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Advanced Lithium Ion Battery Materials Prepared with Atomic Layer Deposition

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Advanced Lithium Ion Battery Materials Prepared with Atomic Layer Deposition

by

Andrew S. Cavanagh

B.S., Fort Lewis College, 2003
M.S., University of Colorado, 2010

A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Physics

2011
This thesis entitled:
Advanced Lithium Ion Battery Materials Prepared with Atomic Layer Deposition
written by Andrew S. Cavanagh
has been approved for the Department of Physics

Prof. Steven M. George

Prof. Daniel S. Dessau

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.
As the world consumes the dwindling supply of fossil fuels, an alternative to gasoline powered vehicles will become necessary. Lithium ion batteries (LIBs) are emerging as the dominant power source for portable electronics, and are seen as a promising energy source in the development of electric vehicles. Current LIB technology is not well suited for vehicles, increases in the energy density, power density and durability are needed before LIB are ready for widespread use in electric vehicles.

LiCoO$_2$ and graphite are the dominant cathode and anode active materials, respectively in LIBs. On the cathode side, instabilities in LiCoO$_2$ can lead to the deterioration of the LIB. Decomposition of electrolyte on the graphite anode surface to form a solid-electrolyte interphase (SEI) consumes lithium from the cathode resulting in a lower battery capacity. Instabilities in the SEI can result in catastrophic battery failure. Previous studies have employed metal oxides films, typically grown with wet chemical techniques, to stabilize LiCoO$_2$ and mitigate the formation of the SEI on graphite. The thicknesses of films grown with wet chemical techniques was typically $\sim$50-1000 Å. In order to achieve higher power densities, the particle size of LIB active materials is being scaled down. As active materials get smaller the mass contribution of a protective film can become a significant fraction of the total mass.

Atomic layer deposition (ALD) has been used to grow ultra thin films of Al$_2$O$_3$ on LiCoO$_2$ and graphite. By altering the interaction between the active material and the battery electrolyte it was possible to improve the stability of both LiCoO$_2$ and graphite electrodes in LIBs. In the case of graphite, the Al$_2$O$_3$ film may be thought of as an artificial SEI.

During the initial charge-discharge cycle of a LIB, the electrolyte decomposes on the anode to form the SEI. The formation of the SEI is believed to prevent further decomposition of the
electrolyte on the anode surface. The SEI contains electrolyte decomposition products including Li$_2$CO$_3$, Li$_2$O, LiOH, LiF and R-OLi. In order to grow a truly artificial SEI on the graphite anode, i.e. grow a film that mimics the SEI that forms during charge-discharge cycling, new ALD chemistries for the growth of Li$_2$CO$_3$ and LiOH have been developed. The ALD of an artificial SEI layer may limit lithium loss and improve the capacity stability during charge-discharge cycles.
Dedication

To my family, past, present, and future. I would not be who I am today without you.
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Chapter 1

Introduction

The world runs on nonrenewable fossil fuels [3]. Figure 1.1 shows that 81.3% of the world's total primary energy supply comes from oil, gas, and coal [3]. Renewable energy sources such as geothermal, solar, and wind power account for 0.7% of the world's total primary energy supply. At the current production rates, it has been estimated that the world's supply of oil, gas, and coal will be exhausted in 40, 62, and 224 years respectively [72]. As oil disappears, it will be possible to shift non-mobile users of oil, such as residential heating, to other established technologies. As of 2008, 61.4% of the oil produced was used for transportation [3]. Vehicles do not have an alternative established technology to replace oil.

Running the world on renewable energy sources has one major problem, energy storage. The problem of energy storage stems from two issues. The first issue is portability. In order to replace oil in vehicle applications, energy generated from renewable sources must be stored in such a way that it can safely and efficiently power a vehicle. The second issue is demand. Most renewable energy sources, such as wind power or solar, have their production rate fixed by nature. With wind power and solar, peak production does not necessarily correlate with peak demand. Rather, peak production correlates with windiest or sunniest times of the day. In order to synchronize peak power production from renewable energy sources with peak demand from the population being served, an efficient and durable means of energy storage must be developed.

One proposed solution to the energy storage problem is to use a nation's battery powered fleet of electric vehicles as a collective energy storage system [101]. When a vehicle is plugged
Figure 1.1: World total energy supply by fuel [3].
into the grid it can either be charging or supplying energy depending on consumer demand and the amount of power being generated by renewable energy sources [101]. For batteries to be commercially viable, both for grid storage and electric vehicles, they must have a high energy and power density and be safe and durable [101]. Currently, lithium ion batteries (LIBs) are the most established battery technology for electric vehicles [153, 30]. Due to the low specific energy density and long recharge times, electric vehicles based current LIB technology are limited to small, low daily mileage vehicles [195]. LIBs can be improved by coating the active material with thin films [129, 40]. Significant enhancements are needed to bring LIBs up to the target levels required for practical use and commercial viability.

1.1 Statement of Purpose

This dissertation is concerned with the modification of surfaces of LIB active materials to enhance the performance of the material in a battery cell. The surface modifications were made by growing thin films with atomic layer deposition (ALD). Chapter 2 is an overview of thin film deposition techniques. Chapter 3 is a review of the mechanism by which thin films can enhance a LIB. Chapters 5 and 6 demonstrate that thin films of Al₂O₃ grown with ALD can dramatically enhance the performance of cathode (LiCoO₂) [98] and anode (graphite) [99] materials. Chapter 4 details the development of new ALD chemistries specifically designed to mimic films that grow from the electrochemical decomposition of electrolytes in a LIB [36]. Chapter 7 details ALD on carbon nanotubes (CNTs) [35]. CNTs may serve as conductive scaffolding onto which a LIB active material may be grown with ALD in the future.
Chapter 2

Thin Films

Many technologies rely on thin films of various dimensions and roughnesses [170]. Thin films have a variety of applications and accordingly a variety of deposition techniques. Some common applications of thin films include: semiconductors and dielectrics for microelectronics and energy conversion devices, diffusion barriers for protection against corrosion and oxidation, catalysis, protective layers for lithium ion batteries, and various optical applications.

There are several techniques for depositing thin films. These techniques fall into two classes: chemical deposition and physical deposition [170]. Chemical deposition techniques include wet chemical methods like sol-gel and electroplating as well gas phase methods like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Physical deposition methods employ a variety of techniques to vaporize a material and condense it onto a substrate. This is commonly referred to as physical vapor deposition (PVD).

The various methods to grow thin films produce varying degrees of conformality and step coverage. Step coverage is the ability of a film to grow at the same rate on the face of a step as on the top surface of the step. Figure 2.1(a) shows poor step coverage and Figure 2.1(b) shows good step coverage. Conformality requires good step coverage and that the film be uniform on all surfaces. Figure 2.1(c) shows poor conformality and Figure 2.1(d) shows a conformal film.
Figure 2.1: Varying degrees of conformality, (a) poor step coverage, (b) good step coverage, (c) poor conformality and (d) a conformal film. Adapted from [4].
2.1 Physical vapor deposition

PVD is a thin film deposition technique where physical rather than chemical methods are used to grow the film [170]. PVD includes a variety of methods to vaporize metals which are condensed on the substrate to grow a film. The vaporization methods include heating the metal with a filament, electron beam or laser, or employing a plasma to sputter a metal target. PVD can be employed in the presence of another gas phase precursors such as oxygen or nitrogen to grow metal oxides or nitride respectively.

PVD has limitations in its ability to uniformly deposit films on high aspect ratio structures or structures with complex morphologies. This lack of conformality is derived from the fact that PVD is typically a line-of-sight technique. This means that all of the surfaces of the substrate must be within the view of the metal source in order for the vaporized metal to condense on the surface. If the substrate is not flat, three dimensional structure on the surface may act as masks thereby blocking the line-of-sight path to the metal source. In the case of high aspect ratio structures or porous material it may also be difficult to obtain a uniform film below the surface due to lack of line-of-sight.

2.2 Sol-gel techniques

Sol-gel techniques involve solution based chemistries to grow thin films of metal oxides [196]. During a sol-gel process a metal oxide network is formed by the progressive condensation of metal hydroxides [196]. Typically a metal alkoxide \((\text{M(OR)}_n\), \text{M} = \text{Si, Ti, Zr, Al, Fe, B}) in a solution (sol) of alcohol will first undergo hydrolysis to form \(\text{M(OH)}_n\). The \(\text{M(OH)}_n\) monomers then begin to polymerize via condensation reactions to form particles of the metal oxide [196]. Eventually a continuous network is formed and the solution thickens (gel) [196]. A sol-gel film can be applied to a flat substrate by dip coating or spin coating, or it may be applied to particles by mixing the particles into the sol-gel solution [196].

After the sol-gel coating is applied, a heat treatment removes excess solvent and reaction
byproducts. There are large volume contractions that coincide with the removal of the solvents; these can lead to cracks in the sol-gel film. Depending on the morphology required, great care must be taken during the curing process to avoid cracks [196].

2.3 Chemical vapor deposition

CVD is gas phase method for depositing thin films [48]. In CVD one or more volatile precursors is exposed to a heated substrate surface where it may react with the substrate surface or thermally decompose onto the substrate surface to grow a film. The surface reaction or decomposition produces volatile reaction products that are pumped from the reaction chamber during growth. CVD is capable of growing films with nanometer thickness control[48].

The five classes of CVD reactions are thermal decomposition, reduction, oxidation, hydrolysis and synthesis [48]. Table 2.1 show several example CVD chemistries classified by the reaction type. Thermal decomposition is typically used to make a film consisting of one element. The reaction products in for thermal decomposition reaction do not usually attack the substrate. Reduction reactions are typically used to make a film consisting of one element. The products of the reduction reaction can etch the substrate or drive the reaction in reverse. Hydrogen is the most commonly used reducing agent. Hydrolysis and oxidation reactions are used to deposit metal oxide films. Synthesis reactions are used to grow binary compounds like carbides or borides [48].

