less than half of the lithium present in the structure. Third, the actual reaction time is not symmetric – the insertion time can be drastically different than the extraction time.

As a solution, current density, (mA g$^{-1}$), will be used unless otherwise stated within each chapter. The corresponding theoretical C-rate will also be provided, but only in order to facilitate data comparison. Since current density is an independently defined variable, it is more accurate than C-rate, which depends upon time and theoretical capacity.
Chapter 5

Methods and Theory

This chapter presents the methods and scientific theory for synthesis, material characterization, and electrochemical testing. Material and case specific values, such as current density and specific electrode composition, will be provided in each chapter along with a reference to the experimental section included below. The methods included in this chapter are universal. Experimental methods which are unique to one material or to one experiment will be presented in the appropriate chapter.

5.1 Material Synthesis and Electrode Fabrication

5.1.1 Hot-Wire Chemical Vapor Deposition (HWCVD)

Molybdenum trioxide (MoO$_3$) nanoparticles are synthesized using a hot-wire chemical vapor deposition system (HWCVD). Traditionally, the HWCVD chamber is filled with gaseous precursors, such as NH$_3$ or SiH$_4$, and heated with a tungsten (W) or tantalum (Ta) filament [1]. At elevated temperatures, the precursors will grow on the surface of a substrate, forming a thin film. The rate and uniformity of nucleation can be controlled through variation of chamber pressure and temperature and through additives such as HCl. HWCVD is commonly used for the deposition of crystalline and polycrystalline thin films for high efficiency solar cells. Unlike traditional HWCVD, where the filament acts as a passive catalyst, the nanoparticle MoO$_3$ is formed through direct filament oxidation.
The HWCVD setup (depicted in Figure 5.1) consists of a 5 cm diameter 70 cm long quartz tube enclosed in a clamshell furnace. A 0.5 mm thick Mo metal wire is tightly coiled and then stretched between two terminals, similar to the filament inside a incandescent light bulb. The quartz chamber is filled with a stagnant atmosphere of O$_2$ and Ar at 75 Torr (13% O$_2$). The Mo filament is then resistively heated with a constant current of 15 A and a clamshell temperature of 300 °C. In the presence of O$_2$, the Mo filament is deliberately oxidized and a metal oxide powder collects along the walls of the chamber. An in-depth study by Dillon et al. identified the ideal operating parameters to achieve uniform nanoparticles between 10 and 50 nm [2].

5.1.2 Combustion Synthesis

The reactants are measured out according to the reaction:

\[ \text{LiNO}_3 + \frac{1}{3}\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O} + \frac{1}{3}\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} + \frac{1}{3}\text{Mn(NO}_3)_2 \cdot 6\text{H}_2\text{O} + 1.5 \cdot \frac{7}{24}\text{C}_{12}\text{H}_{22}\text{O}_{11} \]

The nitrates are placed in a large dish and melted together with stirring in an
inert atmosphere. The mixture is allowed to cool and solidify and is then ground into a paste. The sucrose is added along with a small amount of water to facilitate mixing. The final mixture is a thick, red syrup. The mixture is combusted in one of two ways. The mixture, in a shallow dish, is introduced into a 300 °C furnace or the mixture, in a beaker, is introduced into a preheated 300 °C beaker heating mantle. The volume of the dish or beaker must be many times larger than the volume of the syrup. The dish or beaker is covered with a larger beaker up-ended on supports. All combustion is performed with appropriate exhaust handling. After a few minutes the mixture combusts, the power to the furnace or mantle is terminated, and the setup is allowed to cool. The resulting fine, dark brown powder is collected and annealed for 22 hrs at 700 °C (900 °C) (heating rate of 5 °C/min).

5.1.3 **Electrode Fabrication**

Thick film composite electrodes are made from the following three ingredients: 1) An active material (AM) which acts as the storage site for lithium. 2) Acetylene black (AB), a conductive agent which is added to promote the conduction of electrons within composites. 3) Polyvinylidene fluoride (PVDF), a non-reactive polymer binder used to improve adhesion between particles. The AM and AB are first ground in a mortar and pestle until uniformly mixed. After the PVDF is fully dissolved in n-methylpyrrolidone (NMP), the AM/AB powder is added, along with excess NMP, until a desired viscosity is achieved. To prevent the adsorption of water, the composite is mixed within an argon environment. After at least 30 minutes of continual hand-mixing, the slurry is then removed from the glove box and mechanically spread using a notch bar onto a thin, foil current collector. Cathode materials are spread onto aluminum (Al) and anode materials are spread onto copper (Cu). Both sides of the foil are cleaned with acetone and are free from any noticeable bends, wrinkles, or blemishes. Once the slurry is spread onto the foil, excess NMP is removed by electrode drying for 1 hour at 80 °C in air.
Thin film, binderless and conductive additive-free electrodes are fabricated using an electrophoresis deposition process (EDP) [2]. A solution of 20 mg powder and 50 mL methanol were sonicated for 5 minutes to achieve uniform particle suspension. Two stainless steel electrodes were placed 10 cm apart and a voltage of 300 V was applied for one minute. Particle deposition occurs on the negative electrode.

5.1.4 Atomic Layer Deposition (ALD)

Thin conformal surface coatings were grown on both high surface area particles and porous composite electrode described in §5.1.3 using atomic layer deposition (ALD). ALD on powders was performed using a rotary ALD reactor as described by McCormick in Ref. [3]. A schematic of the rotary reactor is shown in Figure 5.2.

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 in §5.1.5 using the ALD-coated particles as active material. For electrode coatings, first the electrode was made as described in §5.1.3. Then, ALD films were grown directly on composite electrodes. The composite electrodes are porous, therefore the internal surfaces are accessible to the ALD precursors.

The Al$_2$O$_3$ ALD reaction sequence was: (1) Trimethylaluminum (TMA) dose to 1.0 Torr; (2) TMA reaction time; (3) evacuation of reaction products and excess TMA; (4) N$_2$ dose to 20.0 Torr; (5) N$_2$ static time; (6) evacuation of N$_2$ and any entrained gases; (7) H$_2$O dose to 1.0 Torr, (8) H$_2$O reaction time; (9) evacuation of reaction products and excess H$_2$O; (10) dose N$_2$; (11) N$_2$ static time; and (12) evacuation of N$_2$ and
Figure 5.2: Experimental setup for atomic layer deposition processes. The apparatus consists of (A) a porous stainless steel cylinder for powder coating (B) with a load lock door, connected to a (C) rotor to agitate the powder. Sensors and operational equipment include (D) a capacitance manometer, (E) a series of pneumatic and (F) needle valves, as well as (G) gate valves and (H) a vacuum pump.
any entrained gases. This sequence constitutes one cycle of Al₂O₃ ALD. The reactor temperature was 180°C.

5.1.5 Coin Cell and Open Cell Architecture

Unless otherwise stated, all thick film electrodes are tested in a typical 2032 coin cell architecture. Electrodes are punched to 1/2" diameter and then vacuum dried at 120 °C before entering the glove box. All anodes undergo additional in-glove box heat treatment, which will be discussed in detail in Chapter NUM. Lithium foil, 9/16” diameter punch, is used as a counter electrode for half cell tests. Electrodes are physically isolated by a thick, porous silica separator and a liquid organic electrolyte of 1 M LiPF₆ in 1:1 EC:DMC (wt. ratio) is used for the fast ion transport through the silica.

Electrode thin films, grown by electrophoresis (Sec. 5.1.3), are tested in an open cell configuration. In an open cells, the two electrodes are suspended in 50 mL 1 M LiPF₆ in 1:1 EC:DMC (wt. ratio) liquid organic electrolyte. Similar to coin cells, a strip of lithium foil is used as the counter electrode. Due to the large physical gap and the vertical orientation of the electrodes, no separator is needed. While electrochemical testing procedures remain the same for both coin and open cells, open cells are required to remain inside the glove box during testing in order to prevent unwanted exposure to air.

5.2 Material Characterization

5.2.1 X-Ray Diffraction (XRD)

A Scintag TPS 4-cycle Gonionmeter (45 kV, 36 mA) with an LN₂-cooled Ge X-ray detector is used to determine phase, degree of crystallinity, and primary crystallographic orientation. MoO₃ powder samples were mounted onto a stainless steel substrate using electrophoresis as described in Sec 5.1.3 and then further annealed for 2.5 hours at 300
°C. All other samples were mounted to a holder using double sided tape. Scans are taken from 10 to 120 ° at a rate of 0.1 °/min with a step size of 0.05 °.

There are two mechanisms for the scattering of incident X-rays that occur by a crystal lattice, depicting the inherent wave-particle duality nature of radiation. The first is the semi-elastic collision, and subsequent transfer of momentum between photons and atoms, also known as Compton scattering. The second is the absorption and re-emission of radiation from the forced vibration of electrons, commonly known as Thomson scattering\[4, 5\]. While both occur to some degree, Thomson scattering is the dominate contributor to the identification of crystalline structure.

Incident X-rays are comprised of of orthogonal electric (E) and magnetic (B) fields. The E field induces the acceleration of electrons according to

\[
\mathbf{F} = \mathbf{E}q_0
\]

(5.1)

where a charge particle \(q_0\) is accelerated by a force, \(\mathbf{F}\). From Maxwell’s equations a moving charges as in the form of a current, \(\mathbf{J}\), can then produce both changing (E) fields and (B) fields [6].

\[
\nabla \times \mathbf{B} - \mu_0 \varepsilon_0 \left[ \frac{\partial \mathbf{E}}{\partial t} \right] = \mu_0 \mathbf{J}
\]

(5.2)

The phase of the emitted electromagnetic field is directly related to phase of the incident electromagnetic field. For free electrons, the phase between the incident and emitted radiation is \(\pi\) [5]. In a complex lattice, radiation emitted from each atom then interferes with all other surrounding atoms producing a similar effect as a diffraction grating. Even though radiation scatters in all directions, the planar spacing of the crystal determines the angle of constructive interference. The constructive angle of scattering is said to follow Bragg’s Law:

\[
2dsin\theta = \lambda
\]

(5.3)
where $d$ is the atomic spacing, $\theta$ is the constructive scattering angle, and $\lambda$ is the radiation wavelength [5]. Since $\theta_{\text{incident}} = \theta_{\text{reflection}}$, measurements are recorded as a function of $2\theta$.

### 5.2.2 Raman Spectroscopy

Unlike XRD (§5.2.1), Raman Spectroscopy measures the frequency of photons inelastically scattered from molecular structures, following the particle nature of light [7]. In general, the rotational and vibrational motion of diatomic molecules can be described as being quantized, in that each mode corresponds to a discrete energy level.

The available energy states are defined by [4]

$$E_{\text{rotational}} = \frac{\hbar^2}{2I} r(r + 1)$$  \hspace{1cm} (5.4)

$$E_{\text{vibrational}} = (\nu + 1/2)h\nu_0$$  \hspace{1cm} (5.5)

where $r$ and $\nu$ are the rotational and vibrational quantum numbers, respectively.

When the incident radiation collides with a molecule, there will be a partial transfer of energy between the photon and the molecule. The transfer of energy needs to correspond to one of the possible discrete values as defined by Eq. 5.4 and 5.5. The scattered photon leaves a molecule with a different energy and therefore a different frequency, $\nu_{\text{scattered}}$.

The change in frequency ($\Delta\nu$), where $\Delta\nu = \nu_{\text{incident}} \pm \nu_{\text{scattered}}$, is known as a Raman shift [8]. Note that the energy can be transferred either to or from the photon. Energy transfered from the photon to the molecule, $\Delta\nu > 0$, is called Stokes scattering, while energy transfered to the photon, $\Delta\nu < 0$ is called anti-Stokes scattering. For fully elastic cases where no energy is transfered, $\Delta\nu = 0$, the process becomes Rayleigh scattering [7].
5.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

Nicolet 510 FT-IR Spectrometer was used to collect Fourier transform infrared (FTIR) spectroscopy data. Due to the opacity of the electrodes, the reflectivity of the samples was measured using a single beam method. Powders were tested... add some more detail here. Excess $\text{H}_2\text{O}$ and $\text{CO}_2$ was purged with nitrogen for at least 20 minutes prior to background collection in order to minimize signal contamination. The spectrometer was run at an average of 128 scans between 4000 and 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

IR is the sister method to Raman Spectroscopy (§5.2.2). Rather than track the frequency shift of scattered radiation, IR varies the radiation frequency and tracks the absorption at each frequency. Each frequency, $\nu$, corresponds to a discrete energy, $E$, by [4]

$$E = h\nu \quad (5.6)$$

Since all possible molecular modes are quantized (§5.2.2), each mode will absorb very specific frequencies of radiation as seen by Eq. 5.4 and 5.5, while other frequencies will be transmitted. Fourier transform IR differs from traditional IR only in the data acquisition method. Traditional IR directs a single beams of radiation, set to a single frequency. Absorption measurements are recorded, and the beam frequency is changed. This processes is completed until a full range of measurements is collected. For FTIR, all radiation between an upper and lower frequency limit are directed into a sample simultaneously. A time delay is introduced using a Michelson interferometer and a Fourier transform is used in order to relate the intensity of the signal to the appropriate frequency.
5.2.4 Brunauer-Emmett-Teller (BET) Adsorption

A computer controlled Autosorb-1 cooled to 75.7 K by liquid nitrogen (LN₂) is used to determine material surface area. A predetermined, small volume of nitrogen (N₂) gas is titrated into the system and the pressure is allowed to equalize. The pressure of the system will become stable once the rate of condensation of N₂ is equal to the rate of evaporation of N₂. After equilibrium is reached, the process of titration is repeated as needed. Using the pressure and N₂ titration volume, the surface area is computer calculated using the Brunauer-Emmett-Teller (BET) relationship [9].

\[
\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0}
\] (5.7)

\(v\) is the total volume of gas adsorbed, \(v_m\) is the volume of gas required to cover the entire surface with a uniform monolayer of N₂, \(p\) is the pressure, \(p_0\) is the saturation pressure, and \(c\) is a constant. The BET method is an extension of the Langmuir isotherm, which describes the adsorption and desorption of a single layer of non-polar molecules onto a free surface [10]. During titration, N₂ condenses onto the surface of the material. Once the entire surface is covered by a single layer of N₂, a second layer is adsorbed, completely independent of the first layer [9]. Since previous layers have no bearing on subsequent N₂ layers, the relationship between pressure and titration volume are linear. The linear relationship between \(p/v(p_0 - p)\) and \(p/p_0\) (Eq. 5.7) for a single isotherm is used to determine the volume of an individual adsorbed monolayer, \(v_m\), and in turn the materials surface area (SA) can be calculated from the molar volume of the titrated gas.