CVD has the advantage of being able to grow relatively thick films quickly. CVD has the limitation that many chemistries must be done at high temperature (> 600 °C). The high temperatures may be incompatible with some substrates. Reactions of CVD precursors in the gas phase can form particles that are then deposited on the surface leading to nonuniform film growth. Since the growth rate of films grown with CVD is proportional to the reactant flux, care must be taken to ensure that a uniform flux reaches every surface in order to grow a uniform film. Obtaining a uniform flux on complex morphologies can be difficult.
Table 2.1: Types of CVD reactions with example chemistries and reaction temperatures.

<table>
<thead>
<tr>
<th>CVD Reaction Type</th>
<th>Example Reactions</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Decomposition</td>
<td>SiH₄ → Si + 2 H₂</td>
<td>600-1150</td>
</tr>
<tr>
<td></td>
<td>TiI₄ → Ti + 2 I₂</td>
<td>1200</td>
</tr>
<tr>
<td>Reduction</td>
<td>SiCl₄ + 2 H₂ ↔ Si + 4 HCl</td>
<td>900-1200</td>
</tr>
<tr>
<td></td>
<td>WF₆ + 3 H₂ ↔ W + 6 HF</td>
<td>550-800</td>
</tr>
<tr>
<td>Oxidation</td>
<td>SiH₄ + 2 O₂ → SiO₂ + 2 H₂O</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>Zn(C₂H₅)₂ + 4 O₂ → ZnO + 2 CO + 5 H₂O</td>
<td>250-500</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>AlCl₃ + 3 CO₂ + 3 H₂ → Al₂O₃ + 3 CO + 6 HCl</td>
<td>800-1150</td>
</tr>
<tr>
<td></td>
<td>2 Al(CH₃)₃ + 3 H₂O → Al₂O₃ + 6 CH₄</td>
<td></td>
</tr>
<tr>
<td>Synthesis</td>
<td>3 TiCl₄ + 2 BCl₃ 5 H₂ → TiB₂ + 10 HCl</td>
<td>1100</td>
</tr>
</tbody>
</table>

2.4 Atomic layer deposition

Atomic layer deposition (ALD) is a gas phase technique for depositing thin films on solid surfaces [79, 125]. ALD relies on sequential, self-limiting, surface reactions. Once a gas phase precursor has reacted with a surface functional group, that surface functional group has been consumed. It does not matter if there is an excess of the gas phase precursor, the limiting reagent in the reaction are the substrate surface functional groups. Typical ALD chemistries employ a binary reaction sequence where the exposure to the first ALD precursor deposits one atomic layer of one component of the binary material being deposited and generates a new surface functionality. This is commonly referred to as the A-step. Exposing the surface to a second ALD precursor deposits one atomic layer of the second binary component of the material being deposited and regenerates the original surface functionality of the substrate. This is commonly called the B step. Repeating the process ABAB… allows for digital thickness control determined by the growth rate per cycle and the number of AB cycles.

The invention of ALD is often dated with a 1974 patent by a Finnish group led by Suntola [182]. The first ALD system studied by the Finnish team was ZnS using Zn and S as reactants. Russian researchers led by Aleskovskii had in fact been studying ALD since the 1960. The first
published account of ALD by the Russian team came in 1974 [5]. Since its inception, the field of ALD has grown rapidly. Figure 2.2 show the number of publications regarding ALD as a function of time.

Figure 2.3 shows a schematic of the most general ALD process. A solid substrate with one surface functionality is exposed to reactant A. This results in the complete consumption of the functional groups on the solid substrate and the generation of a gaseous reaction byproduct. After a sufficient exposure time the excess A reactant and the reactions byproducts are evacuated from the reaction chamber. The new surface functionality is then exposed to reactant B. This results in the complete consumption of the functional groups on the solid substrate left from the exposure to reactant A and the generation of a gaseous reaction byproduct. After a sufficient exposure time the excess B reactant and the reactions byproducts are evacuated from the reaction chamber. Exposure to reactant B has completed one ALD cycle and returned the surface to its original functionality. The A step and the B step of a binary ALD reaction are often referred to as half reactions.

A key characteristic of any ALD process is that the chemistry is self-limiting. The self-limiting nature of ALD is a crucial component for coating porous and high aspect ratio samples. This allows for a uniform film even when the conduction path varies from an exposed surface to a deep trench or otherwise tortuous path. A point at the bottom of a high aspect ratio trench will receive a lower flux of precursor molecules than at the surface of the substrate. Because ALD employs self-limiting chemistries, precursor molecules adsorb and desorb from reacted sites near the top of a high aspect ratio trench as they proceed toward the bottom. This allows for conformal coatings over the full surface of the substrate. To ensure uniform, conformal films, ALD precursors that do not react with themselves must be employed. This allows for an overexposure of any individual precursor without loss of thickness control. Also, great care must be taken to separate the exposure of reactant A and reactant B. Typically this separation is done in time. In this case one reactant is exposed to the substrate surface, excess reactant and reaction byproducts are then removed from the reaction chamber and then at some later time the second reactant is exposed to the substrate surface. Recent advancements in atmospheric ALD separate ALD precursors spatially [128]. In the
Figure 2.2: The number of publications regarding ALD as a function of the year.

Figure 2.3: Schematic of the most general ALD process.
case of atmospheric ALD the ALD precursors are in separate regions and the substrate surface is passed through the distinct regions. The number of ALD cycles completed with atmospheric ALD is determined by the number of A and B regions and by the number of times the sample surface is oscillated beneath the regions.

ALD reactions are temperature dependent [181]. An ideal ALD process only takes place within a specific temperature window. Figure 2.4 illustrates how the growth rate of an ALD chemistry varies with temperature. If the reactor temperature is too low reactants may condense on the substrate leading to a higher growth rate. Conversely, at low temperatures reactant molecules may not have enough thermal energy to drive the reaction to completion. In this case the growth rate will be lower. At temperatures above the ALD window elevated growth rates may be observed if the reactants decompose. This elevated growth rate is similar to unimolecular chemical vapor deposition. Conversely, at higher temperature the ALD precursors may not be stable on the surface leading to a reduced growth rate.

ALD relies on saturation of available surface functionalities. If a film grown by ALD does not go to completion the density of available surface sites will diminish. To ensure the surface reactions run to completion ALD chemistries are typically very exothermic. For example, the chemical reactions to grow Al$_2$O$_3$, ZnO and TiO$_2$ and their reaction enthalpies are [1]:

\[2 \text{Al(CH}_3\text{)}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6 \text{CH}_4, \quad \Delta H = -1574.6 \text{kJ}, \quad (2.1)\]

\[\text{Zn(C}_2\text{H}_5)_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2 \text{C}_2\text{H}_6, \quad \Delta H = -292.9 \text{kJ}, \quad (2.2)\]

\[\text{TiCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{HCl}, \quad \Delta H = -67.4 \text{kJ}. \quad (2.3)\]

Equation 2.1 is a highly exothermic reaction. In many ways the trimethylaluminum (TMA)/H$_2$O chemistry is an ideal ALD process [79, 156]. The growth of Al$_2$O$_3$ is a feature in Chapters 5-7 and will be reviewed briefly here. The sequential, self-limiting reaction sequence during Al$_2$O$_3$ ALD is [58, 84, 149]:

\[A \quad \text{AlOH}^* + \text{Al(CH}_3\text{)}_3 \rightarrow \text{AlO} - \text{Al(CH}_3\text{)}_2 + \text{CH}_4 \quad (2.4)\]
Figure 2.4: Growth per cycle (GPC) as a function of temperature. Adapted from [180].
AlCH₃ + H₂O → Al – OH⁺ + CH₄ (2.5)

where the asterisks denote surface species. Figure 2.5 shows a schematic of the TMA/H₂O reaction to grow Al₂O₃ with ALD. In frame 1 TMA is dosed into the ALD reaction chamber and reacts with the hydroxyl terminated surface to produce CH₄. In frame 2 CH₄ and excess TMA are purged from the reactor. Frames 1 and 2 constitute the A step in the TMA/H₂O ALD reaction. In frame 3 H₂O is dosed into the ALD reaction chamber and reacts with the methyl terminated surface to produce CH₄. In frame 4 CH₄ and excess H₂O are purged from the reactor. Frames 3 and 4 constitute the B step in the TMA/H₂O ALD reaction.
Figure 2.5: Schematic of the TMA/H₂O reaction to grow Al₂O₃ with ALD.
Chapter 3

Thin Films for Lithium Ion Batteries

Since their commercialization in the 1990s lithium ion batteries (LIBs) have been an effective energy storage medium for portable electronics [185, 203, 209]. LIBs have been proposed as a power source for hybrid electric vehicles [34, 179, 178]. Limitations in LIBs such as short lifetimes, low durability, high cost and poor low temperature performance have hindered commercial success in electric vehicles [40].

It has been widely documented in the literature that additions to the LIB active materials can improve the LIB performance. Additions refers to materials that are not intended to store Li but serve to enhance the performance of the materials that do store Li (active materials). These additional materials can take many forms. A few examples include thin films grown on the active material surface that may or may not be conformal; nanoparticles grown on the active material surface that may be uniform and dense enough to be referred to as a film or may be sparsely distributed on the active material surface; or simply mixing in the additional material i.e. not attempting to grow the material on the active material surface. The mechanisms by which these additional materials enhance LIBs is varied. In this chapter a review of the proposed mechanisms for enhancement of LIBs by the addition non-active material substances will be presented.

3.1 Mechanisms for thin films to enhance LIBs

In order to improve the performance of LIBs a variety of surface coating materials have been used to alter the LIB active material interface. The coating materials previously investigated
include metal oxides [45, 39], metal phosphates [8, 20], metal fluorides [176, 175], metal carbonates [221] and carbon [24, 38, 224, 33]. The proposed mechanisms for the enhanced performance of coated active materials include: acting as a sacrificial scavenger for HF; enhancing electron conduction at the active material surface; changing the active material surface chemistry; acting as a physical barrier between the active material and the electrolyte.

3.1.1 Thin films for scavenging HF

The primary salt in a LIB electrolyte is Lithium hexafluorophosphate (LiPF$_6$). In the presence of H$_2$O, LiPF$_6$ reacts to form HF according to the following reactions [100]:

$$\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5$$  \hspace{1cm} (3.1)

$$\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF}.$$  \hspace{1cm} (3.2)

The resultant HF can then act to dissolve transition metals in the cathode active material [88, 186, 229]. The dissolution of these transition metals results in structural changes in the cathode material and the degradation the LIB’s capacity [146]. It has been reported that metal oxide particle can be employed to sacrificially react with the HF to form stable insoluble compounds [133]. The metal oxide can be applied in several forms: as a discontinuous thin film [148], as particles mixed in with the active material, as a pretreatment to the electrolyte prior to cell fabrication [133] or as a thin conformal thin film [98]. Examples of of Al$_2$O$_3$ and ZrO$_2$ reacting with HF and the reaction enthalpy are given in equations 3.3 and 3.4.

$$\text{Al}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}, \quad \Delta H = -583.8 \text{kJ}$$  \hspace{1cm} (3.3)

$$\text{ZrO}_2 + 4\text{HF} \rightarrow \text{ZrF}_4 + 2\text{H}_2\text{O}, \quad \Delta H = -303.5 \text{kJ}$$  \hspace{1cm} (3.4)

AlF$_3$, ZrF$_4$ and other metal fluorides are typically insoluble in nonaqueous electrolytes. In the case of thin films of protective metal oxides, as opposed to particles, the subsequent metal fluoride film may act as a protective barrier.
3.1.2 Thin films for enhanced electron conduction

Carbon films have been used to enhance the performance of several phosphate materials, for example LiFePO$_4$ [24, 38]. Typically phosphate materials exhibit low electron conductivity [158, 7]. As such the growth of a conductive carbon film improves the conductivity of the composite material and the overall cathode performance accordingly. There are two proposed mechanisms for the increase in the conductivity. A thin film of a highly conductive carbon material will have a large surface area for interaction with the active material surface. By having a large surface area at the interface between the poorly conducting active material and the highly conductive carbon film the charge transfer at the interface may be improved. Alternatively, a conductive carbon film on the cathode surface may increase the interparticle and particle-current collector conductivity. Both of these mechanisms may play a role in the observed enhanced performance of metal phosphate electrodes.

Carbon films are typically deposited on metal phosphate active material by the thermal decomposition of a carbon source such as a hydrocarbon, acetate or carbohydrate. The deposition is typically carried out while the active material is in particle form. Deposition temperatures range from 500-800 °C. However, higher temperature carbon depositions (> 700 °C) exhibit an increased electronic conductivity as compared with lower temperature depositions (< 600 °C) [223]. The increased conductivity for the higher temperature depositions is attributed to the carbon film being more graphitic in nature [223].

It has also been demonstrated that the deposition of an insulating material, such as Al$_2$O$_3$, followed by annealing can lead to the migration of Al atoms into the active material. Oh et al. argue that LiCoO$_2$ coated with a film of Al$_2$O$_3$ via gas suspension spray techniques and then annealed at 500 °C forms a Li-Al-Co-O on the first 15 nm of the LiCoO$_2$ [148]. Measurements of the composite LiCoO$_2$/Al$_2$O$_3$ displayed an order of magnitude drop in the volume resistivity as compared to the bare LiCoO$_2$. This result is surprising because LiCoO$_2$ is a better conductor than Al$_2$O$_3$. It is postulated that this drop in the resistivity contributed to the improved electrochemical
performance of the LiCoO$_2$ coated with Al$_2$O$_3$ as compared to the bare LiCoO$_2$.

### 3.1.3 Thin films as protective barriers

Thin films on the surface of the battery active material may serve as a physical barrier to separate the active material from the electrolyte. The presence of a barrier means that the surface of the active material cannot react with the electrolyte. Possible reactions include the reduction of the delithiated metal oxide by the electrolyte or the evolution of O$_2$ gas [12]. These reactions occur at or near the surface of the active material particles. For a surface mediated reaction a chemically and electrochemically inert barrier can prevent the two reactants from coming into contact. For reactions within the active material a chemically and electrochemically inert barrier will slow the transport of reactants into the active material.

#### 3.1.3.1 Al$_2$O$_3$

Several metal oxides have been employed on a variety of active materials. Al$_2$O$_3$ has been deposited on LiCoO$_2$ using sol-gel methods [46] and gas suspension spray techniques [148]. Al$_2$O$_3$ has a good Li$^+$ ion conductivity and is chemically and electrochemically stable in LIBs [129]. These qualities make it a good candidate for a physical protection barrier in LIBs. It has been demonstrated that Al$_2$O$_3$ films on LiCoO$_2$ can greatly improve the rate capability, capacity retention with cycling and thermal stability [148, 120].

Films deposited with gas suspension spray techniques did not produce conformal films. On LiCoO$_2$ particles with an average size of 7.7 $\mu$m a range of film Al$_2$O$_3$ thicknesses deposited with gas suspension spray techniques has been explored [148]. It was determined that films accounting 0.2 weight % of the composite LiCoO$_2$/Al$_2$O$_3$ material displayed the best performance [148]. This weight % corresponds to a surface coverage of 13.7%. At a surface coverage of 13.7 % this film is not close to conformal [148]. However, it has been demonstrated that an Al$_2$O$_3$ film can still act as a protective barrier to prevent Co dissolution [148]. In one experiment bare LiCoO$_2$ and LiCoO$_2$ coated with 0.2 weight % of Al$_2$O$_3$ were immersed in a solution 1 M LiPF$_6$ in ethylene carbonate.
dimethyl carbonate : ethylmethyl carbonate (1:1:1) for 1 week [148]. The dissolved Co\textsuperscript{4+} in the solution was measured with atomic adsorption spectroscopy and it was determined that the bare LiCoO\textsubscript{2} had lost 2.3 times more Co\textsuperscript{4+} [148].

### 3.1.3.2 AlPO\textsubscript{4}

AlPO\textsubscript{4} films have been deposited on LiCoO\textsubscript{2} particles. The films were grown by mixing LiCoO\textsubscript{2} particles into a slurry of AlPO\textsubscript{4} nanoparticles, drying the particles in an oven and then heat annealing the particles at elevated temperatures [43]. The thickness of the AlPO\textsubscript{4} film was controlled by changing the concentration of the AlPO\textsubscript{4} in the slurry [42, 122].

It is believed that AlPO\textsubscript{4} films can function in several ways to protect the LiCoO\textsubscript{2} active material. AlPO\textsubscript{4} films serve as a physical protection barrier to prevent reactions between LiCoO\textsubscript{2} and the electrolyte. Cho observed that the thickness of the AlPO\textsubscript{4} films inversely correlated with the amount of electrolyte that exothermically reacted with the LiCoO\textsubscript{2} [42]. Beyond 4.2 V LiCoO\textsubscript{2} begins to undergo rapid side reactions with the electrolyte [146]. In an overcharge experiment designed to test the safety aspects of overcharging LiCoO\textsubscript{2} to 12 V, Cho observed a plateau at 5 V. This plateau was consistent with electrolyte oxidation and reactions between the electrolyte and the LiCoO\textsubscript{2} [42]. For LiCoO\textsubscript{2} that had been coated with 50, 200 and 1000 Å of AlPO\textsubscript{4}, the duration of the 5 V plateau was successively reduced by thicker films [42]. This implies that thicker films are better able to act as a physical barrier between the electrolyte and the LiCoO\textsubscript{2}.

### 3.1.3.3 Carbon

Thermal vapor deposition has been employed to coat protective carbon films onto natural graphite NG to prevent interactions between the NG and a propylene carbonate (PC) electrolyte [218, 217, 198]. Increasing the thickness of the protective carbon film increased the battery performance. For example, Yoshio et al. observed that NG coated with an 8.6 weight % protective carbon coating had a coulombic efficiency on the first charge-discharge of 75.8% [218]. The coulombic efficiency was increased to 92.5% by essentially doubling the weight % of the protective carbon
coating to 17.6% [218]. These two experiments used an electrolyte that was only 20% PC (PC:DMC, 1:4 by volume) [218]. If the concentration of the PC in the electrolyte was increased the battery performance suffered. The first cycle coulombic efficiency for a 17.6 weight % protective carbon film in an electrolyte that was 33% PC (PC:DMC, 1:2 by volume) was only 71.0% [218]. This is a dramatic reduction in the first cycle coulombic efficiency, 92.5% $\rightarrow$ 71.0%, with only a 13% increase in the concentration of the PC in the electrolyte, 20% $\rightarrow$ 33% [218]. Furthermore, the weight % of protective carbon film used in this study, and others, are a significant portion of the mass of the active material [218, 217, 198, 197, 119].

### 3.1.3.4 MgO

MgO has been deposited on LiCoO$_2$ using a Mg(OH)$_2$ solution followed by a heat treatment [199], pulsed laser deposition [93]and sol-gel methods [144, 227]. MgO acts as a barrier between the LiCoO$_2$ and the electrolyte thereby preventing the dissolution of Co$^{4+}$ ions [131]. By preventing Co$^{4+}$ dissolution the structure of the LiCoO$_2$ is maintained and the cell performance is enhanced [131]. It also been noted that Mg$^{2+}$ may migrate into the LiCoO$_2$ during annealing or during charge-discharge cycles [227]. The addition of the Mg$^{2+}$ may help stabilize the delithiated CoO$_2$ [227].

After 40 charge-discharge cycles LiCoO$_2$ coated with 1 mol% of MgO by sol-gel methods had a capacity of 120 mAh/g while bare LiCoO$_2$ had a capacity of 13 mAh/g [227]. For films that were thicker, 2 and 3.8 mol% the charge-discharge performance was drastically worse. This decline in performance was attributed to the low Li$^+$ conductivity of MgO.