5.2.5 Temperature Programmed Desorption

The effects of annealing were examined using temperature programmed desorption (TPD). Electrodes were weighed and placed into a clean custom made tube. The
quartz tube was attached to the TPD and a high vacuum was drawn (10-8 Torr), removing any weakly bound species. After excess water and contaminants were pumped from the vial, the sample was heated from RT to 350 °C at a rate of 50 °/min. A SRS RGA-100 mass spectrometer detected the residual gas concentration desorbed from the sample as a function of temperature. The range of detection was 0-100 a.m.u.

5.3 Electrochemical Testing

5.3.1 Galvanostatic Performance and Stability

Coin cells are electrochemically cycled using an Arbin BT2000. All cells undergo at least 12 hours of rest prior to testing in order to allow for the liquid electrolyte to fully penetrate the porous electrode surface. After resting, half and full cells are cycled with a constant current at a theoretical rate of C/10. The rate is calculated as the time for a single charge (or a single discharge) in order to reach the theoretical expected specific capacity for the given voltage range. Therefore, C/10 implies 10 hours for charge (or discharge). The slow initial charging rate is used to allow the electrode to undergo surface structural changes which normally occur during the first 3 cycles. The current profile is symmetric where the charge current is the same as the discharge current.

For cathode materials, cells underwent a constant-current/constant-voltage (CCCV) profile. A standard galvanostatic symmetric current profile is used, though with an additional voltage hold for 1 hour after lithium extraction. The voltage hold helps to ensure that lithium is completely removed and is important for materials with low lithium ion diffusion rates. Further details about experiment specific electrochemical tests are described in chapter.
5.3.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is performed using AC impedance on a Solatron 1280C over a frequency range of 20,000 Hz to 100 mHz. After resting, the coin cell is charged and discharged to the desired voltage and cycle number. The voltage is held constant for at least 1 hour in order to assure for complete solid state diffusion of lithium through the active material. No external voltage is applied, so all experiments are run at the current open circuit potential.

The purpose of AC Impedance is to further identify the electron and ion transport properties of multi-layered structures in-situ. Coin cells can be thought of in terms of a linear combination of layers: A current collector, a composite, a surface oxide, a liquid electrolyte, and a lithium metal counter electrode. When subjected to a constant, direct current (DC), the multi-layered materials act as a single resistor and the measured resistance is the sum of the individual resistances of each component. Interesting effects occur, however, when DC is replaced with AC. As the frequency is increased, the materials begin to act as capacitors when the rate of change in current becomes faster than the motion of charges. Materials with slower kinetics, such as insulators, and processes which depend upon chemical reactions, such as charge-transfer, display capacitor-like behavior at low alternating frequencies. The faster processes, such as the motion of ions through liquid electrolyte and the conduction of electrons in carbon additive, do not exhibit capacitance until much higher frequencies. The impedance of the entire cell is determined for different frequencies ($\omega$) and is a function of the resistance ($R$) and the capacitance ($C$), $Z(\omega) = Z_{\text{real}} - jZ_{\text{imaginary}}$, where,[11]

$$Z_{\text{real}} = R \quad (5.8)$$

$$Z_{\text{imaginary}} = 1/\omega C \quad (5.9)$$

Eq. 5.8 & 5.9 reveal that a purely resistive-like behavior will only yield a real impedance component while purely capacitor-like behavior will only produce an imaginary impedance.
A Nyquist plot \((Z_{\text{imaginary}} \text{ versus } Z_{\text{real}})\) can then be used in order to determine the equivalent resistor and capacitor values based upon the real and imaginary impedance. Each material’s frequency response is governed by a unique time constant, \(\tau = RC\). The peak for each semicircle occurs when \[\omega \tau = 1 \quad (5.10)\] which can also be written as,

\[Z_{\text{real}} = Z_{\text{imaginary}} \quad (5.11)\]

Each layer, with unique values of \(R\) and \(C\), will require a different frequency, \(\omega\), to satisfy Eq. 5.10. Therefore, each semicircle corresponds to the impedance of a single material/charge-transfer process within the composite. The proper identification of each feature strongly depends on the conductive properties of the individual materials, as described earlier.

The final common Nyquist feature normally occurs at low frequencies and is called the Warburg impedance, \(Z_w\). The Warburg impedance describes the impedance due to mass transfer derived from Fick’s Law for a concentration gradient. For all intensive purposes, this work will use the following definition,

\[Z_w = A_w \omega^{-1/2} - j A_w \omega^{-1/2} \quad (5.12)\]

where \(A_w\) is called the Warburg constant, and \(j\) is the imaginary unit length. Notice that at high frequencies, the value of \(Z_w\) is small. Only at low, near-DC frequencies, is the impedance of mass transfer measurable with EIS.

An alternative to the Nyquist plot is the Bode plot. A Bode plot displays the phase angle \((\theta)\) and impedance magnitude, \(|Z|\), given by \[|Z|^2 = Z_{\text{real}}^2 + Z_{\text{imaginary}}^2 \quad (5.13)\]

Purely resistive behavior can be identified by a change in phase of 0° from the input wave. An ideal capacitor can be identified by a change in phase of \(\pi/2\) (90°). Phase
angles between 0 and 90° indicate the combination of both resistive and capacitive behavior.
References


Chapter 6

Optimization of MoO$_3$ Nanoparticles as Negative-Electrode Material in High-Energy Lithium Ion Batteries

As industry and consumers shift towards implementation of alternative energy sources for both homes and in transportation, there is a greater need for the safe storage of electrical energy. Lithium-ion batteries (LIBs) have shown a strong potential for high performance applications such as in plug-in hybrid electric vehicles (PHEVs) and hybrid electric vehicles (HEVs). Despite their commercial popularity, graphite anodes demonstrate relatively low electrochemical capacities (372 mAh g$^{-1}$) [1, 2]. In order to be PHEV and HEV compatible, novel electrode materials are needed to improve both energy density and power.

Recent work has focused on nanostructures for improving capacity and rate capability in LIB electrodes [3]. Alcantara et al. fabricated nanocrystalline CoSn by one pot synthesis method and tested the material as an anode [4]. When the particle size was reduced from micron-CoSn, the initial capacities were improved by 500%, close to the theoretical capacity of 664 mAh g$^{-1}$. Similar results were obtained using Fe$_2$O$_3$ as well as CoSb$_3$ [5, 6, 7]. Superior rate capabilities for cathodes were achieved by Shaju et al. by using a disordered form of nano-Li[Ni$_{0.5}$Mn$_{1.5}$]O$_4$ [8]. Our most recent work has employed thin film anodes comprised of nanoparticle MoO$_3$ [9]. Using electrophoresis deposition on a stainless steel substrate, a stable capacity of 630 mAh g$^{-1}$ was obtained for 150 cycles between 0.005 and 3.5 V. In contrast micron-sized particles of MoO$_3$
Figure 6.1: Specific capacity of nanoparticles with diameters ranging from 5 - 20 nm and the µm-sized particles [9].

showed significant capacity fade after only several cycles (Fig. 6.1). These thin films employed neither conductive additive nor binder as in traditional electrodes. Despite stable cycling at a rate of C/2, the reversible capacity was only 60% of the theoretical maximum of MoO$_3$, 1117 mAh g$^{-1}$. Also, while thin films may have application in small electronic devices, vehicular applications will likely be comprised of conventional electrodes. Here we report on the optimization of thick (35 µm) electrodes made with MoO$_3$ as the active material and employing polyvinyl fluorine (PVDF) and acetylene black (AB). The electrodes are tested in a coin cell configuration, that is more relevant to commercial applications. It is found that both the ratio of AB:PVDF and electrode pre-heat treatment are critical to obtaining high reversible capacities and stable cycling. Optimized performance is demonstrated for electrodes that are binder rich (AB:PVDF ratio of 1:2) and heated to 250 °C. The increase in reversible capacity compared to the thin film electrode is attributed to an improved conductive path due to the presence of the AB and melted PVDF polymer chains.
6.1 Results of MoO$_3$ Optimization

6.1.1 Analysis of MoO$_3$ nanopowder

The material produced and collected from HWCVD is a fine, black powder, indicating that the particles are sub-stoichiometric. Thus the particles were baked in air at 250 °C to convert the particles to MoO$_3$. TEM for the MoO$_x$ nanospheres before (Fig. 6.2a) and after (Fig. 6.2b) baking indicates that the average particle diameter increases from 10 up to 40 nm after annealing. Despite initial signs of particle agglomeration, individual spheres remain identifiable after oxidation. The ideal powder baking temperature and duration were found to be 300 °C for 2.5 hours in air. Baking at higher temperatures and/or longer times results in the observance of large micron-sized rods due to increased surface mobility of the atoms. Consistent with the TEM, BET analyses confirm a reduction in surface area of the nanospheres (with the optimal oxidation time) from 49.31 to 28.77 m$^2$g$^{-1}$. The change corresponds to an expected 41.65% loss in surface area. After baking, the powder visually transforms from black to a whitish-blue, which is an indication of oxidation. XRD patterns, in Figure 6.3,
Figure 6.3: XRD of nanoparticle powder a) as-synthesized and b) after baking in air at 250 °C. Prior to baking, the powder is a mixture of MoO$_2$ and Mo Metal. After baking, all of the powder is converted to MoO$_3$. 
were used to identify the composition and crystalline structure of the sample. The raw, unbaked powder collected from the HWCVD is indexed as a combination of MoO$_2$ and Mo metal. Peaks at 44.5° and 65° represent the stainless steel substrate. After baking, the XRD peaks correspond to pristine orthorhombic $\alpha$-MoO$_3$ with no significant traces of MoO$_2$ or Mo metal [10]. The sharp peaks indicate a highly uniform and crystalline structure.

6.1.2 Determination of AB:PVDF Ratio

In the electrodes the AB:PVDF ratio was optimized using 70 wt. % MoO$_3$ to allow for adequate volume expansion during lithiation. Similar to Fe and Si, MoO$_3$ has a large theoretical volume expansion as lithiation goes to completion which is perhaps tolerated only by nanoparticles [9]. The cells were cycled at room temperature at a charge-discharge rate of C/10 from 3 V to 0.005 V. Electrochemical stability and capacity (Fig. 6.4) were tested using four cell compositions of AB:PVDF (1:2, 1:1.25, 1:1, 2:1). Binder rich electrodes of a 1:2 ratio showed the greatest electrochemical stability near the theoretical capacity, which is in good agreement with previous investigations [11, 12]. It appears that large surface area materials such as nanospheres require additional binder in order to maintain physical contact between the active material and the conductive additive. Cell compositions with lower binder content of 1:1 and 2:1 show rapid failure after only eight cycles presumably due to a reduction in conductive pathways for electrons and ions through the electrode.

6.1.3 Effects of Electrode Heat Treatment

Electrodes of 70:10:20 composition underwent a minimum of eight hour glove box heat treatment at various temperatures prior to cell construction. As seen in the voltage profiles (Fig. 6.5a), both no heat treatment and heat treatment at 150 °C result in large first cycle irreversible capacities of nearly 60% likely due to Li$^+$ reaction
Figure 6.4: Effect of AB:PVDF ratio on cycle stability and capacity for 70 wt. % MoO$_3$. 

![Graph showing the effect of AB:PVDF ratio on cycle stability and capacity for 70 wt. % MoO$_3$.]
with water. Likewise, both cases show poor cycling stability (Fig. 6.5b) and rapid degradation. When the pre-annealing temperature was increased beyond 150 °C, the irreversible capacity is significantly reduced. For a heat treatment temperature of 250 °C a stable capacity of 1050 mAh g⁻¹ is observed for 30 cycles. This high reversible capacity corresponds to 80% of the initial capacity of 1400 mAh g⁻¹. The initial capacity of 1400 mAh g⁻¹ exceeds the theoretical maximum capacity expected for 6 Li⁺/MoO₃ presumably due to initial surface side reactions. Similar results but at a lower capacity can be seen when the temperature is raised to 300 °C.

Fig. 6.6 shows how the heat treatment affected the AC impedance of the various electrodes. A decrease in the radius of the first semicircle represents a relative decrease in electronic resistance. Apparently, heating electrodes above the binder’s melting temperature of 170 °C redistributes and unfurls long chains to allow for improved electrical contact between active material and conductive additive.

The high reversible capacity of 1050 mAh g⁻¹ corresponds to the insertion of 5.7 Li⁺/MoO₃ which approaches the theoretical maximum (6 Li⁺/MoO₃). It has been previously suggested that during the first lithium insertion, MoO₃ undergoes an irreversible structural change from the α-phase to an amorphous phase followed by a conversion reaction to form Li₂O and Mo metal [13]

\[
MoO₃ + 6Li⁺ + 6e^- \leftrightarrow Mo + 3Li₂O
\]  

(6.1)

However, the amorphization of the material does not alter the overall electrochemical performance of the electrode. Presumably as Li₂O forms and decomposes, the conversion reaction yields nanodispersed particles of Mo metal [14]. Poizot has purposed that small particles, with an increased total number of surface atoms, in turn increase the electrochemical reactivity and make the conversion process reversible [3]. We also suggest that starting with nanoparticles initially better allows for the formation of small metal clusters during the conversion process. This is consistent with the data
Figure 6.5: (a) Cycling profile; and (b) electrochemical performance for cells compositions of 70:10:20 as a function of heat treatment temperature.
Figure 6.6: AC Impedance as a function of heat treatment for a 70:10:20 cell composition using MoO$_3$
presented in Fig. 6.1, where the nanoparticles out perform the larger commercial metal oxide particles in reversibility.

6.1.4 PVDF Binder Decomposition

Additional evidence of water removal for both the electrodes with no heat treatment and heat treatment at 150 °C is exhibited in the FTIR spectra in Fig. 6.7. The pristine MoO$_3$ powder after exposure to air is shown to have neither adsorbed molecular water that would be indicated by the H$_2$O scissors mode at 1640 cm$^{-1}$ nor hydrogen bonded hydroxyl groups that would be indicated by a broad O-H stretching vibration (3200 – 3500 cm$^{-1}$). When the active material is mixed with AB:PVDF and deposited onto a copper substrate, both the scissors mode of molecular water and the broad peak associated with the O-H stretching vibration are observed indicating that the water source is actually the AB or PVDF. Peaks between 841 and 1,403 cm$^{-1}$ are characteristic of the $\beta$-phase PVDF [15, 16]. After electrode heat treatment to 250 °C, the FTIR shows almost no sign of the scissors mode at 1640 cm$^{-1}$ indicating that molecular water has been removed. The smaller broad feature between 3200 – 3500 cm$^{-1}$ is consistent with stable surface hydroxyl species, possibly now present on the MoO$_3$ nanoparticle surfaces.

6.1.5 Species Desorption During Heat Treatment

As noted previously, the irreversible Li-insertion that exceeds the theoretical capacity for MoO$_3$ is most likely due to reactions with surface species. The irreversible insertion is largest for the electrodes not subjected to heat treatment and for the electrode that was only annealed to 150 °C (Fig. 6.5). Figure 6.8a depicts the TPD spectra of gaseous species desorbing from the electrode while heating in vacuum. Water is observed to desorb from the sample above 70 °C with peak desorption occurring at two temperatures, 100 and 200 °C. The lower desorption peak most likely corresponds to
Figure 6.7: FTIR of 70:10:20 electrodes on Cu substrate. Molecular water, present prior to heat treatment, is fully removed when annealed up to 250 °C.
Figure 6.8: TPD Mass Signal as a function of temperature for MoO$_3$:AB:PVDF composition of 70:10:20 for: (a) select desorbed gas species; and (b) binder decomposition.

Physisorbed H$_2$O bound to the high surface area MoO$_3$ and AB. Given the high temperature of the second peak (200 °C), it is likely that stable surface hydroxyl species exist on the MoO$_3$ nanoparticles. These hydroxyl species then decompose to form water at high temperature. A mechanism for the surface hydroxyl decomposition is shown below:

$$Mo - OH + Mo - OH \rightarrow Mo - O - Mo + H_2O$$  \hspace{1cm} (6.2)

The absence of hydrogen evolution with the water desorption supports this surface decomposition mechanism. Water evolution at higher temperature then causes oxidation of the carbon present in the binder and acetylene black, and CO$_2$ is observed to desorb in the TPD spectrum (Fig 6.8a) with the desorption also peaked at 200 °C. The presence of both stable molecular water and surface OH groups inhibit the removal of lithium after initial intercalation, producing the large irreversibility seen in Fig. 6.5a at lower heat treatment temperatures. For the higher heat treatment temperature of 300 °C, the irreversible capacity is minimized but the total reversible capacity of the material also decreases to ~850 mAhg$^{-1}$ (Fig 6.5b). PVDF is a polymer binder consisting of a chain of carbons, alternating with hydrogen and fluorine terminations. As a commercial powder, PVDF melts around 170 °C and decomposes at 375 °C. Independent of MoO$_3$, AB:PVDF electrodes show initial signs of decomposition, indicated by the
desorption of HF, at 350 °C. However, when the metal oxide is added to the composition, binder decomposition begins at a significantly reduced temperature slightly above 250 °C. Previous studies have shown that the addition of metal oxides and nitrides to various polymer compounds accelerates the chain scission within the binder, reducing the decomposition temperature [17, 18, 19]. The actual binder degradation temperature is thus dependent upon the active material and its ability to unzip polymer chains [20].

6.1.6 Thermal Gravimetric Analysis of MoO$_3$

The water removal and early binder decomposition is also supported by TGA (Fig 6.9). At 200 °C, the large peak in the weight derivative curve is attributed to both water loss and the conductive additive decomposition due to oxidation. A saddle for the weight change occurs just after 250 °C, followed by a rapid weight loss consistent with the complete binder breakdown. Full decomposition is observed at 350 °C. As identified by TPD in Fig. 6.8b and supported by the cycling data in Fig. 6.5, the ideal heat treatment temperature occurs just prior to binder decomposition. For the MoO$_3$ electrodes, the optimal temperature is 250 °C. Li et al. determined that the ideal
heat treatment for Si:PVDF electrodes occurred at 300 °C [21]. We believe that each active material will require a unique optimal annealing temperature that can be easily determined through thermal analysis.

6.2 Summary of MoO₃ Optimization

In summary, by using thick, more conventional electrodes of MoO₃ along with AB and PVDF a near-theoretical reversible capacity of ~1050 mAhg⁻¹ is obtained. Employing deep charge/discharge, the electrodes maintain a stable capacity for nearly 40 cycles. The optimized electrode composition is 70:10:20 corresponding to MoO₃:AB:PVDF with a preheat treatment of 250 °C. A combination of TPD, TGA and IR analyses indicate that water and surface hydroxyl groups may be effectively removed up to 250 °C while annealing the electrode to 300 °C results in binder decomposition.
References


[18] P. Malik, M. Castro, and C. Carrot, “Thermal degradation during melt processing of poly(ethylene oxide), poly(vinylidenefluoride-co-hexafluoropropylene) and


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 Li\(_2\)O as shown in Eq. 7.1 [3].

\[ MO_x + 2xLi^+ + 2xe^- \leftrightarrow xLi_2O + M \]  

(7.1)

However, for materials, such as silicon and transition metal oxides, which can
accommodate more than 4 Li\(^{+}\) 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, 5, 6], nano-arrays [7, 8, 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 \(\alpha\)-Fe\(_2\)O\(_3\) 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 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 \(\leq 40\) wt.% to allow for volume expansion. Li et al. demonstrated that binder choice and electrode pre-heat treatment could stabilize \(\mu\)-sized particles of \(\alpha\)-Fe\(_2\)O\(_3\) 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-Co\(_3\)O\(_4\) by sol-gel [14]. The coating improved the 12\(^{th}\) 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 $\alpha$-MoO$_3$ was first proposed as a material of interest for Li-ion batteries as a cathode in the 1970’s [17], but was not demonstrated as an anode material due to the volume expansion occurring for high Li-loading at lower potential. Using nanoparticle $\alpha$-MoO$_3$ for an anode, we previously demonstrated an anomalous reversible capacity as a thin film electrode and then achieved improved reversible capacity (1000 mAh g$^{-1}$) in a traditional electrode architecture [18, 19]. Our electrode composition contained only 10 wt.% conductive additive, 20 wt.% binder and 70% active material. We also established a necessary electrode heat treatment at 250 °C, unique to MoO$_3$, 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 hours each for charge and discharge).

This chapter focuses on improving the durable high-rate capability of high volume expansion nanoparticle MoO$_3$ 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.

7.1 Experimental Methods

Electrode fabrication: Active material (AM), nano-MoO$_3$, was obtained using a hot-wire chemical vapor deposition method as described by Riley et al [18]. 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 hours to obtain a fully oxidized $\alpha$-MoO$_3$ sample. Electrodes were made using a 70:10:20 composition of AM:AB:PVDF dissolved in N-methyl-2-pyrrolidone. Upon spreading on 20 nm thick Cu foil, the NMP was evaporated at 120 °C for 1 hour in air and then again for 8 hours under vacuum. All electrodes were then heat treated at 250 °C on a hot plate in an Ar glove box overnight.

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-MoO$_3$ 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 Al$_2$O$_3$ ALD reaction sequence was: (1) Trimethylaluminum dose to 1.0 Torr;
(2) TMA reaction time; (3) evacuation of reaction products and excess TMA; (4) N\textsubscript{2} dose to 20.0 Torr; (5) N\textsubscript{2} static time; (6) evacuation of N\textsubscript{2} and any entrained gases; (7) H\textsubscript{2}O dose to 1.0 Torr, (8) H\textsubscript{2}O reaction time; (9) evacuation of reaction products and excess H\textsubscript{2}O; (10) dose N\textsubscript{2}; (11) N\textsubscript{2} static time; and (12) evacuation of N\textsubscript{2} and any entrained gases. This sequence constitutes one cycle of Al\textsubscript{2}O\textsubscript{3} ALD. The reactor temperature was 180 °C.

*Material characterization:* The Al\textsubscript{2}O\textsubscript{3} ALD coated and bare MoO\textsubscript{3} nanoparticles were examined by transmission electron microscopy using a FEI Tecnai F20 UT microscope operated at 200 kV. The presence of Al\textsubscript{2}O\textsubscript{3} layer on the surface of MoO\textsubscript{3} nanoparticles was confirmed by nano-probe energy dispersive X-ray spectroscopy (EDS).

*Electrochemical testing:* All electrodes were electrochemically tested in coin cells (CR2023) using LiPF\textsubscript{6} in 1:1 ethylene carbonate: dimethyl carbonate (EC:DMC) 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-designated 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.

## 7.2 Results from ALD Coatings on MoO\textsubscript{3}

As discussed previously in detail [18, 19, 20], the crystalline MoO\textsubscript{3} is grown using a unique hot-wire chemical vapor deposition (HWCVD) technique. In this study, self-limiting ALD is performed using trimethylaluminum (TMA) and H\textsubscript{2}O 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 H\textsubscript{2}O 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 [21].

A transmission electron microscope (TEM) image of a bare MoO₃ nanoparticle (prior to the application of an ALD coating) is shown in Figure 7.1a. 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 7.1b). Figure 7.1c 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 Fig. 1a and 1c. However for the coated particle (Fig. 7.1c), 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 bare sample confirms that the bright film is a very thin layer of Al₂O₃ upon the surface of the nanoparticle (Figure 7.1d). Note that the ALD coating also appears to improve the surface roughness of the particles.

7.2.1 Improvements to Electrochemical Performance

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 Fig. 7.2a. 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 1117 mAh g⁻¹ represents the theoretical maximum capacity of MoO₃ when completely lithiated (6 Li⁺ per MoO₃ formula unit as given by Eq. 7.1). After the first two cy-
Figure 7.1: Graphs showing: (a) TEM of bare MoO$_3$ nanoparticle; (b) EDS of the circular area marked p1 shows no aluminum present on the surface of the bare sample; (c) TEM of a MoO$_3$ nanoparticle coated by ALD with 4 monolayers of Al$_2$O$_3$ on the surface; and (d) EDS of area labeled as p1 confirms the presence of alumina at a monolayer level.
Figure 7.2: Comparison between bare, 4-cycle ALD coated MoO$_3$ nanoparticles and 4-cycle ALD coated electrodes in a composition of 70:10:20 (MoO$_3$: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 nMoO$_3$. 
cles at C/10, each sample is cycled at a rate of C/2 (only 2 hours for each charge and discharge) from 3.0 to 0.001 V at room temperature. As shown in Fig. 2a, the bare MoO$_3$ nanoparticles exhibit a progressive capacity fade after only 15 cycles. Consistent with the onset of stability loss, the Coulombic efficiency of the electrode also degrades (Fig. 7.2b). The gradual capacity loss and poor efficiency is attributed primarily to mechanical degradation due to volume expansion with surface decomposition / reaction with the liquid electrolyte also playing a role. Interestingly, individual nanoparticles coated with 4 cycles of Al$_2$O$_3$ ALD show inferior performance to the bare nano-MoO$_3$ (Fig. 7.2a) as the Coulombic efficiency drops from 74% to 63% in the first cycle (Fig 7.2b). The CP then exhibits a rapid drop in capacity upon further cycling, finally stabilizing around the 10$^{th}$ cycle, with a low reversible capacity of 380 mAh g$^{-1}$.

Unlike the individual particle coated sample, dramatically improved cycling performance is observed (Fig. 7.2a) when the entire electrode is coated with 4 cycles of Al$_2$O$_3$ ALD. The CE shows no capacity fade for over 50 cycles at C/2 rate and maintains a stable reversible capacity of 900 mAh g$^{-1}$ corresponding to an uptake of 4.8 Li$^+/\text{MoO}_3$. By the 40$^{th}$ cycle the Coulombic efficiency of the electrode coated sample is 97.5% compared to the bare sample with a Coulombic efficiency of 94%. The improved durability of the ALD coated electrodes is even more dramatically depicted by exploring the rate capability as depicted in Fig. 7.2c. At a rate of 2C (30 minutes for both charge and discharge) the surface coated electrode delivers a capacity of nearly 800 mAh g$^{-1}$ while the bare exhibits only 400 mAh g$^{-1}$. Also the coated electrode delivers 600 mAh g$^{-1}$ in only 12 minutes when cycled at 5 C. Thus, and perhaps surprisingly, the electrode coating provides beneficial protection against capacity degradation while the individual particle coating appears detrimental to overall performance. The voltage profiles depicted in Fig 7.2d compare the 1$^{st}$ cycle (C/10) to the 40$^{th}$ 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.

7.2.2 Volume Change Effect on Al₂O₃

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 channel 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 7.2.2. 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 [15]. 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 Fig. 7.3a-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 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 (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 7.3c. 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.

7.2.3 Electrochemical Impedance Spectroscopy

The electronic conductivity of each electrode was studied with electrochemical impedance spectroscopy (EIS). Fig. 7.4 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 re-
Figure 7.3: 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.
sistance 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 to the CP, is indicative of the physical interface caused by the Al$_2$O$_3$
insulation of the individually coated nanoparticles. The extra resistive layer indicated
in Fig. 7.4b decreases ion mobility and limits conductive electron pathways.

### 7.2.4 Importance of Carbothermal Reduction

Physical contact between MoO$_3$ nanoparticles and the conductive additive /
binder ensures proper electron conduction and is necessary to achieve good cycling
stability. If carbothermal reduction to MoO$_3$$_{-y}$ during the electrode pre-heat treatment
is observed, it suggests that good conductivity is maintained. This is consistent with
previous studies indicating that slightly reduced MoO$_3$$_{-y}$, that occurs upon ball milling,
exhibits enhanced cycling stability [25]. Here the carbothermal reduction occurs upon
heat treatment at 250 °C in Ar prior to coin cell assembly [18]. When heated, the surface
oxygen of MoO$_3$ reacts with both the melted polymer binder chains (T$_{melt}$ 170 °C),
as well as the carbon additive to form CO and CO$_2$, 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 po-
tentials, and in general, negative peak shifts can be attributed to two factors: kinetics
or change in oxidation state. Figure 7.5 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 MoO$_3$, represented by the non-
Figure 7.4: First cycle discharge/charge Bode plots for: (a) bare MoO$_3$; (b) ALD coated MoO$_3$ electrode; (c) ALD coated MoO$_3$ particles.
Figure 7.5: First cycle differential discharge capacity MoO$_3$ electrodes undergoing no heat treatment and overnight heat treatment at 250 °C.
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, 27, 28]. The second phase, common to transition metal oxides, is the conversion stage described in Eq. 7.1, where MoO$_3$ undergoes a displacement reaction to form Mo metal and Li$_2$O creating a highly disordered and amorphous structure at low voltages (< 1.0 V) [25, 29]. 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 Fig. 7.5, observed for the non-heat treated electrode, is typical of pure MoO$_3$. 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 MoO$_3$ 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 7.6. 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 MoO$_3$ 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 -0.08V 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 MoO$_3$ in Figure 7.5. Unlike the bare heat-treated MoO$_3$ 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 MoO$_3$ and AB / binder. Thus ALD coatings to the entire electrode are necessary to enable
Figure 7.6: Comparison of bare and ALD coated first cycle differential discharge capacity (dQ/dV) at a rate of C/10.
favorable reactions that occur during electrode pre-heat treatment.