### 3.1.3.5 TiO$_2$

TiO$_2$ coated LiNi$_{0.8}$Co$_{0.2}$O$_2$ has been produced by the hydroxylation of tetra-n-butyl titanate on the LiNi$_{0.8}$Co$_{0.2}$O$_2$ surface under ambient conditions. The coated material then underwent a heat treatment at 400 °C. Under these conditions a TiO$_2$ film of 50 nm was produced [225]. In electrochemical studies it was demonstrated that TiO$_2$ coated LiNi$_{0.8}$Co$_{0.2}$O$_2$ had improved
capacity retention. This was attributed to suppressed decomposition of the electrolyte on the TiO$_2$ as compared to the LiNi$_{0.8}$Co$_{0.2}$O$_2$ surface [226, 132].

### 3.1.4 Enhanced Surface Chemistry with Thin Films

The role of the surface chemistry of cathode active materials and their interaction with the electrolyte plays a significant role on the electrochemical performance of the active material [40]. The correlation between electrochemical performance of cathode active materials and the effect of the active material surface chemistry are not well characterized in the LIB literature [40]. Much of the LIB literature involves active materials that were recently synthesized and stored under ideal conditions. Many of the techniques used to coat LIB active materials involve a heat treatment. In contrast to fresh active materials or active materials that have been subject to a coating technique that involved a heat treatment, it has been observed that LiCoO$_2$ that is exposed to H$_2$O displays a large loss in specific capacity [37]. The loss in capacity could be recovered in part by either by heat treating the LiCoO$_2$ at 550 °C or by grinding the LiCoO$_2$ into a fine powder [37]. Grinding the LiCoO$_2$ powder exposes fresh LiCoO$_2$ surfaces, this implies that the the loss of capacity upon H$_2$O exposure is mediated by the surface of the LiCoO$_2$. 
Chapter 4

Atomic Layer Deposition of LiOH and Li$_2$CO$_3$ Using Lithium t-butoxide as the Lithium Source

4.1 Abstract

Atomic layer deposition (ALD) was utilized to grow LiOH and Li$_2$CO$_3$ films using lithium tert-butoxide, H$_2$O and CO$_2$. Film growth was monitored with a quartz crystal microbalance between 100-295 °C. At 225 °C LiOH ALD had a growth rate of 7.6 ng·cm$^{-2}$·cycle$^{-1}$ before displaying evidence for hygroscopic behavior. At 225 °C Li$_2$CO$_3$ ALD had a growth rate of 10.4 ng·cm$^{-2}$·cycle$^{-1}$. H$_2$O production during the conversion of LiOH to Li$_2$CO$_3$ by exposure to CO$_2$ was monitored with quadrupole mass spectrometry. The film identities were confirmed using Fourier transform infrared and X-ray photoelectron spectroscopies. Lithium-containing films are present in the solid-electrolyte interphase (SEI) on graphite anodes of Li-ion batteries. The ALD of an artificial SEI layer may limit lithium loss and improve the capacity stability during charge-discharge cycles.

4.2 Introduction

Lithium ion batteries (LIBs) are the dominant power source for portable electronics, laptops, mobil phones etc. [11]. However, in order to realize LIBs in large-format technologies, such as power grid storage and electric vehicles, significant progress must be achieved in making them safer [81, 2]. The safety, shelf life and power capability of a LIB are determined in large part by the solid-electrolyte interphase (SEI) on the anode [142]. The SEI is formed by the reductive decomposition
of the electrolyte on the anode surface during the first few charge-discharge cycles [17, 92, 22].

The safety issues that arise for LIBs in large-format technologies are brought on by the requirement the LIBs be capable of fast charging and the elevated temperatures that coincide with fast charging. For example, in an electric vehicle the battery must be able to charge at the rate at which power is generated by regenerative breaking. If the LIB can dissipate the heat generated by fast charging the cell temperature will not rise dramatically. If the LIB cannot dissipate heat fast enough then a threshold under which the SEI can start to undergo a rapid exothermic decomposition may be crossed [173, 159]. The destruction of the SEI provides for direct contact between the lithiated anode and the electrolyte leading to more exothermic reactions. The further rise in temperature from the exothermic reactions will accelerate more chemical reactions in a process known as thermal runaway [173, 21]. Pressure generated during these reactions can cause mechanical failures resulting in the rupture of cell casing [21]. Most LIB employ flammable electrolytes. Upon the rupture of the cell casing, heat and flammable electrolytes can lead to fire and explosion [21]. A stable SEI is critical to the safety of LIBs [142].

Graphite is a common anode material in LIBs [73, 185]. With its high reversible capacity (372 mA h g\(^{-1}\), assuming a stoichiometry of LiC\(_2\)), low cost, moderate volume change, and low and flat voltage range, natural graphite (NG) is a promising anode material [217, 77, 165]. The SEI layer restricts lithium diffusion and electron conductivity to the graphite electrode [151, 214]. Lithium bound in the SEI layer is no longer free to participate in charge transfer and as such lowers the battery capacity [151, 214]. The composition of the SEI layer includes various lithium compounds such as Li\(_2\)CO\(_3\), Li\(_2\)O, LiOH, LiF and R-OLi [151, 60]. The deposition of an artificial SEI layer on the graphite anode may be useful to prevent lithium loss and limit capacity reduction during charge-discharge cycling [105].

In this paper, two possible artificial SEI materials, LiOH and Li\(_2\)CO\(_3\), are grown with atomic layer deposition (ALD) techniques using lithium tert-butoxide (LTB), H\(_2\)O and CO\(_2\) as the reactants. ALD is a thin film deposition technique based on sequential, self-limiting surface reactions [78, 161]. ALD can deposit atomic layer controlled and conformal films on very high aspect sub-
strates [64]. In addition, ALD can be employed to deposit films on particles and on porous substrates [70]. ALD could be used to deposit artificial SEI layers either on graphite particles used to make the anode or on the porous anode formed from graphite particles.

4.3 Experimental

4.3.1 Chemicals and Materials

Lithium tert-butoxide (LiOC(CH$_3$)$_3$, LTB) with a purity of 98+\% was obtained from Strem Chemicals (Newburyport, MA). HPLC (high performance liquid chromatography) grade H$_2$O was obtained from Honeywell International Inc. (Morristown, NJ). Ultra high purity N$_2$ and bone dry CO$_2$ were obtained by Matheson Trigas (Newark, CA). Trimethylaluminum (Al(CH$_3$)$_3$, TMA) with a purity of 97\% was obtained from Sigma-Aldrich (Saint Louis, MO).

In order to remove dissolved gases the H$_2$O underwent 5 cycles of freeze-pump-thaw. All other precursors were used without further purification. The LTB was transferred into a stainless steel dosing vessel in a glove box under an Ar environment (Vacuum Atmosphere's Inc., Amesbury, MA). The H$_2$O and O$_2$ concentrations in the glove box were typically under 0.1 and 0.5 ppm respectively.

For ex situ analysis, LiOH and Li$_2$CO$_3$ were deposited on $\sim$ 1 x 1 inch Si wafers with a thin native oxide. The Si wafers were obtained from Silicon Valley Semiconductors, Inc. (Santa Clara, CA). The Si were cleaned with deionized water, acetone and isopropyl alcohol prior to film deposition. LiOH and Li$_2$CO$_3$ were also grown on KBr slides obtained from International Crystal Laboratories (Garfield, NJ). The KBr slides were used without further cleaning.

4.3.2 Deposition Parameters

The LiOH and Li$_2$CO$_3$ films were grown in a viscous flow ALD reactor that is described elsewhere [62]. A schematic of the reactor is shown in Figure 4.1. The reactor was operated at a pressure of $\sim$1 Torr with a total nitrogen carrier gas flow of 170 sccm. Nitrogen flow was
controlled with a mass flow controller (MKS Instrument, Andover, MA). The reactor was heated with two ceramic heaters (Watlow Electric Manufacturing Co., St. Louis, MO). The temperature was monitored with an external thermocouple and was controlled via PID loop with a temperature controller (Eurotherm U.S.A., Ashburn, VA). The pressure was measured using a Baratron capacitance manometer (MKS Instrument, Andover, MA). The precursors were introduced in the ALD chamber through a series pneumatic and needle valves. To prevent precursor condensation, the dosing line from each precursor vessel to the reactor was heated with a gradient of increasing temperature toward the reactor.

Unless otherwise noted, the following dosing conditions were used. The LTB source was held at 165 °C and the reactor was maintained at 225 °C. The LTB dose was 3 s with a partial pressure of 35 mTorr. The H$_2$O dose was 1 s with a partial pressure of 250 mTorr. The CO$_2$ dose was 1 s with a partial pressure of 500 mTorr. The purge times after the reactant exposures were 60 s. LiOH and Li$_2$CO$_3$ films were grown on a fresh Al$_2$O$_3$ film.

4.3.3 Dosing Low Vapor Pressure Precursors

H$_2$O and CO$_2$ have excellent vapor pressures and can simply be dosed onto a stream of N$_2$ gas that entrains the precursor and carries it into the ALD reactor. This dosing scheme has been described in detail elsewhere [62]. When the vapor pressure of a precursor is low relative to the ALD reactor pressure it is difficult to dose the precursor onto a stream of N$_2$ gas. This was the case for the LTB. In order to dose low vapor pressure precursors the N$_2$ gas flowing into the ALD reactor was diverted over the headspace of the low vapor pressure precursor. This enables the entrainment of the low vapor pressure precursor by the N$_2$ gas. This dosing arrangement is depicted in Figure 4.2. A metered flow of N$_2$ gas was sent through a needle valve such that when the pneumatic valves bith in and out of the precursor vessel were opened, the change in conductance resulted in a only a small amount of N$_2$ gas being diverted over the head space of the precursor.

The custom dosing vessel was comprised of two 2.75” Conflat flanges. The lid flange was fitted with two 0.25” welded stainless steel lines that had VCR fitting on the ends of the tubes.
Figure 4.1: Schematic of viscous flow ALD reactor with a quart crystal microbalance and a quadrupole mass spectrometer.

Figure 4.2: Schematic representation of bubbler used for dosing low vapor pressure precursors.
These comprised the inlet and outlet ports of the vessel. The lid also had a vacuum sealed stainless finger into which a thermocouple could be placed to monitor the precursor temperature. The vessel was a Conflat nipple that had been welded shut at a height of 2”.

In a typical commercial dosing vessel of this type the inlet port does not stop at the bottom surface of the lid. Instead it continues down below the level of the precursor. This allows the entraining gas to actually bubble through a liquid precursor. In an ALD process this is not ideal because the bubbling process may entrain small droplets of liquid precursor which can result in undesirable dosing conditions. In the case of solid precursors a bubbling may entrain particles of the precursor which can also result in undesirable dosing conditions.

The pneumatic valves used to dose the precursor have open/close times on the order of 1 s. In order to ensure that the precursor only flowed forward toward the ALD reactor and not backwards into the N\textsubscript{2} gas line care was taken in the order in which the valves were opened. At the start of a dose the outlet (precursor to ALD reactor) pneumatic valve was opened 500 ms before the inlet (N\textsubscript{2} gas to precursor) pneumatic valve. At the end of a dose the inlet pneumatic valve was closed 500 ms before the outlet pneumatic valve.

4.3.4 Quartz Crystal Microbalance Monitoring

The reaction was monitored in situ with a quartz crystal microbalance (QCM). A detailed description on using QCM to monitor in situ ALD reactions is given elsewhere [62]. A Maxtek, Inc. BSH-150 (now owned by Inficon, East Syracuse, NY) sensor head was modified such that the cooling line could be used to flow N\textsubscript{2} gas over the back side of the QCM crystal. This gas flow prevented film growth from taking place on the back side of the crystal and minimized the pressure difference across the crystal. The N\textsubscript{2} gas flow was \(\sim\) 20 sccm. This resulted in a pressure increase in the reactor of \(\sim\) 100 mTorr. AT-cut quartz crystals with a polished gold surface and a frequency of 6 MHz were obtained from the Colorado Crystal Corp (Loveland, CO). The QCM crystals were sealed into the BSH-150 sensor head with a conductive epoxy obtained from Epoxy Technology, Inc. (Billerica, MA). During growth, the QCM was positioned horizontally and facing downward
in the middle of the ALD reactor.

Film growth was monitored with a Maxtek TM-400 (now owned by Inficon, East Syracuse, NY). QCM performance and health was monitored by the growth of Al₂O₃ with TMA and H₂O. The QCM crystal was replaced when the behavior of the Al₂O₃ growth deviated from acceptable values [208]. In between every experiment where LiOH or Li₂CO₃ was grown, 200 cycles of Al₂O₃ were grown on the QCM sensor. This allowed for verification of the sensor health and ensured that every LiOH and Li₂CO₃ started on an identical surface. The observed Al₂O₃ ALD growth rates were also used to calibrate the mass gains observed during LiOH and Li₂CO₃ growth.

4.3.5 Quadrupole Mass Spectrometry

Quadrupole mass spectrometry (QMS) was performed on the vapor phase species in the ALD reactor. Measurements were performed with a Stanford Research Systems RGA 200 (Sunnyvale, CA). The gases were sampled via an aperture shown in Figure 4.1. The aperture separated two distinct pressure regions, the ALD reactor (∼1 Torr) and the QMS region (∼1 × 10⁻⁷ Torr). In order to maintain these pressures with an open conductance between the two regions, the QMS region was differentially pumped with a Varian V70LP turbo molecular pump (Palo Alto, CA). The aperture radius \( r \) was determined by Equation 4.1, where \( S \) is the pumping speed of the turbo molecular pump, \( P_{QMS} \) and \( T_{QMS} \) are the pressure and temperature in the QMS region, \( P_{ALD} \) and \( T_{ALD} \) are the pressure and temperature in the ALD reactor, \( m \) is the mass of the molecule being conducted and \( k \) is the Boltzmann constant.

\[
r = 2 \sqrt{\frac{S P_{QMS}}{\pi P_{ALD} T_{QMS}}} \left( \frac{m T_{ALD}}{3 k} \right)^{1/4}
\]  

Equation 4.1

From Equation 4.1 it was determined that an aperture with a radius of 25 μm was appropriate. A dual thoriated-iridium (ThO₂/Ir) filament was used for electron emission in the mass spectrometer. The ionization energy was 70 eV. A Faraday cup was used as the detector. Data was collected as a function of time for mass to charge ratios (m/z) of 18.
4.3.6 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to determine the film identity. LiOH and Li$_2$CO$_3$ ALD films were grown on KBr slides (International Crystal Laboratories) and characterized \textit{ex situ} with a Nicolet Avatar 360 FTIR (Thermo Fisher Scientific Inc.). Excess H$_2$O and CO$_2$ was purged with nitrogen for at least 20 minutes prior to background collection in order to minimize signal contamination. The spectrometer collected 100 scans and then took the average. Data was collected between 4000 and 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

Due to the instability of LiOH in air, LiOH films were also grown in an ALD reactor equipped with \textit{in situ} FTIR analysis that has been described elsewhere [216]. The \textit{in-situ} FTIR studies were performed with a Nicolet Nexus 870 FTIR spectrometer equipped with a liquid-N$_2$ cooled mercury-cadmium-telluride infrared detector. Spectra were collected with a mirror speed of 1.8 cm s$^{-1}$, and averaged over 100 scans. The resolution of the spectrometer was cm$^{-1}$. The IR transparent windows were KBr disks supplied by International Crystal Laboratories. The \textit{ex situ} IR beam path between the reactor and the KBr window was purged with H$_2$O and CO$_2$-free air delivered from a purge gas generator.

4.3.7 X-ray Photoelectron Spectroscopy

The LiOH and Li$_2$CO$_3$ films were also characterized \textit{ex situ} with X-ray photoelectron spectroscopy (XPS). Measurements were performed with a Perkin-Elmer 5600 XPS using a monochromatic Al K$_\alpha$ source (1486.6 eV). The base pressure in the vacuum chamber during XPS analysis was $3 \times 10^{-10}$ Torr. A constant analyzer energy mode was employed at a pass energy of 58.7 eV with a step size of 0.25 eV. All spectra were calibrated to the adventitious carbon peak at 285 eV. An electron beam neutralizer was employed at 17.8 mA. Data was collected with Auger Scan (RBD Instruments, Inc., Bend, OR). XPS data was analyzed in CASA XPS (Casa Software Ltd, UK).
4.4 Results and Discussion

4.4.1 LiOH ALD

LiOH film growth was monitored on the QCM. The overall binary reaction is LiOC(CH\(_3\)_3) + H\(_2\)O → LiOH + HOC(CH\(_3\)_3). The AB binary reaction sequence during LiOH ALD is proposed to be:

A \[ \text{LiOH}^* + \text{LiOC(CH}_3)_3 \rightarrow \text{LiOH} - \text{LiOC(CH}_3)_3 \]  

B \[ \text{LiOH} - \text{LiOC(CH}_3)_3^* + \text{H}_2\text{O} \rightarrow \text{LiOH} - \text{LiOH}^* + \text{HOC(CH}_3)_3 \]  

where an asterisk is used to denote surface species. LiOH-LiOC(CH\(_3\)_3)* is postulated to be a molecularly adsorbed species that reacts with H\(_2\)O to form LiOH.

The first 3 cycles during LiOH ALD on a fresh Al\(_2\)O\(_3\) surface are shown in Figure 4.3. During the first 10 ALD cycles, the mass gain during the LTB exposure was \( \Delta m_A = 18.9 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{cycle}^{-1} \) and the mass loss during the H\(_2\)O exposure was \( \Delta m_B = -11.7 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{cycle}^{-1} \). The \( \Delta m_A/\Delta m_B \) ratio was -1.62. This ratio is close to the predicted ratio of -1.43 based on Equations 4.2 and 4.3. The growth rate during first 10 cycles of LiOH was 7.6 ng·cm\(^{-2}\)·cycle\(^{-1}\). Assuming a LiOH bulk density of 1.45 g·cm\(^{-3}\) [202], the mass gain of 7.6 ng·cm\(^{-2}\)·cycle\(^{-1}\) is equivalent to a LiOH ALD growth rate of 0.5 Å/cycle\(^{-1}\).

LTB has a molecular mass of 80.06 AMU. A mass gain of 30.1 ng·cm\(^{-2}\) corresponds to 1.4 × 10\(^{14}\) LTB molecules cm\(^{-2}\). Al\(_2\)O\(_3\) grown with ALD has a density of 3.0 g·cm\(^{-3}\) [84]. This equates to an Al\(_2\)O\(_3\) density \( (\rho_{\text{Al}_2\text{O}_3}) \) of 1.8 × 10\(^{22}\) Al\(_2\)O\(_3\) units cm\(^{-3}\). An estimate of the density of hydroxyl groups on the Al\(_2\)O\(_3\) after a H\(_2\)O dose is given by \( (\rho_{\text{Al}_2\text{O}_3})^{2/3}/2 \). The estimated value of the density of hydroxyl groups is 3.4 × 10\(^{14}\) hydroxyl groups cm\(^{-2}\). This value is in close agreement with the density of LTB molecules on the surface. This may indicate that the adsorbed monolayer of LTB may be interacting with hydroxyl groups on the Al\(_2\)O\(_3\).