ALD coatings were also applied on commercial MoO$_3$ electrodes. Figure 7.7 displays results from coating the electrodes of commercially available micron sized MoO$_3$ with 4 cycles of Al$_2$O$_3$ using ALD. Despite the tremendous improvements reported above for coating high surface area nanoparticle electrodes, a similar benefit is not observed for micron-sized particles. Again the rapid failure of micron-sized particles is due to the extreme fracturing upon volume expansion during cycling [19]. For the micron-sized particles the thin ALD coating is not prolific enough to provide any significant adhesion to the conductive additive. Additionally, the dQ/dV remains unchanged after an overnight 250 °C heat treatment of the micron-sized MoO$_3$ 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 MoO$_{3-y}$ 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 Fig. 7.2a,
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
$\text{Al}_2\text{O}_3$ coating that is 4-8 Å thick on an $\text{MoO}_3$ 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.

7.3 Summary of ALD coatings on High Volume Expansion $\text{MoO}_3$
Nanoparticles

Molybdenum trioxide nanoparticles and electrodes have been coated with $\text{Al}_2\text{O}_3$
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 $\text{Al}_2\text{O}_3$
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 $\text{MoO}_3$ 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.
References


Chapter 8

Improved mechanical integrity of ALD-coated composite electrodes

High capacity anode materials for lithium ion batteries, such as silicon, iron oxide, and molybdenum oxide, have been plagued by detrimental changes in volume during lithium insertion and extraction. Material expansion can cause the displacement of electrode material, breaking electron and ion pathways. Research has circumvented the expansion issue through the creative use of nano-structures [1], the use of carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) binders [2], heat treatment [3] and carbon-based matrices [4]. Unfortunately, many of these methods are either time consuming, costly, or difficult to scale for mass production. In Chapter 7 considerable improvement to the cycle stability and rate capacity of high capacity nano-MoO$_3$ was achieved through the application of 4-monolayers of alumina on the electrode surface using the roll-to-roll friendly method of atomic layer deposition (ALD). This chapter focuses on the enhanced mechanical properties ceramic coated, composite polymer-based electrodes determined by nanoindentation and nanoscratch.

8.1 Experimental Methods

Composite electrodes (15 $\mu$m thick) were composed of MoO$_3$, acetylene black, and poly(vinylidene fluoride) (PVDF) binder on 20 $\mu$m copper foil. Nanoparticle MoO$_3$ synthesized by hot-wire chemical vapor deposition (HWCVD) and electrode fabrication followed similar procedures described in previous work [5, 6]. Post-fabrication,
electrodes were then coated with 4-monolayers of Al$_2$O$_3$ by atomic layer deposition.

Both indentation and adhesion scratch tests were performed at room temperature on an MTS NanoIndenter XP with a standard triangular pyramidal Berkovich diamond indenter (maximum load = 500 mN, resolution = 50 nN). Electrodes were mounted to an aluminum holder by commercial adhesive and allowed to dry prior to testing. Indentation depth was limited to 1.5 µm, not exceeding 10% of the total electrode thickness. Continuous Stiffness Measurement (CSM) was also applied during the loading segment. CSM applies a very small oscillating force in order to measure both the instantaneous elasticity and the contact stiffness at all depths. Multiple indentations were performed to account for variations in surface roughness, sink-in, and pile-up. Nanoscratch testing consisted of a common three-segment profiling technique [7, 8]: pre-profiling at 20 µN for 700 µm, linear ramping scratch segment to 40 and 80 mN for 500 µm, and post-profiling at 20 µN. The scratch tip was oriented for face-forward operation, corresponding to orientation (II) from Ref. [9], with a horizontal profile velocity set to 10 µm/s. Images were taken using an optical microscope included with the NanoIndenter.

8.2 Mechanical Properties of Composite Electrodes

8.2.1 Results from Nanoindentation

Typical load-displacement curves obtained by nanoindentation for the bare and Al$_2$O$_3$ coated electrodes are shown in Fig 1. For identical indentation depths, the peak load for the ALD-coated MoO$_3$ electrode is over twice that of the bare sample. The horizontal plateau represents the viscoelastic creep associated with the PVDF binder [10, 11]. The corresponding mechanical properties for the composite electrodes and PVDF and ALD grown Al$_2$O$_3$ from literature are listed in Table 8.2.1. The bare MoO$_3$ electrode exhibits a similar mechanical response to bulk PVDF. Differences in mechanical properties between bulk PVDF and composite are attributed to the heavy loading
Figure 8.1: Indentation profile for bare and ALD coated MoO$_3$ electrodes. The initial loading consists of CSM, followed by a hold to compensate for viscoelastic creep, and finally unloading.
Table 8.1: Mechanical properties of MoO$_3$ electrodes during nano-indentation compared with PVDF and Al$_2$O$_3$ films from literature

<table>
<thead>
<tr>
<th></th>
<th>Bare</th>
<th>4-Al$_2$O$_3$</th>
<th>PVDF[12]</th>
<th>ALD Al$_2$O$_3$[13]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus from Unloading (GPa)</td>
<td>2.1642</td>
<td>3.5013</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Modulus during CSM (GPa)</td>
<td>1.6819</td>
<td>2.4808</td>
<td>3.44 ± 0.14</td>
<td>180 ± 8.2</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>0.26</td>
<td>0.65</td>
<td>0.24 ± 0.01</td>
<td>12.3 ±1.0</td>
</tr>
<tr>
<td>Stiffness (kN/m)</td>
<td>21.6</td>
<td>32</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

of both MoO$_3$ nanoparticles and carbon additive and the resulting scission of the polymer chains. As expected, bulk ALD-Al$_2$O$_3$ exhibits a much higher elastic modulus and hardness than the polymer binder. The 150% increase in hardness and 44% increase in Young’s modulus of the Al$_2$O$_3$ coated electrode correlates with the improved mechanical properties of bulk alumina 8.2.1.

### 8.2.2 Results from Nanoscratch

Resultant damages to the bare and ALD coated electrodes during nanoscratch tests recorded by optical microscope are shown in Figure 8.2. Scratch direction is from left to right. Complete delamination of the bare electrode from the copper current collector is observed midway during the linear ramp scratch segment for $P_{max} = 80$ mN. Loss of adhesion to the copper substrate is confirmed by the tip penetration depth 8.3a.

The complete delamination seen in Figure 8.2a is marked on Fig. 8.3a by an arrow. Notice that the tip depth at failure (15 $\mu$m) is equal to the composite thickness. Unlike the bare sample, complete delamination is found not to occur in the ALD coated sample, even for $P_{max} = 80$ mN. Short portions of ribbing, caused by partial-delamination or localized failure within the sample, are observed prior to bare delamination and throughout Al$_2$O$_3$-coated electrodes. Despite partial-delamination, the ALD coated electrode remains adhered to the copper substrate for the entire scratch.

The frictional coefficient (COF) during the linearly increasing application of load
Figure 8.2: Optical images of damage caused by nanoscratching with a maximum load of 80 mN for: (a) bare; and (b) 4-Al$_2$O$_3$ ALD coated MoO$_3$ composite electrode;

Figure 8.3: (a) Depth profile; and (b) friction coefficient as a function of penetration depth;
is shown in Figure 8.3b. COF is defined as a ratio between the force required to move the tip laterally and the load applied normal to the surface [14]. To our surprise, despite significant differences in mechanical properties from nanoindentation, the COF at a given depth remains unchanged after ALD coating. It is known that the lateral force required depends upon the friction of abrasion between the tip and the surface and the friction associated with material adhesion. We assume that by reducing the elasticity and increasing electrode brittleness, the Al₂O₃ layer decreases the material adhesion to the scratch tip but increases the friction of abrasion. Without the coating, the material is noticeably more elastic, increases the friction due to adhesion and lowering the abrasion between the tip and the composite. So, while elastic properties are desirable for high volume expansion materials in theory, a harder, more brittle composite with better current collector adhesion is superior.

8.3 Summary Nanoindentation and Nanoscratch Techniques for Electrodes

In conclusion, we have demonstrated the improved mechanical stability and volume expansion tolerance afforded by the application of only 4 monolayers of alumina to MoO₃ composite electrodes. After coating, adhesion of the composite electrode onto the current collector more than doubles, while the electrode hardness increases by close to 50%. These results are promising for the implementation of high capacity anodes in commercial lithium ion batteries and provide insight to the benefits of CMC over the more elastic PVDF binder.
References


High capacity Li$_2$MnO$_3$-stabilized LiMO$_2$/Al$_2$O$_3$-coated MoO$_3$ Li-ion batteries without a pre-lithiation step

Li$_2$MnO$_3$-stabilized LiMO$_2$ lithium rich cathodes were successfully paired with a high-capacity Al$_2$O$_3$-coated MoO$_3$ anode. The reversible capacity of the full cell was found to be over 150 mAh g$^{-1}$ for over 20 cycles, considerably greater than the commercially available 80 mAh g$^{-1}$. Unlike other possible counter electrodes, these materials may be paired such that the cathode excess Li perfectly matches the irreversible capacity loss of the anode, eliminating pre-lithiation. The limiting factor is found to be the metal oxide anode with a large hysteresis causing a low operating voltage. However, significant stability improvements have been demonstrated through the application of only 4-monolayers of Al$_2$O$_3$ on the surface of the MoO$_3$ electrode by atomic layer deposition.

High energy-density anodes, such as silicon (theoretical capacity 4200 mAh g$^{-1}$) and metal oxide conversion materials (theoretical capacity around 1000 mAh g$^{-1}$) have recently become extremely popular in the research community [1, 2, 3, 4, 5]. Exhibiting capacities 3, 4, and even 10 times greater than graphitic electrodes, these materials are thus considered as plausible replacements for traditional graphite electrodes. However, even when silicon is paired with a traditional LiCoO$_2$ electrode and cycled in a safe voltage window, the theoretical capacity increases from a commercially available 80 mAh g$^{-1}$ to only mAh g$^{-1}$ (Table 9) [6]. In order to fully utilize and properly benefit from high capacity anodes, the counter electrode needs to be replaced with a high capacity...
Table 9.1: Theoretical full cell capacities for given electrodes. **Bold** values represent anode (left) and cathode (top). Values represent the theoretical full cell capacity for the anode/ cathode combination. All values are in mAh g\(^{-1}\).

<table>
<thead>
<tr>
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<th>100</th>
<th>150</th>
<th>170</th>
<th>200</th>
<th>220</th>
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<tr>
<td>300</td>
<td>75.00</td>
<td>100.00</td>
<td>108.51</td>
<td>120.00</td>
<td>126.92</td>
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<td>382</td>
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<td>131.27</td>
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<tr>
<td>1000</td>
<td>90.91</td>
<td>130.43</td>
<td>145.30</td>
<td>166.67</td>
<td>180.33</td>
</tr>
<tr>
<td>4000</td>
<td>97.56</td>
<td>144.58</td>
<td>163.07</td>
<td>190.48</td>
<td>208.53</td>
</tr>
</tbody>
</table>

cathode. Here we report on a high capacity full cell made from an Al\(_2\)O\(_3\) surface coating grown by atomic layer deposition (ALD) on electrodes containing nano-MoO\(_3\) (ALD-MoO\(_3\)) with a reversible capacity 1000 mAh g\(^{-1}\) and a Li\(_2\)MnO\(_3\)-stabilized LiMO\(_2\) (M = Mn\(_{0.31}\)Ni\(_{0.44}\)Co\(_{0.25}\)) lithium excess cathode (ANL-NMC) with a reversible capacity 220 mAh g\(^{-1}\) [7, 8]. Successful demonstration of this unique full cell has important implications for the use of high capacity materials as viable replacements for graphite and LiCoO\(_2\).

### 9.1 Experimental Methods

#### 9.1.1 Li\(_2\)MnO\(_3\)-stabilized LiMO\(_2\) synthesis

MoO\(_3\) was synthesized by hotwire chemical vapor deposition (HWCVD) as previously described in §5.1.1. The average particle size was 40 nm and could be controlled by both temperature and pressure during synthesis [9]. 0.5Li\(_2\)MnO\(_3\)•0.5LiNi\(_{0.44}\)Mn\(_{0.31}\)Co\(_{0.25}\)O\(_2\), synthesized with 5 mol% fluorine as an anion substituent was synthesized from stoichiometric amounts of Li\(_2\)CO\(_3\) (Sigma-Aldrich), (Mn\(_{0.656}\)Ni\(_{0.219}\)Co\(_{0.125}\))(OH)\(_2\) and NH\(_4\)F (Sigma-Aldrich) precursors. The (Ni\(_{0.219}\)Co\(_{0.125}\)Mn\(_{0.656}\))(OH)\(_2\) precursor was prepared by a coprecipitation method as follows. A 2 M aqueous solution of Ni-, Co-, and Mn-sulfate (Mn:Co:Ni=0.656:0.219:0.125) was pumped into a 2 M aqueous solution of NaOH with a desired amount of NH\(_4\)OH under flowing nitrogen atmosphere. The pH, temperature, and stirring speed at 12, 55 °C, and 1000 rpm, respectively, were controlled...
throughout the co-precipitation process. The co-precipitated nickel-cobalt-manganese hydroxide was filtered, dried, and then mixed with appropriate amounts of Li₂CO₃ and NH₄F, followed by calcination at 800 ºC for 12 h in an air atmosphere.

### 9.1.2 Electrode Fabrication

Composite electrodes were fabricated with active material (AM), acetylene black (AB, Alfa Aesar) conductive additive, and poly-vinylidene fluoride (PVDF, Alfa Aesar) binder. The anode composition was 70:10:20 (AM:AB:PVDF) and the cathode composition was 83:7.5:9.7. AM and AB powders were mixed using a mortar and pestle then added to PVDF dissolved in n-methyl pyrrolidinone (NMP, Alfa Aesar). The slurry was then mechanical spread onto a current collector (copper for anode, aluminum for cathode) using a notch bar. Both electrodes were dried in air for 1 hour at 80 ºC, calendared to 75% of the total thickness, and then vacuum dried at 125 ºC overnight. Four atomic layers of Al₂O₃ was grown directly onto the prefabricated MoO₃ electrode using the ALD technique found in Ref. [7]. The anodes then underwent additional heating overnight in an argon glove box at 250 ºC as previously described. Electrodes were punched to diameter and tested in a 2032 coin cell architecture with a thick, porous silica separator and 1M LiPF₆ 1:1 EC:DMC electrolyte. Cells were allowed to rest for at least 12 hours and then electrochemically cycled on an Arbin at a rate of C/10 (10 hours per charge/discharge). The average open circuit potential was 300 mV.

### 9.2 Half cell comparison

As a metal oxide, the anode undergoes the following conversion reaction at low voltages: [10]

\[ MoO_3 + 6Li^+ + 6e^- \leftrightarrow Mo + 3Li_2O \]  

(9.1)

Bulk LiMO₂ undergoes a standard intercalation reaction, coupled with Li₂MnO₃ activation [8]
\[ \text{LiMO}_2 + \text{Li}_2\text{MnO}_3 \leftrightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + \text{MnO}_2 + \text{Li}_2\text{O} \quad (9.2) \]

\[ \text{Li}_{1-x}\text{MO}_2 + \text{MnO}_2 + (1+x)\text{Li}^+ \leftrightarrow \text{LiMO}_2 + \text{LiMnO}_2 \quad (9.3) \]

After the first complete cycle, the final composition of the intercalation cathode is LiMO₂ and LiMnO₂.

Differential capacity plots for the anode and cathode half cells, electrochemically tested versus a lithium metal counter electrode, are depicted in Fig. 9.1. Complete lithium insertion during the first cycle for ALD-MoO₃ occurs below 0.5 V versus Li⁺ as the metal oxide undergoes the conversion reaction. The corresponding first cycle extraction for the ANL-NMC occurs at 3.95 V, expected for the LiMO₂, followed by the additional irreversible removal of Li₂O from Li₂MnO₃ at > 4.4 V. For subsequent cycles, the ALD-MoO₃ insertion profile remains similar to that of the first cycle with the insertion potential predominantly below 0.5 V. The ANL-NMC gains an additional feature at 3.55 V, corresponding to the reversible electrochemical intercalation for LiMnO₂, and the high voltage feature (>4.4 V) now as expected.

Both the anode and the cathode are shown to be electrochemically stable versus Li⁺ for 25 cycles in Fig. 9.2. Importantly, both materials have similar irreversible capacity losses in the first cycle (25%). High capacity metal oxide anodes normally exhibit a large first cycle irreversible capacity loss associated with either surface reactions or the known phase change from crystalline to amorphous. Cathodes, such as LiCoO₂, exhibit very small irreversible capacities (10%), making them difficult to pair with non-graphitic counter electrodes. The ANL-NMC, on the other hand, has an inherent capacity loss associated with the activation of Li₂MnO₃ to LiMnO₂, that strategically off-sets the irreversible capacity loss of ALD-MoO₃ and eliminates any need for pre-lithiation.
Figure 9.1: 1\textsuperscript{st} and 2\textsuperscript{nd} cycle differential capacity profiles for Al\textsubscript{2}O\textsubscript{3}-coated MoO\textsubscript{3} vs. Li\textsuperscript{+} and Li\textsubscript{2}MnO\textsubscript{3}-stabilized LiMO\textsubscript{3} vs. Li\textsuperscript{+}. 
Figure 9.2: Electrochemical stability and performance of ANL-NMC and ALD-MoO3 half-cells. The voltage window of the ANL-NMC was increased from 3.0-4.6 V to 2.0-4.6V after 4 cycles.
9.3 ALD-MoO$_3$/ANL-NMC Pairing Results

9.3.1 Differential Capacity Analysis

Figures 9.3a and 9.3b depict the differential capacity plots and the voltage profiles for the ALD-MoO$_3$/ANL-NMC full cell. That shape of the curves match with what is expected from the half-cell results. The peaks around 2.5 V in Fig. 9.3a and small plateaus in Fig. 9.3b during the first cycle are consistent with the lithium extraction from LiMnO$_2$ and subsequent intercalation into crystalline MoO$_3$ from Fig 9.1 [11]. The sharp differential peak and corresponding voltage plateau beginning at 4.0 V can be attributed to the activation of the stabilizing Li$_2$MnO$_3$ cathode component and the majority of the MoO$_3$ lithium insertion resulting in the conversion reaction. The notable full cell hysteresis in the voltage discharge/charge profiles of approximately 1.7 V is primarily attributed to the large hysteresis of the ALD-MoO$_3$.

9.3.2 Electrochemical Performance and Stability

Finally, the electrochemical performance and stability of the ALD-MoO$_3$/ANL-NMC full cell is exhibited in Fig. 9.4. Even after 20 cycles, the full cell maintains a capacity above 150 mAh g$^{-1}$. The first cycle irreversible capacity loss measured to be 32% is slightly higher than either half-cell. In addition, the cell undergoes a slow but steady loss in capacity during cycling. Due to the large voltage window (0.01-4.55 V) it remains a possibility that lithium plating could occur, regularly causing a reduction in the available lithium. This phenomenon was not observed in the ALD-MoO$_3$ half cell (Fig. 9.2) since the lithium metal counter electrode provides an excess supply of lithium.
Figure 9.3: First and second cycle (a) differential capacity plots; and (b) voltage profiles for ALD-MoO$_3$/ANL-NMC full cell.
Figure 9.4: Electrochemical stability of ALD-MoO$_3$/ANL-NMC compared with bare MoO$_3$/ANL-NMC full cells.
9.3.3 Importance of Al$_2$O$_3$-coating on MoO$_3$

The application of ALD on MoO$_3$ is essential to achieving durable high-capacity, as depicted by the open triangles in Fig. 9.4. These points represent a full cell made with a bare, uncoated MoO$_3$ anode and ANL-NMC. Our previous study verified that bare MoO$_3$, with a lithium metal counter electrode, is stable for over 40 cycles with the identical appropriate ratio of AM:AB:PVDF [12]. However, when the lithium metal is replaced with the ANL-NMC, the reversible full cell capacity drops 30% in only 20 cycles. When the MoO$_3$ electrode is coated by ALD, the capacity loss after 20 cycles is only 11%. From these results, it is evident that the ALD coating is necessary in order to protect the anode surface from undesirable, lithium side-reactions at low voltages (and possible mechanical failure during volume expansion [11]).

9.4 Summary of ALD-MoO$_3$/ANL-NMC Pairing

This study demonstrates initial electrochemical performance of a novel high capacity, battery and clearly elucidates the importance of material selection. Electrode materials were chosen so that the anode and cathode exhibit a very similar first cycle irreversible capacity loss. By matching active materials based upon the first cycle irreversible losses, all material is then becomes active during the reversible electrochemical process. Importantly no prelithiation of either is required before cell fabrication. A stable capacity approximately twice that of most commercial cells is achieved with surface passivation of MoO$_3$. The ALD coating is necessary for to enable electrochemical anode stability while the Li$_2$MnO$_3$, containing excess lithium, allows for pre-lithiation to be avoided despite the irreversible first cycle capacity loss of the MoO$_3$ anode material.
References


Chapter 10

Surface Modification of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ Particles by ALD

In the past few years, there has been a large influx of papers published on replacements for LiCoO$_2$ cathodes. Despite the stability and high rate capability of LiCoO$_2$, LiCoO$_2$ is plagued by issues such as low operating potential, rapid phase change, and high cost. To offset dissolution and reduce overall cost, Co has been both partially and fully replaced with Ni and/or Mn. One viable LiCoO$_2$ replacement material is Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ layered structures.

A variety of fabrication techniques have been used to yield Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$. Ohzuku et al. produced pure Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ with a first cycle capacity of 165 mAh g$^{-1}$ using a solid state reaction [1]. Later, Park et al. employed spray pyrolysis in order to achieve a more uniform, homogeneous distribution of nanospherical particles [2]. High purity, spray pyrolysis Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ also performed well at high temperatures (173 mAh g$^{-1}$) while maintaining cycle stability (94% after 50 cycles). More recently, Sclar et al. reported on Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ fabrication by self-combustion reaction. By tailoring the temperature during an anneal, Sclar improved both the capacity and the rate capability of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ [3].

Despite performance gains through changes in synthesis methods, high surface area metal oxides continue to strongly react with standard electrolyte solutions.[3] One solution to prevent electrode/electrode interfacial reactions is to passivate the surface with a coating. A variety of coatings, such as ZrO$_2$, Al(OH)$_3$, CeO$_2$, and SnPO$_4$
have recently been shown to improve both the thermal stability and the rate capability of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ [4, 5, 6, 7, 8]. However, Al$_2$O$_3$ continues to be the most popular protective surface coating due to the high abundance of aluminum, the low cost of materials, and ease of film deposition. Using wet-chemical methods, Al$_2$O$_3$ has been successfully applied to high voltage cathode materials such as LiCoO$_2$, LiMnO$_2$, and Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ [9, 10, 11, 12]. Myung et al. speculates that Al$_2$O$_3$ may act as a scavenger of F$^-$ ions through the formation of Al-O-F and Al-F layers, limiting the concentration of harmful HF species [13].

However, with the exception of Martha et al. and Sclar et al., there is limited data beyond 50 cycles and up to 4.5V, indicating that the long term reversibility of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ might fall short of that for LiCoO$_2$. Likewise, surface films grown using most wet-chemical techniques either i) are unable to grow a uniform thin film, ii) operate at high temperatures or iii) require long growth time. In order to help improve the electrochemical performance of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$, we have chosen to use atomic layer deposition (ALD) to provide controllable, thin, uniform, conformal surface coverage rapidly and at a low temperature of 180 °C [14].

Here we report large gains in cycle stability through the growth of alumina directly on combustion synthesized (900 °C anneal) Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ powders using ALD. With as little as 4 Å of Al$_2$O$_3$, we increased stability and decreased resistance, with minimal change to overpotential and rate capability. We will show that the conformal, thin coating of alumina on Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ by ALD is one of the more promising commercial replacements for LiCoO$_2$.

10.1 Synthesis and Experimental Methods

Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ particles are synthesized from the procedures described in §5.1.2 and coated by Al$_2$O$_3$ by §5.1.4. A thick film, composite AM:AB:PVDF ratio was set to 83:7.5:9.5 by weight and deposited on an aluminum current collector (§5.1.3).
Electrochemical tests were performed in a closed CR-2032 coin cell configuration using lithium foil as a counter electrode (§5.1.5). Stability tests were cycled between 3.0 and 4.5 V using a constant current-constant voltage (CCCV) profile (§) consisting of a charge/discharge current density of 16 mA g$^{-1}$ (corresponding to C/10) for the first two formation cycles, an increase to 80 mA g$^{-1}$ (corresponding to C/2) for subsequent cycles, and a 1 hour voltage hold at 4.5 V. Rate studies were tested (3.0–4.5 V) using a symmetric galvanostatic profile with the current systematically increased from C/4 up to 2.5C every three cycles. Electrochemical impedance spectroscopy measurements were taken on every sixth cycle (100 mA g$^{-1}$) at 3.2 and 4.2 V on both charge and discharge. A one hour hold prior to measurement was employed to ensure constant voltage. The cyclic voltammogram measurements were taken at a scan rate of 0.1 mV/sec between 3.0 and 4.6V.

10.2 Results and Discussion

10.2.1 Characterization

Combustion synthesis (T$_c$ = 900 °C) of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ yields a fine, uniform, black powder. SEM images, shown in Figure 10.1, show the size distribution and the individual particle morphology. Particle size of the bare Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ ranges from 200 to 400nm in diameter. At a lower synthesis temperature of 700 °C, SEM images reveal a decrease in uniformity. Small, nano-sized particles become intermixed by larger formations made from long, platelet shaped Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$. Due to size homogeneity, Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ synthesized at 900 °C as seen in Fig. 10.1 was chosen as the active cathode material in this study.

Successful growth of Al$_2$O$_3$ on the surface of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ particles is confirmed from TEM and EDS. Preceding deposition, the bare surface is smooth with no distinct features present in TEM (Fig. 10.2a). Further elemental analy-
Figure 10.1: SEM images of combustion synthesized, bare Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$, annealed at 900 °C.
Figure 10.2: Bare Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ (a) TEM image; and (b) EDS elemental analysis. Al$_2$O$_3$ coated Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ (c) TEM image; and (d) EDS elemental analysis.
sis indicates high concentrations of Ni, Mn, Co, and O (Fig. 10.2b). Additional peaks labeled Cu are due to the copper sample mounting grid. Once alumina has been grown, TEM in Fig. 10.2c shows a uniform, conformal, white layer covering the \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) surface. The difference in TEM contrast between the surface film and the bulk \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) is attributed to compositional differences after coating. EDS (Fig. 10.2d) supports the presence of aluminum along the surface of the \( \text{Al}_2\text{O}_3 \)-coated sample that is not found in the bare sample. The metal peaks in the \( \text{Al}_2\text{O}_3 \)-\( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) identified by EDS remain similar in relative intensity to bare \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) and are a strong indicator that the ALD process does not change the elemental composition of the local structure. Unlike the metal counts, the relative intensity of oxygen after ALD increases by nearly 50% along the particle surface. Both the appearance of Al and the increase in O validates that the white coating visible by TEM is the ALD grown \( \text{Al}_2\text{O}_3 \) surface film.

The XRD pattern for bare and alumina coated combustion synthesized \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) is shown in Figure 10.3. The material is a highly crystalline layered structure, with diffraction peaks corresponding to the R-3m space group (166). The alumina coating (Fig. 10.3b) grown by ALD is amorphous and yields minimal changes to the material structure. Table 10.2.1 summarizes characterization differences between the bare and ALD coated \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \). The splitting of the (108), (110) and (006),(102) peaks seen in XRD as well as an integrated ratio of \( I(003)/I(104) > 1.2 \) indicate a well-ordered \( \alpha \)-NaFeO2 structure, with limited cation mixing [3].