After the first 10 LiOH ALD cycles, the mass changes evolve and display a much different behavior. Figure 4.4 shows the QCM results during cycles 198-200. LiOH is hygroscopic and can
Figure 4.3: Mass gain during LiOH ALD using LTB and H₂O at 225 °C for cycles 1-3.
easily adsorb H₂O and form a hydrate [204]. The hygroscopicity is reversible and H₂O can desorb from the LiOH-hydrate during the purge times [204]. This H₂O desorption leads to the mass decays observed after both the LTB and H₂O exposures in Figure 4.4. To confirm the presence a LiOH-hydrate, films grown using 200 AB cycles were subjected to an extended N₂ purge at 225 °C. The LiOH film lost ~32% of its mass in 2 hours before reaching a stable value, this is shown in Figure 4.5. This mass loss is attributed to H₂O desorption from the LiOH-hydrate. A mass loss of 32% means that the LiOH film was initially 74% hydrated, i.e. 76% LiOH-H₂O and 24% H₂O.

The presence of H₂O in the ALD reactor during an LTB dose may have increased the growth rate of the LiOH by the process of chemical vapor deposition. For LiOH to be grown in true ALD fashion all excess water must be completely purged from the reactor after the H₂O dose. The time scale for this should be short at high temperatures with thin LiOH films, as was observed for the initial several cycles shown in Figure 4.3. After the appearance of the LiOH-H₂O, starting around 10 LiOH ALD, H₂O purge time in excess of 1000 s were still insufficient at completely dehydrating the LiOH-H₂O.

4.4.2 Li₂CO₃ ALD

LiOH is highly reactive with CO₂ to form Li₂CO₃ and H₂O [204]. The reaction enthalpy for this reaction is -134.3 kJ [1]. The reaction is so efficient that LiOH is used as a CO₂ scrubber by NASA in the shuttle spacecraft [94].

Li₂CO₃ ALD is based on a ternary ABC reaction sequence that utilizes the LTB and H₂O reactions given in Equations 4.2 and 4.3. In addition, a third reaction is added where LiOH can react with CO₂ to form Li₂CO₃ according to [204]:

\[
\text{C} \quad \text{LiOH} - \text{LiOH}^\ast + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3^\ast + \text{H}_2\text{O},
\]

(4.4)

where an asterisk is used to denote surface species. The reaction in Eqn. 4.4 relies on the presence of H₂O and has been shown to involve LiOH-H₂O (lithium hydroxide hydrate) according to [204]:

\[
\text{C1} \quad 2\text{LiOH} + 2\text{H}_2\text{O} \leftrightarrow 2\text{LiOH} \cdot \text{H}_2\text{O},
\]

(4.5)
Figure 4.4: Mass gain during LiOH ALD using LTB and H$_2$O at 225 °C for cycles 198-200.
Figure 4.5: Mass gain during LiOH ALD using LTB and H\textsubscript{2}O at 225 °C followed by mass loss as the LiOH film was dehydrated.
Although \( \text{H}_2\text{O} \) is required to initiate the reaction, \( \text{H}_2\text{O} \) products sustain the reaction.

### 4.4.2.1 Converting LiOH to Li\(_2\)CO\(_3\) with CO\(_2\) Exposures

After depositing 8873.1 ng cm\(^{-2}\) of dehydrated LiOH onto the QCM sensor, the sensor was exposed to repeated doses of CO\(_2\). Figure 4.6 shows that with each CO\(_2\) dose there is a mass gain on the QCM as the LiOH is converted to Li\(_2\)CO\(_3\). After \( \sim \)31 CO\(_2\) doses the mass on the QCM leveled off indicating that the conversion reaction had run to completion. The stoichiometric prediction for 100% conversion of LiOH to Li\(_2\)CO\(_3\) is also shown in Figure 4.6. The actual mass change on the QCM is close to the stoichiometric prediction. It is possible that the initial mass of LiOH was overestimated due to some degree of hydration of the LiOH; this may account for the difference between the stoichiometric prediction and the final QCM mass.

Equation 4.4 indicates that the conversion of LiOH to Li\(_2\)CO\(_3\) should produce H\(_2\)O as a reaction byproduct. Figure 4.7 shows the partial pressure of the mass fragment associated with H\(_2\)O (\( m/z = 18 \)), as monitored with QMS. The production of H\(_2\)O correlated with the CO\(_2\) doses and the mass increases on the QCM. As the mass increases on the QCM tapered off with subsequent CO\(_2\) doses so did the signal for \( m/z = 18 \) mass fragment. The \( m/z = 18 \) mass fragment did not go to zero after the QCM mass increases leveled off. This may be due to an artifact from the CO\(_2\) that appears at \( m/z = 18 \).

### 4.4.2.2 Li\(_2\)CO\(_3\) ALD as an ABC Process

The first 3 cycles during Li\(_2\)CO\(_3\) ALD on a fresh Al\(_2\)O\(_3\) surface are shown in Figure 4.8. During the first 10 ALD cycles, the mass gain during the LTB exposure was \( \Delta m_A = 19.8 \text{ ng cm}^{-2} \cdot \text{cycle}^{-1} \), the mass loss during the H\(_2\)O exposure was \( \Delta m_B = -14.2 \text{ ng cm}^{-2} \cdot \text{cycle}^{-1} \) and the mass gain during the CO\(_2\) exposure was \( \Delta m_C = 4.9 \text{ ng cm}^{-2} \cdot \text{cycle}^{-1} \). The \( \Delta m_A/\Delta m_B \) ratio was -1.39. This ratio is close to the predicted ratio of -1.43 based on Equations 4.2 and 4.3. The initial growth
Figure 4.6: Mass increases on the QCM as LiOH is converted to Li$_2$CO$_3$ with doses of CO$_2$. The stoichiometric prediction for 100% conversion of LiOH to Li$_2$CO$_3$ is shown in orange.
Figure 4.7: Mass increases on the QCM as LiOH is converted to Li$_2$CO$_3$ with doses of CO$_2$. The stoichiometric prediction for 100% conversion of LiOH to Li$_2$CO$_3$ is shown in orange. The partial pressure of H$_2$O ($m/z = 18$) from QMS correspond to the CO$_2$ doses and mass increase on the QCM.
rate during the first 10 cycles of Li$_2$CO$_3$ ALD was 13.4 ng·cm$^{-2}$·cycle$^{-1}$.

After $\sim$10-15 cycles of Li$_2$CO$_3$ ALD on a fresh Al$_2$O$_3$ surface the growth rate decreased slightly to 10.4 ng·cm$^{-2}$·cycle$^{-1}$ and was stable.

Figure 4.9 shows the QCM results during cycles 198-200 for the growth of Li$_2$CO$_3$ with ALD. The mass gain during the LTB exposure was $\Delta m_A = 25.7$ ng·cm$^{-2}$·cycle$^{-1}$, the mass loss during the H$_2$O exposure was $\Delta m_B = -19.3$ ng·cm$^{-2}$·cycle$^{-1}$, and the mass gain during the CO$_2$ exposure was $\Delta m_C = 3.4$ ng·cm$^{-2}$·cycle$^{-1}$. Compared with the nucleation regime, the magnitude of the mass gain per cycle of the LTB and the H$_2$O increased and the magnitude of the mass gain per cycle of the CO$_2$ decreased. The differences in the magnitudes of the mass gains and losses began to evolve after $\sim$10-15 cycles of Li$_2$CO$_3$ ALD on a fresh Al$_2$O$_3$ surface. This difference was attributed to nucleation on the Al$_2$O$_3$. After $\sim$10-15 cycles the growth rate decreased slightly to 10.4 ng·cm$^{-2}$·cycle$^{-1}$ and was stable. Assuming a Li$_2$CO$_3$ bulk density of 2.11 g·cm$^{-3}$ [202], the mass gain of 10.4 ng·cm$^{-2}$·cycle$^{-1}$ is equivalent to a Li$_2$CO$_3$ ALD growth rate of 0.5 Å/cycle$^{-1}$.

Throughout the 200 cycles of Li$_2$CO$_3$ ALD the ratios of the mass gains, $\Delta m_A/\Delta m_B$, $\Delta m_C/\Delta m_A$ and $\Delta m_C/\Delta m_B$, stayed relatively constant. Figure 4.10 shows the mass ratios versus the number of ALD cycles. The mass ratios are $\Delta m_A/\Delta m_B = -1.47$, $\Delta m_C/\Delta m_A = 0.14$ and $\Delta m_C/\Delta m_B = -0.20$. In comparison, the mass ratios calculated from Equations 4.2-4.4 are $\Delta m_A/\Delta m_B = -1.43$, $\Delta m_C/\Delta m_A = 0.16$ and $\Delta m_C/\Delta m_B = -0.23$. These predicted ratios are given by the solid lines in Fig. 4.10. The agreement between the predicted mass ratios and the measured mass ratios is excellent and supports the reaction mechanism proposed in Equations. 4.2-4.4.

The mass gain per cycle (MGPC) as a function of the ALD reactor temperature for growth of Li$_2$CO$_3$ is shown in Figure 4.11. Below 130 °C the growth rate rapidly increased due to condensation of the LTB precursor on the QCM sensor. Above 250 °C the growth rate decreased. This decrease in growth rate was attributed to the inability to form an adsorbed monolayer of LTB on the surface of the QCM sensor. At 295 °C the growth rate rose, which may be due to the decomposition of the LTB precursor. Between 130-250°C the growth rate was relatively stable, this temperature range is the ALD window. The average growth rate in the ALD window 9.2 ng·cm$^{-2}$·cycle$^{-1}$ with a
Figure 4.8: Mass gain during Li$_2$CO$_3$ ALD using LTB H$_2$O and CO$_2$ at 225 °C for cycles 1-3.
Figure 4.9: Mass gain during Li$_2$CO$_3$ ALD using LTB H$_2$O and CO$_2$ at 225 °C for cycles 198-200.
Figure 4.10: Mass ratios of the mass changes during the LTB (A), H\(_2\)O (B) and CO\(_2\) (C) exposures versus the number of ALD cycles. The solid lines indicate the predicted values expected from Equns. 4.2-4.4.
standard deviation of 0.6 ng·cm$^{-2}$·cycle$^{-1}$. Assuming that ALD Li$_2$CO$_3$ has the density of bulk Li$_2$CO$_3$, this growth rate equates to 0.44 Å·cycle$^{-1}$ with a standard deviation of 0.03 Å·cycle$^{-1}$.