### Table 10.1: Lattice constants and structural properties of bare and alumina-coated \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a (\text{Å}) )</th>
<th>( c (\text{Å}) )</th>
<th>( c/a )</th>
<th>( V (\text{Å}^3) )</th>
<th>( I_{003}/I_{104} )</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare ( \text{L333} )</td>
<td>2.863</td>
<td>14.219</td>
<td>4.97</td>
<td>100.94</td>
<td>1.25</td>
<td>0.52</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )-coated ( \text{L} )</td>
<td>2.860</td>
<td>14.231</td>
<td>4.98</td>
<td>100.80</td>
<td>1.30</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Figure 10.3: XRD spectra of a) bare and b) Al\(_2\)O\(_3\)-coated Li\(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\)O\(_2\) particles.
Selective regions of Raman and FT-IR are shown in Figure 10.4. Similar to XRD, alumina is assumed to be inactive for Raman and IR at low wavenumbers [15, 16]. We assume that the structure of Li(Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\))O\(_2\) is layered with a space group of R-3m, similar to that of LiCoO\(_2\). Therefore, the corresponding optical vibrational modes are [17],

\[ \Gamma = A_{2g} + E_g + 2A_{2u} + 2E_u \]  

(10.1)

The first two modes are visible only by Raman while the second two modes can be measured with IR. In theory, two Raman bands and four IR bands, two for each mode, should be visible. The active M-O symmetrical stretching and bending vibrational Raman modes of A\(_{1g}\) and E\(_g\) are labeled accordingly in Fig 10.4a. Both samples clearly show the two active Raman modes. However, bare Li(Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\))O\(_2\) Raman peaks are broader compared to after ALD-coating. Peak broadening is normally associated with increased structural disorder caused by the different cation-anion bond lengths of the metals [18, 19]. Commonly, broadening is accompanied by a red shift, a result of cation replacement, which is can be seen for the A\(_{1g}\) peak but is not as clear in the E\(_g\) mode. The ALD coating may help to increase the order of the surface structure of the Li(Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\))O\(_2\). For both samples, a small shoulder in near 640 cm\(^{-1}\) is visible that is not inherent to the Raman vibrational modes for a layered structure. A band at 630 cm\(^{-1}\) may strongly correlate to the F\(_{2g}\) mode of a cubic spinel structure as often found in LiMn\(_2\)O\(_4\) [20]. However, a spinel structure (Fd3m space group) has three vibrational modes and four defined Raman bands (\(\Gamma_{\text{raman}} = A_{1g} + E_g + 2F_{2g}\)) between 400 and 700 cm\(^{-1}\) [17]. Since a fourth peak is not visible in either of the Raman samples, we can assume that the presence of this feature does not indicate a local spinel structure. An alternate explanation is that the Raman shoulder may be due to the inherent disorder complex-layered structures compared to simple-layered structures, such as LiCoO\(_2\). As explained above, the structural disorder found naturally
Figure 10.4: (a) Raman spectra and; (b) FT-IR spectra of bare and ALD coated Li(Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3})O\textsubscript{2} powder
in poly-metal oxide structures has been shown to broaden Raman peaks. As the disorder increases, the symmetry may in turn decrease. Li et al. predicted that the additional Raman mode may be an artifact from this lowered symmetry [10]. The second two optical observable modes, $A_{2u}$ and $E_u$, consist of four bands visible by IR, three of which can be seen between 400 and 800 cm$^{-1}$ (Fig. 10.4b). The change in IR spectra due to alumina surface coating is identical to that recorded by Ref. [21]. Prior to an alumina coating, the bare Li(Ni$\frac{1}{3}$Mn$\frac{1}{3}$Co$\frac{1}{3}$)O$_2$ shows two clear peaks (540 and 610 cm$^{-1}$) corresponding to the M-O stretching and O-M-O bending. A smaller feature at 425 cm$^{-1}$ is the only visible LiO$_6$ line in the given range. As seen in both Raman and FTIR, and supported by XRD, even though the ALD coating alters the surface chemistry, the local structure remains constant.

### 10.2.2 Electrochemical Performance

Figure 10.5 compares the steady-state cyclic voltammagram (CV) for bare, 4-, 6-, and 10-layers of Al$_2$O$_3$, at a rate of 100 µV/s. Typical of Li(Ni$\frac{1}{3}$Mn$\frac{1}{3}$Co$\frac{1}{3}$)O$_2$, the bare sample displays a sharp cathodic peak at 3.90 V followed by a broader anodic feature during delithiation at 3.71 V. The bare peak separation potential is 190 mV. As expected, for 4- and 6-layers of Al$_2$O$_3$ (Fig 10.5b, 10.5c), the cathode peak is shifted to a higher overpotential of 3.91 and 3.92 V, respectively. When the particles are coated lithium ion kinetics slow through the alumina increasing polarization. Peak separation potentials increase to 200 mV (5% increase) for 4-layers of alumina and 210 mV (10% increase) for 6-layers of alumina. Surprisingly, despite the positive shift in the cathodic peak potential, no significant change in anodic peak potential is observed with 4- and 6-layers of alumina. Change in the anodic peak potential is not evident until 10-layers of alumina are grown on the Li(Ni$\frac{1}{3}$Mn$\frac{1}{3}$Co$\frac{1}{3}$)O$_2$ particles (Fig 10.5d). The reduced ionic mobility accompanied by a 10-layer thick alumina coating decreases the anodic peak to 3.69V and increases the total peak separation potential to 300 mV (58%
Figure 10.5: Li(Ni$^{1/3}$Mn$^{1/3}$Co$^{1/3}$)O$_2$ Cyclic Voltammogram (a) bare; (b) 4-Al$_2$O$_3$; (c) 6-Al$_2$O$_3$; and, (d) 10-Al$_2$O$_3$ coated Li(Ni$^{1/3}$Mn$^{1/3}$Co$^{1/3}$)O$_2$. 
The stability enhancement of the ALD coating is most visible from the electrochemical performance (Fig 10.6a). After three cycles, the current rate was increased from $C/10$ to $C/2$ at room temperature ($1C = 160 \text{ mAh g}^{-1}$). The bare Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ displays a stable capacity of $150 \text{mAh g}^{-1}$ for 15 cycle, after which the capacity begins to steadily drop, retaining only 103 mAh $g$ by the 100$^{th}$ cycle. However, upon the application of 2-ALD layers of Al$_2$O$_3$, the Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ retains 140mAh/g after 100 cycles and exhibits no change in initial capacity. Similar improvements are also observable when the coating thickness is increased to 4- and 6-layers. For thicker films, the decrease in first cycle specific capacity can be associated with slower ionic mobility through the Al$_2$O$_3$ to reach the Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ core. Despite a lower initial capacity from the additional mass of the inactive alumina, the capacity after 40 and 70 cycles of 4- and 6-Al$_2$O$_3$ Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ is greater than the bare due to the improved electrochemical stability. Of the ALD coatings tested, only 10-Al$_2$O$_3$ is found to be detrimental to the overall performance of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$. Since alumina is a both an electronic and ionic insulator, the thicker coating tends to physically isolate individual particles from direct contact with conductive acetylene black. Figure 10.6b further examines the effect ALD coating thickness on Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ capacity retention when cycled with an upper cutoff of 4.5 V. The capacity retention was measured after 20, 40 and 110 cycles for coated samples. ALD thicknesses were calculated assuming each layer of alumina is 2.2 Å. The data was then fit with an exponential curve. 2-, 4-, and 6- layers of ALD grown Al$_2$O$_3$ all remain electrochemically stable by retaining $>80\%$ of their initial capacity after 110 cycles. Once the coating thickness exceeds 12 Å, the electrochemical stability is significantly affected by ion and electron mobility and kinetics. However, similar to previous studies on ALD coated LiCoO$_2$, graphite, and MoO$_3$, our maximum allowed thickness (1.2 nm) is significantly less than all other coatings grown using other deposition meth-
Figure 10.6: Bare and Al$_2$O$_3$ coated Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ particles at room temperature: (a) Electrochemical performance and stability at C/2; and (b) Capacity retention as a function of alumina film thickness measured during electrochemical testing at specific cycles.
ods [9, 22, 23]. Alumina coatings grown by wet-chemical techniques with thickness of 4 nm, 5 nm, and even 1.2 µm (10 times greater than ALD maximum thickness) displayed notable improvements in stability after 40 cycles [12, 13, 24]. At the time, we are unable to provide a concrete explanation for the difference in performance as a function of coating method. Possible factors include differences in density of the grown films, diffusion of aluminum into the active material at high temperatures, film defects and impurities, and coverage area. However, it is clear that the high purity and conformal nature of Al₂O₃ grown by ALD is able to protect material surfaces by using less material than conventional deposition techniques.

Rate capability of bare and 4-Al₂O₃ coated Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂ is shown in Figure 10.7. The rate performance of the bare sample is found to be comparable to recently reported Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂ combustion synthesis with a 900 C anneal [3]. Even at a rate of 2.5C (400mA g⁻¹), our bare sample maintains a capacity of 120 mAh g⁻¹. The high rate capability of bare Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂ is attributed to the small particle size. Similar to results in a reported study by Hu et al., the alumina coating improves total stability and cycle life, though produces a small decrease in capacity at higher rates when compared to bare samples [5]. We can conclude that the maximum capacity at high rates for bare Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂ nanoparticles is determined by the bulk material properties, such as the coefficient of diffusion, and not on surface degradation mechanisms. After ALD coating, the alumina serves as a barrier to ion mobility which decreases the total capacity. This is especially evident at higher rates as the capacity difference increases between bare and ALD coated samples.

10.2.3 Electrochemical Impedance Spectroscopy

The failure of high voltage cathodes is normally attributed to dissolution or the side reaction between the liquid electrolyte and the active material [25]. In order to further explain the electrochemical performance results, electrochemical impedance spec-
Figure 10.7: Rate capability comparison between bare and 4-Al$_2$O$_3$ coated Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$. A rate of 1C is assumed to be equivalent to a current density of 160 mA g$^{-1}$. 
troscopy (EIS) measurements were recorded after lithium extraction for 100 cycles (4.2 V). Figure 10.8 shows the Nyquist plots for bare and Al₂O₃ coated Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂. Frequency increases from right to left, with the inset depicting the high frequency region of the bare sample, consisting of two overlapping semicircles. The Nyquist is divided into distinct sections and labeled in Fig. 10.8a as,

(i) the ohmic resistance of the liquid electrolyte ($R_{\text{sol}}$)

(ii) the impedance of the natural and artificial solid electrolyte interface ($R_{sf} \parallel C_{sf}$)

(iii) the impedance of electrons through the active material ($R_b \parallel C_b$)

(iv) the charge-transfer resistance and the double layer capacitance ($R_{ct} \parallel C_{dl}$)

(v) the impedance to the solid-state diffusion of lithium ($Z_w$)

as introduced by Warburg [26, 27]. Sections (ii) and (iii) are considered the high frequency region (HFR), (iv) as the mid frequency region (MFR), and (v) as the low frequency region (LFR). The scale for Figs 10.8a & 10.8b is identical in order to provide a more accurate visual comparison between the bare and the alumina coated Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂. For $R \parallel C$ impedance features, the resistance is closely related to the circle diameter. The most prominent difference between Fig 10.8a and 10.8b is in the charge-transfer impedance feature (iv).

The impedance spectra were fit to the equivalent circuit model seen in Figure 10.8c. The model consists of a series of frequency-independent circuit elements, each one identified as a component on the Nyquist. Due to non homogeneity of the composite, capacitor elements were replaced with constant phase elements (CPE). The impedance for CPE is defined as

$$Z_{CPE} = 1/B(j\omega)^n$$  \hspace{1cm} (10.2)

where $\omega$ is angular frequency, $j = \sqrt{-1}$, $B$ is a constant, and $n$ represents the distortional effects due to non homogeneity of the electrode surface. As $n$ approaches a value of 1,
Figure 10.8: Electrochemical impedance spectroscopy (EIS) Nyquist plots of: (a) bare; and (b) 4-Al$_2$O$_3$ coated Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$. Z indicates the imaginary axis while Z indicates the real axis. The curves were fit with a (c) Voigt-type equivalent circuit.
the frequency response of a CPE is equivalent to that of a capacitor, where \( B \rightarrow C \). Impedance for the Warburg-like element is defined by

\[
Z_W = A_w \omega^{-1/2}(1 - j)
\]  

(10.3)

where \( A_w \) is the Warburg coefficient [28]. Previously explained by Franceschetti and Macdonald, the proposed Voigt-type circuit model in Fig 10.8c can be accurate and used to fit impedance data under loosely couples conditions [29]. So initial parameters were chosen based results from an in-depth study of bare \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) by Shaju et al. under the assumption our impedance values would be of similar order of magnitude to those by Shaju [30].

Results of equivalent circuit fitting are depicted in Figure 10.9a and 10.9b. Trends for \( R \), \( C \), and \( n \) during the first 40 cycles of bare \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) closely match the results reported by Shaju. The constant values of \( C_b \) and \( n_b \) indicate no significant changes in porosity of conductivity, while the steady increase in \( R_{ct} \) may indicate changes in lithium diffusion [30]. After 4-layers of \( \text{Al}_2\text{O}_3 \) grown on \( \text{Li(Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) particles, the double layer capacitance (\( C_{dl} \) and \( n_{dl} \)) and the bulk electronic resistance (\( R_b \)) remain unchanged. However, the charge-transfer resistance (\( R_{ct} \)) actually decreases in value as a function of cycle number. Since the ALD coating merely protects the surface from electrolyte/electrode interfacial interaction and does not suppress changes in phase, we do not attribute changes in bare-\( R_{ct} \) to natural changes in phase during the cycling process, but rather possibly due to material property changes occurring as a result of dissolution or HF attack. The constant value of ALD-\( R_{ct} \) is attributed to the added protection of the material from the liquid electrolyte and supports the improved cycling stability seen in Fig. 10.8.

Despite alumina being an ionic and electronic insulator, extensive studies on \( \text{LiCoO}_2 \) have shown similar EIS results when surface coatings of \( \text{Al}_2\text{O}_3 \) are converted to a thin layer of \( \text{Li-Al-Co-O} \) after heat treatment [11]. This layer is found to decrease
Figure 10.9: Equivalent circuit values fit to Fig. 10.8c: (a) bare Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2; and (b) ALD-coated Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2.