Figure 4.12 shows the MGPC of Li$_2$CO$_3$ ALD as a function of reactor temperature during nucleation on a fresh Al$_2$O$_3$ surface. The nucleation regime was defined as the first 10 ALD cycles. The data is somewhat irregular and is peaked at 205 °C. The clear trends for condensation, desorption, and decomposition that were observe in the growth regime (Figure 4.11) beyond ~10-15 ALD cycles were not apparent in the nucleation regime. It should be noted that overall the MGPC was higher in the nucleation regime than in the growth regime; this result is consistent with Figures 4.8 and 4.9.

Figure 4.13 shows the MGPC recorded by the in situ QCM as a function of the LTB exposure time for the nucleation regime (1$^{st}$ 10 ALD cycles) and the growth regime at 225 °C. After a ~2 s dose of LTB the the QCM sensor surface was saturated both in the nucleation regime and in the growth regime. Ignoring any pressure transients from the change in the conduction path as the N$_2$ was shifted from flowing directly into the ALD reactor to flowing into the ALD reactor and across the LTB bubbler headspace in parallel, a dose time of 2 s is equivalent to 70 mTorr·s.

### 4.4.3 Fourier Transform Infrared Spectroscopy

LiOH and Li$_2$CO$_3$ ALD films were also grown on KBr slides and characterized using ex situ FTIR. Removal of the LiOH film from the reactor resulted in the conversion of LiOH to Li$_2$CO$_3$ by ambient CO$_2$. Figure 4.14 shows an ex situ FTIR spectrum of Li$_2$CO$_3$. It did not matter whether LiOH or Li$_2$CO$_3$ ALD was grown on the KBr slide, Li$_2$CO$_3$ was observed after both LiOH and Li$_2$CO$_3$ ALD. The main absorption bands of Li$_2$CO$_3$ were observed at 1475 cm$^{-1}$ and 1429 cm$^{-1}$ for antisymmetric C-O stretching vibrations, 1088 cm$^{-1}$ for symmetric C-O stretching vibrations, and 870 cm$^{-1}$ for out of plane deformation modes [29]. All of these features are from the carbonate CO$_3^{2-}$ ion. For comparison, Figure 4.14 also shows a reference spectrum of Li$_2$CO$_3$ from the NIST Chemistry WebBook [174].

Figure 4.15 shows an in situ FTIR spectrum approximately 30 hours after 100 cycles of LiOH
Figure 4.11: Mass gain per cycle (MGPC) of Li$_2$CO$_3$ in the growth regime.
Figure 4.12: Mass gain per cycle (MGPC) of Li$_2$CO$_3$ ALD as a function of reactor temperature during nucleation on a fresh Al$_2$O$_3$ surface.
Figure 4.13: Mass gain per cycle (MGPC) as a function of the LTB exposure time for the nucleation regime (1st 10 ALD cycles) and the growth regime.
Figure 4.14: *Ex situ* FTIR spectrum of Li$_2$CO$_3$. For comparison a reference FTIR spectrum of Li$_2$CO$_3$ from NIST is also shown.
ALD on ZrO2 nanoparticles at 225 °C. After deposition, the LiOH ALD film was maintained in the ALD reactor under vacuum. A sharp absorption peak was observed at 3672 cm$^{-1}$ that is consistent with hydroxyl stretching vibrations from unhydrated LiOH [171, 97]. The O-H stretching vibration from H$_2$O in LiOHH$_2$O is not observed at 3570-3574 cm$^{-1}$ [171, 97]. The absence of this hydrate feature supports the identification of this film as LiOH.

There is also a broad absorbance feature from O-H stretching vibrations at 3720-3220 cm$^{-1}$ in Figure 4.15. This absorbance could be caused by some hydrogen-bonded LiOH hydroxyls or some H$_2$O in the LiOH film [171, 97]. This absorbance feature also increased with subsequent H$_2$O exposure and decreased with purging time after H$_2$O exposure. However, the O-H stretching vibration from H$_2$O in LiOHH$_2$O was never observed at 3570-3574 cm$^{-1}$ after H$_2$O exposures to the LiOH ALD film.

The strong absorbances at 1496 and 1450 cm$^{-1}$ in Figure 4.15 are assigned to antisymmetric C-O stretching vibrations from some Li$_2$CO$_3$ in the LiOH film [171, 29]. This feature is explained by the facile reaction of LiOH with background CO$_2$ in the ALD reactor [204, 171]. In addition, absorbance from C-H stretching vibrations at 3000-2817 cm$^{-1}$ and C-O stretching vibrations at 1200 cm$^{-1}$ indicates that some unreacted tert-butoxide groups remain in the film.

### 4.4.4 X-ray Photoelectron Spectroscopy

Figure 4.16 shows *ex situ* XPS spectra of the Li 1s, C 1s and O 1s peaks from LiOH and Li$_2$CO$_3$ films before and after Ar ion sputtering. For the LiOH film, conversion to Li$_2$CO$_3$ occurred upon exposure to CO$_2$ in air. The adventitious C 1s peak at 285.0 eV was removed with 1 minute of Ar ion sputtering. The Li 1s peak at 55.2 eV, the C 1s peak at 289.5 eV and the O 1s peak at 531.6 eV were attributed to the formation of Li$_2$CO$_3$ [50, 51]. The stoichiometry of sputtered LiOH and Li$_2$CO$_3$ films is summarized in Table 4.4.4. The uncertainty of these atomic percentages is <2%. In comparison, stoichiometric Li$_2$CO$_3$ has a composition of 33.3% lithium, 16.7% carbon and 50.0% oxygen. This excellent agreement argues that the Li$_2$CO$_3$ ALD film is close to stoichiometric Li$_2$CO$_3$. The slightly higher levels of carbon and decreased levels of oxygen in the Li$_2$CO$_3$ ALD
Figure 4.15: *In situ* FTIR spectrum of a LiOH ALD film grown using 100 cycles of LTB and H$_2$O at 225 C. The absorbance from O2C-O stretching vibrations indicates the presence of some Li$_2$CO$_3$ from reaction with CO$_2$. 
films may result from some unreacted tert-butoxide groups.

Table 4.1: Atomic percentage of Li, C and O in Li$_2$CO$_3$. For comparison, the atomic percentage of stoichiometric Li$_2$CO$_3$ are also presented.

<table>
<thead>
<tr>
<th></th>
<th>Stoichiometric Li$_2$CO$_3$</th>
<th>Air Exposed ALD LiOH</th>
<th>ALD Li$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>33.3%</td>
<td>30.7%</td>
<td>32.7%</td>
</tr>
<tr>
<td>C</td>
<td>16.7%</td>
<td>20.1%</td>
<td>19.0%</td>
</tr>
<tr>
<td>O</td>
<td>50.0%</td>
<td>49.3%</td>
<td>48.3%</td>
</tr>
</tbody>
</table>

4.5 Conclusions

ALD techniques have been demonstrated for depositing LiOH and Li$_2$CO$_3$ using LTB, H$_2$O and CO$_2$ reactants. The QCM results illustrate the initial growth of LiOH with sequential LTB and H$_2$O exposures and reveal the very hygroscopic nature of LiOH. The reaction of LiOH with CO$_2$ is facile as observed by QCM and FTIR investigations. Li$_2$CO$_3$ ALD growth was also accomplished using sequential LTB, H$_2$O and CO$_2$ exposures. The identity of the Li$_2$CO$_3$ films was confirmed by FTIR and XPS investigations. LiOH and Li$_2$CO$_3$ ALD films may serve as artificial SEI layers to enhance the performance of graphite anodes in LIBs.

4.6 Acknowledgements

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Figure 4.16: *Ex situ* XPS spectra of LiOH and Li$_2$CO$_3$. 
Chapter 5

Enhanced Stability of LiCoO$_2$ Cathodes with thin films of Al$_2$O$_3$ Grown with Atomic Layer Deposition

5.1 Abstract

It has been widely demonstrated in the literature that metal oxide films grown with wet chemical techniques enhance the performance of LIBs. Films grown with wet chemical techniques typically have thicknesses with the range 50-1000 Å. Here we demonstrate that ultrathin films grown with atomic layer deposition (ALD) enhanced the capacity retention of LiCoO$_2$ in lithium-ion battery (LIB) half cells. Depending on the number of ALD cycles, the Al$_2$O$_3$ films grown on LiCoO$_2$ particles in this study had thickness in the range of 3-22 Å. Al$_2$O$_3$ coated LiCoO$_2$ particles had a capacity retention of 89% after 120 charge-discharge cycles, with respect to the third charge-discharge cycle, in the range of 3.3-4.5 V (versus Li/Li$^+$). Bare LiCoO$_2$ exhibited a capacity retention of only 45%. In addition to coating LiCoO$_2$ particles, Al$_2$O$_3$ ALD was coated on composite electrodes consisting of LiCoO$_2$ particles, acetylene black and poly(vinylidene fluoride). The improvements from the ultrathin Al$_2$O$_3$ films may stem from a variety of mechanisms including: minimizing the interactions between the LiCoO$_2$ and the electrolyte thereby reducing reactions between the two, Al$_2$O$_3$ may act as a sacrificial scrubber for HF, or the film may block the dissolution of Co ions. In addition to Al$_2$O$_3$, films of ZnO ALD on LiCoO$_2$ were also characterized. ZnO did enhance the performance of the LiCoO$_2$. 
5.2 Introduction

The traditional means for producing energy, such as coal or hydroelectric, can be tuned to meet the power demand of the population being served. In contrast, most renewable energy sources, such as wind power or photovoltaics, have their production rate fixed by nature. With wind power and photovoltaics, peak production does not necessarily correlate with peak demand. Rather, peak production correlates with windiest or sunniest times of the day. In order to synchronize peak power production from renewable energy sources with peak demand from the population being served, an efficient and durable means of energy storage must be developed. Lithium ion batteries (LIBs) have emerged as a vital energy storage technology for portable electronics [185, 203, 209]. The high energy densities that make LIBs suitable for portable electronics may allow for the practical use of LIBs for power storage for the electric grid, hybrid electric vehicles or all-electric vehicles. In order to implement LIBs in vehicles or the power grid the durability of the LIBs must be dramatically improved.