Values were collected at 4.2 V on during lithium extraction (charging) after a one hour voltage hold.
surface resistance and improve cycle stability. A previous study by Kim et al. showed that the EIS response of alumina-coated Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ particles by sol-gel method is extremely sensitive to the coating thickness [31]. The authors surmise that a heavy coating of 5 wt.% Al$_2$O$_3$ inhibits the movement of Li$^+$ ions while the lighter coating of 3 wt.% Al$_2$O$_3$ provides optimal protection and Li-Al-M-O formation. While similar on many levels, the most notable difference between the sol-gel studies cited and this work is the absence of heat treatment of our ALD-coated particles. In order to form the lithium-bearing surface film through ion migration, sol-gel coated particles need to be heated at temperatures above 500 °C. Thicker films or films not undergoing heat treatment fail to form a uniform ion conductive surface. ALD-grown Al$_2$O$_3$ does not require heat treatment to obtain improved conductivity. By eliminating heat treatment, surface coating of powders by ALD becomes both faster and less expensive than by wet-chemical methods. The enhanced performance and lower resistance seen in EIS reported in this work are attributed to the formation of a lithium-bearing surface film which occurs during electrochemical cycling. Further studies are currently underway to extensively examine the electrochemical evolution of conformal ALD coatings.

10.3 Summary of Surface Modified Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$

Here we have shown that conformal and uniform coatings are highly important to performance optimization of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$. Even after 100 cycles, the frequency response of the coated Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ remains unchanged and suitably protected from physical contact with the liquid electrolyte even with only 4 monolayers of conformal alumina. As evidenced by electrochemical performance and CV, the stability and retention can be greatly improved. Changes to the overpotential are extremely sensitive to film thickness. Large variations in film thickness seen from wet chemical coating methods could create a wide range of potential drops along the surface of a single particle. We believe that only through layer-by-layer controllable coverage, such
as ALD, can the maximum efficiency and stability be achieved with minimum addition of non-reactive material.
References


Chapter 11

Summary and Concluding Remarks

11.1 Contributions to the Field of Electrochemistry

The goal for this research was to help stabilize high energy density materials for commercial use in lithium-ion batteries (LIBs). This goal has been achieved through the completion of three primary objectives as discussed in Chapters 6, 7, 8, 9 and 10.

The initial objective focused on improving the electrochemical stability and rate capability of MoO$_3$, a replacement anode material for graphite using two methods: first, through the optimization of composition and heat treatment temperature and second, by coating electrodes with Al$_2$O$_3$ using ALD. The optimal electrochemical composition of MoO$_3$ electrodes is binder-rich (70:10:20 MoO$_3$:AB:PVDF). The excess binder is necessary due to the high surface area to volume ratio found in nanoparticles. For improved performance, the binder-rich electrodes require an additional pre-anneal at 250 °C to remove unwanted chemisorbed water just prior to polymer decomposition. Surface passivation on both individual particles and pre-fabricated electrodes were tested. Despite particle-coated success in cathode materials, the high energy density, high volume expansion MoO$_3$ showed an unstable and detrimental response to thin layers of Al$_2$O$_3$ directly on the particle surface. Significant improvements were obtained only through complete electrode coating with 4-layers of amorphous Al$_2$O$_3$ by atomic layer deposition. The Al$_2$O$_3$ conformal ultrathin layers protect against electrolyte/electrode interfacial reactions while providing mechanical stability and adhesion to the current
collector. This work was a collaboration between the National Renewable Energy Laboratory (NREL) and the University of Colorado at Boulder.

A direct extension of the initial objective, the second objective was to fully utilize the optimized, ALD-coated MoO$_3$ anode in a lithium-metal free, secondary lithium-ion battery. Commonly referred to as full cells, secondary batteries are advantageous due to increased safety and engineering design control. Full cells present new issues and considerations since an infinite supply of lithium is no longer available. Small losses and side reactions have a greater effect on the overall stability and reversibility. The counter electrode was a state-of-the-art lithium excess cathode, Li$_2$MnO$_3$-stabilized LiMO$_2$ (M = Mn$_{0.31}$Ni$_{0.44}$Co$_{0.25}$) or ANL-NMC, by Argonne National Laboratory (ANL). The ANL-NMC supplies additional lithium through the activation of lithium-bearing metal-oxide octahedral sites. Upon the removal of lithium, the metal-oxide layers are then capable of undergoing stable and reversible lithium insertion and extraction. Through proper and precise pairing, the 4-Al$_2$O$_3$ coated MoO$_3$ electrodes were successfully cycled against the high voltage ANL-NMC. Even for a severe, deep discharge down to 0 V versus lithium, the ALD-MoO$_3$/ANL-NMC maintained a capacity over 150 mAh g$^{-1}$ over 10 cycles. This is unmatched by commercially available C$_6$/LiCoO$_2$ with a maximum reversible capacity of only 80 mAh g$^{-1}$. The success of the stability is attributed both to the groundbreaking cathode chemistry and the ALD surface protection and mechanical enhancement of the MoO$_3$ electrodes. This work was completed as a strong collaboration between the NREL, CU Boulder and ANL.

The final objective was to improve the capacity retention and stability of Li(Ni$_{1/3}$ Mn$_{1/3}$Co$_{1/3}$)O$_2$ cathode at high voltages up to 5.0 V versus lithium. At potentials above 4.2 V versus lithium metal, the non-aqueous, organic, ionically conductive liquid salt decomposes forming CO, CO$_2$, O$_2$ and a slew of other undesirable compounds. These products further react with the electrode surfaces causing accelerated decomposition, dissolution and self-sustaining HF formation. Both Li(Ni$_{1/3}$ Mn$_{1/3}$Co$_{1/3}$)O$_2$ particles
and pre-fabricated electrodes were coated by amorphous Al₂O₃ using ALD. When cycled up to 4.5 V, both the particle coated and the electrode coated exhibited identical behavior and electrochemical stability over the bare sample. When cycled up to 5.0 V, the particle coating only protects the active material but not the binder and conductive additive. On the other hand, ALD coated electrodes show a strong reversible performance even up to 5.0 V. The conformal nature of ALD on all electrode materials, including the aluminum current collector, provides the necessary stability for long cycle life.

11.2 Challenges for Future Research

This work is the first in-depth study on the use of atomic layer deposition as method to grow protective surface films on materials and electrodes for lithium secondary batteries. The results help to provide insight to the function of the ALD surface layer and allows for the further study using alternative coatings as well as active materials and compositions. Only two materials (MoO₃ and Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂) have been tested in addition to two previously in literature (LiCoO₂ and graphite). These materials happen to stable in air and safe to handle. Unlike the work done in this study, large scale commercialization of battery materials tend to be handled in a dry room rather than a glove box. The in-air synthesis and fabrication process eliminates many viable materials due to reactivity. Materials which are air sensitive, such as sulfur compounds, are ideal candidates for surface protection.

Tests were also performed using only Al₂O₃ as the coating material. Atomic layer deposition has been used and researched for nearly 40 years. There exists a wide range of chemistries to synthesize oxides, phosphates, sulfates, fluorites and even metals. Al₂O₃ is a well known chemistry and well researched as a coating using wet-chemical techniques. Now that initial demonstrations have shown the viability of ALD for lithium ion batteries, research can focus on experimenting with new ALD chemistries
to help promote lithium ion transfer while retaining high electrical conductivity. For high volume expansion materials, the use of ductile more rubber-like materials would resist mechanical failure under expansion stress.

11.3 Concluding Remarks

Since it’s first development in the early 1970’s, there has never been as much money and interest in the use and research of lithium battery technology. While decades of results have yielded many answers they have also produced an array of new and exciting questions. It is this author’s hope that this thesis will help others answer their own questions down the road.

I think I cannot deceive myself in considering the doctrine of definite electrochemical action as of the utmost importance. It touches by its facts more directly and closely than any former fact, or set of facts have done, upon the beautiful idea, that ordinary chemical affinity is a mere consequence of the electrical attractions of the particles of different kinds of matter; and it will probably lead us to the means by which we may enlighten at which is at present so obscure, and either fully demonstrate the truth of the idea or develop that which ought to replace it.

Michael Faraday (On Electrochemical Decomposition, 1834)
Appendix A

Publications and Presentations

A.1 Scholarly Publications


A.2 Conference Presentations


A.3 Poster Presentations


Appendix B

Ultrathin Direct Atomic Layer Deposition on Composite Electrodes for Highly Durable and Safe Li-Ion Batteries

B.1 Introduction

In order to employ Li-ion batteries (LIBs) in next-generation hybrid electric and/or plug-in hybrid electric vehicles (HEVs and PHEVs), LIBs must satisfy many requirements: electrodes with long lifetimes (fabricated from inexpensive environmentally benign materials), stability over a wide temperature range, high energy density, and high rate capability. Establishing long-term durability while operating at realistic temperatures (5000 charge-depleting cycles, 15 year calendar life, -46 °C to 66 °C) for a battery that does not fail catastrophically remains a significant challenge [1].

Recently, surface modifications of electrode materials have been explored as viable paths to improve the performance of LIBs for vehicular applications [2, 3, 4, 5]. The cycle life and safety issues have been largely satisfied for LiₓMO₂ (M = Co, Ni, Mn, etc.) cathodes by coating the active material particles with a metal oxide and/or metal phosphate [2, 3, 6, 7]. For anode, state-of-the-art materials such as Si, suffer from significant volume expansion/contraction during charge-discharge leading to rapid capacity fade [8, 9]. Natural graphite (NG) is a realistic candidate anode, for vehicular applications, due to its high reversible capacity, low and flat potential relative to Li/Li⁺, moderate volume change, and low cost [10, 11, 12]. In previous reports, the performance of NG was improved by surface modifications with mild oxidation [13], coating with amorphous
carbon [12], metal oxides (Al₂O₃, ZrO₂) [10, 14, 15] and metal phosphate (AlPO₄) [11]. These efforts were performed in order to mitigate the solid electrolyte interphase (SEI) [16, 17, 18] that is formed on the NG surface by reductive decomposition of the electrolyte during initial charge/discharge especially at elevated temperatures. The decomposition of the SEI at elevated temperature (80 °C) is exothermic and initiates thermal runaway [19, 20]. In most previous reports films of metal oxides and metal phosphates have been deposited on powder electrode materials with ‘sol-gel’ wet-chemical methods [2, 3, 6, 7, 10, 11, 12, 14, 15]. Unfortunately, sol-gel methods require large quantities of solvents as well as multiple complex steps. Also, these chemical techniques may only be employed for powders (i.e. a fully fabricated electrode cannot be coated).

Here we clearly demonstrate that conformal ultrathin protective coating by inactive metal oxide without disrupting inter-particle electronic pathway can be realized by atomic layer deposition (ALD) directly performed on a composite electrode, which leads to significant improvement of both long-term durability and safety of NG anode. Also ALD coatings are significantly more promising than efforts that have been previously reported.

Atomic layer deposition is a well established method to apply conformal thin films on high-surface area tortuous networks using sequential, self-limiting surface reactions [21]. Also, the thickness of ALD coatings is easily tailored at the atomic level (Å-level control). Recently, we reported that Al₂O₃-coated LiCoO₂ electrodes display superior electrochemical performance in comparison to LiCoO₂ electrodes that were not coated with ALD [22]. We employed a simple, well-known ALD process utilizing trimethylaluminium (TMA) and H₂O as precursors [23]:

\[
\text{AlOH}^* + \text{Al(CH₃)₃} \rightarrow \text{AlO} - \text{Al(CH₃)₂}^* + \text{CH₄} \quad \text{(B.1)}
\]

\[
\text{AlCH₅}^* + \text{H₂O} \rightarrow \text{Al} - \text{OH}^* + \text{CH₄} \quad \text{(B.2)}
\]
The performance of both of these steps constitutes one ALD cycle.

In all of the previous efforts to apply protective coatings, the coatings were applied to powders, that then comprise the active material in the electrode, but not directly on the composite electrode, containing conductive additive and binder [2, 3, 6, 7, 10, 11, 12, 14, 15]. (Commercial LIBs are comprised of composite electrodes containing an active Li-ion insertion/extraction compound, carbon as a conductive additive, and a polymeric binder.) We have demonstrated that applying a conformal coating directly to the electrode is critical to achieving optimal electrochemical performance for LIB vehicular applications.

B.2 Experimental

B.2.1 Atomic layer deposition

Al₂O₃ ALD films were grown directly on NG and LiCoO₂ particles using a rotary reactor. For the Al₂O₃ ALD, TMA (97%) and HPLC (high performance liquid chromatography) grade H₂O was obtained from Sigma-Aldrich. The typical growth rate for the chemistry is 1.1 Å per cycle [24]. However, due to the large surface area of the LiCoO₂ and NG powders, it is difficult to completely purge H₂O from the reactor. The presence of H₂O in the reactor during the TMA reaction leads to slightly enhanced growth per cycle resulting from some chemical vapor deposition.

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

For the NO₂ nucleation treatment, commercial purity grade NO₂ (99.5%) was acquired from Airgas. In this work, 10 cycles of NO₂/TMA functionalized the NG. This
NO$_2$/TMA functionalization was performed with the following sequence: (1) exposure to NO$_2$ to set pressure; (2) evacuation of excess NO$_2$; (3) exposure to TMA to set pressure; and (4) TMA excess evacuation. This sequence defines one AB cycle of the NO$_2$/TMA functionalization layer.

**B.2.2 Electrochemical characterization.**

The LiCoO$_2$ composite electrode was prepared by spreading LiCoO$_2$ powder (7-10 µm, L106, LICO Technology), acetylene black (AB), and PVDF (poly(vinylidene fluoride), binder) (83.0:7.5:9.5 weight ratio) on a piece of Al foil. The NG composite electrodes were composed of NG (5 µm, HPM850, Asbury Graphite Mills Inc.) and PVDF (90:10 weight ratio) on Cu foil. Cells were assembled in an Ar-dry box and tested in a temperature-controlled oven. The galvanostatic charge-discharge cycling was performed in 2032-type coin cells. The LiCoO$_2$/Li cells were cycled between 3.3-4.5 V at 0.1 C-rate (14 mA g$^{-1}$) for the first two cycles and 1 C-rate for the subsequent cycles at room temperature. The NG/Li cells were cycled between 0.005-1.500 V at 0.1 C-rate (37 mA g$^{-1}$) for the first two cycles and 0.5 C-rate for subsequent cycles. LiCoO$_2$/NG full cells were cycled at 3.30-4.45 V, 0.1 C-rate (14 mA/g of LiCoO$_2$)$^{-1}$) for the first two cycles and 1C for subsequent cycles. The weight ratio of LiCoO$_2$/NG was 1.4. 1.0 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v). As the separator, a glass fiber sheet and a porous 20 µm thick polypropylene (PP)/polyethylene/PP trilayer film were used for NG/Li and NG/LiCoO$_2$ cells, respectively.

**B.2.3 Thermal properties.**

Perkin-Elmer DSC experiment were conducted on fully lithiated bare NG electrodes and NG electrodes coated with 5 Al$_2$O$_3$ ALD cycles with NO$_2$ pretreatment. The scan rate and measurement temperature range were 10$^\circ$C min$^{-1}$ and 50-350 $^\circ$C, respec-
tively. The fully lithiated electrodes were prepared in lithium cells by cycling four times between 0.005 and 1.5 V at 0.063 mA cm$^{-2}$ and charging to 0.005 V before DSC sample preparation. The electrolyte used for the DSC experiment was 1.2 M LiPF$_6$ in a mixture of EC and ethyl methyl carbonate (EMC) (3:7 wt %). The cells were disassembled and a portion of the fully charged electrode was scraped from the Cu current collector and hermetically sealed inside high-pressure stainless steel crucibles. Preparation of the DSC samples was conducted in an Ar-filled dry box. An empty, sealed stainless steel crucible was used for the reference pan of the calorimeter. To ensure reproducibility of the experimental data the DSC measurement was duplicated for each sample.

**B.3 Results and Discussion**

Figure B.1a displays a scanning electron microscope (SEM) cross-sectional image of a NG composite electrode following 5 cycles of Al$_2$O$_3$ ALD. The cross section was fabricated with focused ion beam (FIB) gallium milling. As depicted in Fig B.1a, the electrode is very porous. Seven regions of the electrode were analyzed with energy dispersive spectroscopy (EDS) to acquire elemental analysis data. Fig. B.1b is a plot of the weight fraction of Al (Al/(C + Cu + Al)) as a function of the EDS depth profile in the NG composite electrode. Note, the Al content remains constant throughout the NG electrode (regions 1-6) and is negligible on the face of the Cu foil (region 7). The absence of the Al on the surface of the Cu foil and the relatively constant concentration of Al demonstrates that the Al is deposited conformally with ALD and not inadvertently sputter deposited during the FIB process. This was also confirmed by employing FIB milling to sputter through the Cu foil from the backside of the electrode. It was then possible to detect Al at only the Cu/NG interface. This conclusively shows that ALD precursors can diffuse through the pores of composite electrodes to deposit a conformal Al$_2$O$_3$ film in the torturous path of the entire electrode structure.

As discussed in more detail below, we have also demonstrated that in most cases
Figure B.1: SEM/EDS analyses of Al$_2$O$_3$ ALD electrodes. a) FE-SEM cross-sectional image of a NG composite electrode coated with 5 cycles of Al$_2$O$_3$ ALD. Numbers indicate regions in which Al was analysed with EDS. b) Weight fraction of Al as a function of depth.
it is critical to apply an ALD coating directly to a fabricated electrode rather than to powders of active materials. We believe that when ALD is performed directly on powders, slower Li-ion diffusion as well as $e^-$ transport through the $\text{Al}_2\text{O}_3$ layer is observed. Conversely when ALD is employed on the composite electrode the $\text{Al}_2\text{O}_3$ is not deposited at contact points between active material particles and the current collector, maintaining electrical conductivity and enabling rapid electron transport. Figure B.2a displays a schematic representation of Li-ion and electron transport through LiCoO$_2$ particles in an electrode fabricated from ALD coated powders and an ALD coated composite electrode.

Figure B.2b compares the charge-discharge voltage profiles of bare LiCoO$_2$ and LiCoO$_2$ (commercial cathode technology) coated with 20 cycles of ALD on the powder and also directly on the electrode. The additional overpotential (‘*’) with respect to bare LiCoO$_2$ for ALD on the powder is larger than that observed (‘**’) for ALD directly on the electrode. The difference between the overpotential of the ALD on the powder and the ALD directly on the electrode may be attributed to the hindrance of $e^-$ transport in the $\text{Al}_2\text{O}_3$ film resulting from the complete ALD coverage on the active material powder. Figure B.2b also suggests that the kinetics is actually improved by growing the ALD $\text{Al}_2\text{O}_3$ film directly on the composite electrode.

Typically the first ALD $\text{Al}_2\text{O}_3$ reaction requires a hydroxyl-terminated surface, which is present on metal oxides. However, the conjugated carbon bonds in the graphitic planes of NG are relatively inert. Thus in order to perform ALD on the NG surface, it was necessary to pre-treat the NG with NO$_2$ prior to TMA exposure [25, 26]:

\begin{align}
\text{NG}^* + \text{NO}_2 & \rightarrow \text{NG} - \text{NO}_2^* \\
\text{NG} - \text{NO}_2^* + \text{TMA} & \rightarrow \text{NG} - \text{NO}_2^* - TMA^* 
\end{align}

Following this process, the NO$_2$ nitrogen behaves as a Lewis base and is attached to the NG surface via strong van der Walls interactions leaving oxygen atoms accessible
Figure B.2: a) Schematics of transport in LiCoO$_2$ composite electrodes when ALD is performed first on the powder versus when ALD is performed directly on the composite electrode. b) Charge-discharge curves at 1 C-rate (140 mA g$^{-1}$) at room temperature. Note the polarization increase ("\(^{\wedge}\)" and "\(^{*}\)"") observed for Al$_2$O$_3$ coatings with respect to the curve for bare LiCoO$_2$. 
to reaction with TMA. In order to demonstrate the effect of the NO\textsubscript{2} pretreatment, Al\textsubscript{2}O\textsubscript{3} ALD on NG was performed with and without NO\textsubscript{2} pretreatment. The electronic conductivity was then measured for each sample to verify thickness and conformity of the ALD coating (Supplementary Fig. S1). As expected, the ALD Al\textsubscript{2}O\textsubscript{3} coated NG showed decreased conductivity with increasing number of ALD cycles, and the NO\textsubscript{2} pretreated NG was less conductive than non-treated NG.

Furthermore, NG electrodes prepared with Al\textsubscript{2}O\textsubscript{3} ALD coatings on powder and also directly on the electrodes were tested using charge-discharge cycling at a highly elevated temperature of 50 °C. As a control sample, bare NG was also tested at 50 °C. The bare NG displays a relatively rapid decay in reversible capacity versus the number of charge-discharge cycles (Fig. 3a), attributed to instability of a SEI layer [18]. Conversely, the capacity retention is dramatically improved by performing only 5 cycles Al\textsubscript{2}O\textsubscript{3} ALD directly on the electrode. Highly improved electrochemical performance was obtained both with and without the use of a NO\textsubscript{2} surface nucleation pretreatment. The charge-discharge capacity retention for the electrode coated with 5 Al\textsubscript{2}O\textsubscript{3} ALD cycles with NO\textsubscript{2} is 98% for 200 charge-discharge cycles, normalized to the reversible capacity at the 3\textsuperscript{rd} charge-discharge cycle, with negligible kinetic hindrance. Surprisingly, the electrode coated with 5 cycles Al\textsubscript{2}O\textsubscript{3} ALD without NO\textsubscript{2} pretreatment also displayed excellent capacity stability indicating that the NG must have enough edge and/or defective sites to allow for TMA nucleation. The improved cycle life achieved via ALD directly on the electrode is believed to result from a stable ‘artificial’ thin film SEI of Al\textsubscript{2}O\textsubscript{3} that protects the NG surface from undesirable decomposition reactions with the electrolyte.

In an extensive comparison of the charge-discharge cycle retention relative to the number of ALD cycles for samples with and without the NO\textsubscript{2} pretreatment, thicker conformal coatings exhibit slightly better electrochemical performance (Table B.3). At room temperature, ALD Al\textsubscript{2}O\textsubscript{3} coated NG also exhibits excellent cycling retention with
Table B.1: Cycle performance of Al₂O₃-coated NG electrodes.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>ALD Cycle number</th>
<th>NO₂/TMA</th>
<th>Capacity retention [%]</th>
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<td></td>
<td></td>
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<td>100th</td>
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<tr>
<td>RT</td>
<td>Bare</td>
<td></td>
<td>90</td>
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<tr>
<td>RT</td>
<td>2</td>
<td>No</td>
<td>100</td>
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<tr>
<td>RT</td>
<td>5</td>
<td>No</td>
<td>104</td>
</tr>
<tr>
<td>RT</td>
<td>5</td>
<td>Yes</td>
<td>104</td>
</tr>
<tr>
<td>50 °C</td>
<td>Bare</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>50 °C</td>
<td>2</td>
<td>No</td>
<td>96</td>
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<tr>
<td>50 °C</td>
<td>5</td>
<td>No</td>
<td>97</td>
</tr>
<tr>
<td>50 °C</td>
<td>5</td>
<td>Yes</td>
<td>99</td>
</tr>
</tbody>
</table>

negligible kinetic limitations (Supplementary Fig. S2). When compared with the previous results obtained from NG coated by wet chemical methods (Table S1), ALD-coated NG delivers much more promising performance even at elevated temperature (50 °C).

In contrast with the Al₂O₃ ALD coating on the NG electrode, Fig. B.3a shows that NG particles coated with 5 cycles of Al₂O₃ ALD, subsequently fabricated into electrodes, display significantly decreased capacity retention compared to bare NG. The degradation in performance is attributed to the insulating property of the Al₂O₃ film. The insulating Al₂O₃ layer inhibits electron conduction paths between NG particles and the current collector. A schematic of this effect is illustrated in Fig. 3b. We also note that NG experiences an ~13% volume change during a charge-discharge cycle [27]. For the ALD powder, the NG particles and the current collector are isolated by the insulating Al₂O₃ film and therefore even a slight volume change in the NG disrupts the electrical conductivity between the particles and current collector. The repeated volume expansion and contraction subsequently accelerates loss of electronic conduction pathways. Importantly, ALD performed directly on the electrode enables the electrical pathways between particles to not be coated with an insulating layer allowing for necessary conductivity (Fig. B.3b).

The irreversible capacity observed upon the first charge is undoubtedly attributed
Figure B.3: Electrochemical performance for ALD coated NG composite electrodes. a) Cycle performance at 50 °C. b) Schematic representation transport in NG composite electrodes prepared by ALD on powder and ALD directly on the electrode. c) Differential first charge voltage profiles at room temperature. d) Coulombic efficiency (CE) at the first charge-discharge cycle. e) Voltage profiles at room temperature when using 1 M LiPF₆ in PC as electrolyte.
to the formation of an SEI layer [16, 17, 18, 28]. However, this large irreversible reaction is undesirable because it results in large impedance and also causes loss of valuable Li$^+$ from the cathode material, which results in ultimately lower full cell capacity. The intensity of the differential charge peak at 0.7 V during the first charge (Fig. B.3c) indicates that the irreversible reductive decomposition of the electrolyte decreases for NG coated with ALD Al$_2$O$_3$ and further decreases if the NO$_2$ pretreatment is employed (Bare $>$ 5 ALD cycles $>$ 5 ALD cycles with NO$_2$ pretreatment). Accordingly, the coulombic efficiency (CE), the ratio of discharge capacity to charge capacity, significantly increases (Fig. B.3d) for the NO$_2$ treated sample. Furthermore, the conformal Al$_2$O$_3$ coating on the composite NG electrodes allows propylene carbonate (PC) to be employed as the electrolyte. Due to its low melting point ($\sim$49 °C) [12] PC is essentially only employed for operating LIBs at low temperatures and is thus particularly important for cold weather operation of HEVs. The voltage plateau at 0.8 V for bare NG is indicative of electrochemical exfoliation by PC molecules.[12, 29] In contrast, NG electrodes coated with 5 cycles of Al$_2$O$_3$ ALD with the NO$_2$/TMA process allows for reversible Li$^+$ insertion/extraction without an irreversible plateau related to exfoliation (Fig. B.3e) and importantly reveals stable cycling performance (Supplementary Fig. S3). Furthermore, PC-NG compatibility achieved by ALD confirms the conformity of the ALD coating and also suggests commercialization of ALD processes for a variety of electrode materials.

Figure B.4 shows differential scanning calorimetry (DSC) curves of the fully lithiated bare NG electrode (dashed line) and NG electrode coated with 5 Al$_2$O$_3$ ALD cycles with the NO$_2$/TMA process (solid line) in the presence of electrolyte. The fully lithiated, ALD coated NG electrode exhibits significantly lower heat generation between 100-150 °C compared to bare NG electrodes. The heat generation in this temperature range is attributed to conversion of a meta-stable SEI to a more stable SEI layer or further electrolyte decomposition at the graphite surface, which may in turn significantly
Figure B.4: DSC curves of fully lithiated electrodes in the presence of electrolyte. Bare NG electrode (dotted line) and NG electrode coated with 5 Al₂O₃ ALD cycles with NO2 pretreatment (solid line).
affect the LIB safety performance [19, 20]. The results in Fig. B.4 indicate that the SEI layer formed on the ALD coated NG electrode is smaller and/or more stable than that formed on bare NG electrodes, consistent with the results in Fig. B.3c.

Finally, a LiCoO$_2$/NG full cell cycled in the 3.30-4.45 V range is provided in Supplementary Fig. S4. The full cell was made from LiCoO$_2$ coated with 2 cycles of ALDAl$_2$O$_3$ on powder and NG coated with 2 cycles of ALDAl$_2$O$_3$ on the electrode. The coated full cell shows a dramatically enhanced cycling performance.

**B.4 Conclusion**

In conclusion, we have demonstrated that ALD deposited directly on electrode surfaces may protect the surface of the active powders in electrodes while maintaining an inter-particle electronic pathway. The anomalous cycling performance at elevated temperatures, PC-compatibility, and improved safety performance of Al$_2$O$_3$ coated NG composite electrodes suggests viability for next generation electric vehicles. Furthermore, the versatility of direct ALD on composite electrodes may be employed to develop coatings for any advanced battery materials.
References