Most LIBs employ LiCoO$_2$ as the cathode active material. LiCoO$_2$ has practical limitations that limit the voltage range over which it may be cycled. At voltages higher than $\sim 4.2$ V (versus Li/Li$^+$), Co can be dissolved from LiCoO$_2$, LiCoO$_2$ can react with the electrolyte and structural changes may occur in the LiCoO$_2$ [146]. These changes are detrimental to the LiCoO$_2$ and result in a decreased capacity of the LIB [146]. It has been demonstrated in the literature that these problems can be mitigated by coating the LiCoO$_2$ powders with metal oxides: Al$_2$O$_3$ [46, 45, 120], ZrO$_2$ [131, 106], ZnO [177], SiO$_2$ [13] and TiO$_2$ [132, 225]; metal fluorides: AlF$_3$ [228]; and metal phosphates: AlPO$_4$ [42, 122]. These films were typically deposited with wet chemical techniques such as the sol-gel method, followed by a heat treatment [44, 129, 47, 176, 45]. The typical thickness of these coatings is $\sim 50$-1000 Å [44, 129].

Atomic layer deposition (ALD) is a thin film growth technique where gas phase precursors react with the surface of the substrate [79, 161]. Because ALD uses sequential, self limiting surface reaction it is possible to grow conformal films on high aspect ratio structures with digital thickness
control [79, 161]. The precise control of film thickness, morphology and stoichiometry offered by ALD makes it an excellent choice for coating LIB active materials. Films grown by ALD have been employed in a variety of industries [103, 111, 138, 147, 152]; however, ALD has not been widely used to modify the surfaces of active materials for LIBs [172].

In this study ALD, rather than wet chemical techniques, ALD was used to grow metal oxide films on LiCoO₂. ALD does not use the large amount of solvents required for wet-chemical techniques and ALD allows for precise control of the amount of precursor used. In these two regards ALD can be seen as more environmentally benign than wet chemical techniques.

In this study, Al₂O₃ and ZnO films grown with ALD on LiCoO₂ are characterized. Films were grown both on the LiCoO₂ powders prior to electrode assembly and on assembled electrodes consisting of LiCoO₂, acetylene black (conductive additive) and poly(vinylidene fluoride) (polymer binder). The presence and conformality of the Al₂O₃ and ZnO were measured with X-ray photoelectron spectroscopy. The electrochemical performance for the coated, particle and electrodes, and bare LiCoO₂ was measured by cycling against Li metal. The effect of the thickness of the Al₂O₃ film on the electrochemical performance was evaluated.

5.3 Experimental

5.3.1 ALD on LiCoO₂ powders

The LiCoO₂ used in these experiments was obtained from LICO Technology (Tao-Yuan Hsien, Taiwan). The LiCoO₂ particle size (D₅₀) was 7-10 µm, as reported by the manufacturer. The manufactures grade for the LiCoO₂ was L106. For the Al₂O₃ ALD and ZnO ALD, (Al(CH₃)₃ (TMA, trimethylaluminum) (97%) and Zn(C₂H₅)₂ (DEZ, diethylzinc) were obtained from Sigma-Aldrich (St. Louis, MO). HPLC grade H₂O was also from Sigma-Aldrich and was further purified by 5 cycles of freeze-pump-thaw.

ALD on particles is possible using either fluid bed reactors [201, 200] or rotary reactors [139, 140]. A schematic of the rotary reactor used in this work is shown in Figure 5.1. In order
to perform ALD on powders, the powders were placed in a porous stainless steel cylinder (A). The porous stainless steel cylinder was placed in the chamber onto a magnetically coupled axel via an O-ring sealed door (B). A motor rotated the axel and porous stainless steel via a magnetically coupled rotary feed through (Transfer Engineering and Manufacturing, Inc., Fremont, CA)(C). This served to agitate the LiCoO$_2$ during the ALD process. A dual range, 0-10 and 0-100 Torr, Baratron capacitance manometer (MKS Instrument, Andover, MA)(D) was used to measure the pressure in the reaction chamber. Each reactant entered the reaction chamber through a series of pneumatic (E) and needle (F) valves that were attached to 0.25” welded ports on a custom 6.0” to 2.75” Conflat zero length reducer. In order to evacuate the chamber a gate (G) was opened to connect the reactor to an corrosion resistant dual-stage rotary vane pump (Alcatel Vacuum Technology, Annecy, France) (H). A ceramic heater (Watlow Electric Manufacturing Co., St. Louis, MO) (J) on the rotary reactor was employed to heat the reactor. The temperature was monitored with a thermocouple and was controlled via PID loop with a temperature controller (Eurotherm U.S.A., Ashburn, VA).

During the ALD process on particles the porous metal cylinder was rotated in the rotary reactor at $\sim$150 rpm. Given the diameter of the rotating porous cylinder, this rotational frequency is consistent with a centripetal force of $\sim$0.5g. Reasonable results were obtained using rotational frequencies from 140-180 rpm. Rotational frequencies $<$140 rpm led to less agitation and agglomeration during ALD.

Al$_2$O$_3$ ALD was performed on gram quantities of LiCoO$_2$ in the rotary reactor. The Al$_2$O$_3$ ALD surface chemistry employs Al(CH$_3$)$_3$ (trimethylaluminum, TMA) and H$_2$O as the reactants. The sequential, self-limiting reaction sequence during Al$_2$O$_3$ ALD is [58, 84, 149]:

\begin{align}
A & \quad \text{AlOH}^* + \text{Al(CH$_3$)$_3$} \rightarrow \text{AlO} - \text{Al(CH$_3$)$_2^*$} + \text{CH}_4 \\
B & \quad \text{AlCH}$_3^*$ + H$_2$O $\rightarrow$ Al - OH$^*$ + CH$_4$
\end{align}

where the asterisks denote surface species. The Al$_2$O$_3$ ALD reaction sequence was: (1) TMA dose to set pressure; (2) TMA reaction time; (3) evacuation of reaction products and excess TMA; (4)
Figure 5.1: Schematic of rotary reactor used to coat gram quantities of LiCoO$_2$ powders.
N₂ dose; (5) N₂ static time; (6) evacuation of N₂ and any entrained gases; (7) H₂O dose to pressure, (8) H₂O reaction time; (9) evacuation of reaction products and excess H₂O; (10) dose N₂; (11) N₂ static time; and (12) evacuation of N₂ and any entrained gases. This sequence constituted one AB cycle of Al₂O₃ ALD. This reaction was carried out at 180 °C.

The typical growth rate for Al₂O₃ ALD is 1.1-1.2 Å per ALD cycle [84, 149]. During the water dose a hydroxyl terminated surface is generated. The hydroxyl terminated surface will interact with excess H₂O in the reactor via hydrogen bonding. Due to the large surface area of the LiCoO₂ powders and the large surface area of the porous stainless steel cylinder, H₂O may not be completely purged from the reactor during the evacuation step of the H₂O dose. The presence of H₂O in the reactor during the TMA half reaction may lead increased growth per cycle. This behavior is similar to chemical vapor deposition [83, 139].

ZnO was also grown on LiCoO₂ powders with ALD. The sequential, self-limiting reaction sequence during ZnO ALD is [140, 211]:

A \[\text{ZnOH}^* + \text{Zn(CH}_2\text{CH}_3)_2 \rightarrow \text{ZnO} - \text{ZnCH}_2\text{CH}_3^* + \text{CH}_3\text{CH}_3\] (5.3)

B \[\text{ZnCH}_2\text{CH}_3^* + \text{H}_2\text{O} \rightarrow \text{ZnOH}^* + \text{CH}_3\text{CH}_3\] (5.4)

where the asterisks denote surface species. The ZnO ALD reaction sequence was: (1) DEZ dose to set pressure; (2) DEZ reaction time; (3) evacuation of reaction products and excess DEZ; (4) N₂ dose; (5) N₂ static time; (6) evacuation of N₂ and any entrained gases; (7) H₂O dose to pressure, (8) H₂O reaction time; (9) evacuation of reaction products and excess H₂O; (10) dose N₂; (11) N₂ static time; and (12) evacuation of N₂ and any entrained gases. This sequence constituted one AB cycle of ZnO ALD. This reaction was carried out at 180 °C. The reported growth rate for ZnO ALD is 2.0 Å per ALD cycle [61]. In a similar fashion to the Al₂O₃ ALD chemistry, the presence of H₂O in the reactor during the DEZ half reaction may lead increased growth per cycle.
5.3.2 Materials Characterization

5.3.2.1 X-ray Photoelectron Spectroscopy

Characterization with X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5600 X-ray photoelectron spectrometer with a monochromatic Al Kα source (1486.6 eV). The base pressure in the XPS analysis chamber was $3 \times 10^{-10}$ Torr. XPS spectra were collected using the constant analyzer energy mode with a pass energy between 58.7-93.9 eV. The step size was varied between 0.25-0.4 eV. All spectra were calibrated to the adventitious carbon peak at 285 eV. An electron beam neutralizer was employed at 17.8 mA. Data was collected with Auger Scan (RBD Enterprises, Inc., Bend, OR). XPS data was analyzed in CASA XPS (Casa Software Ltd, UK). By monitoring the attenuation of the Co $2p_{3/2}$ peak with respect to the Al $2s$ peak as a function of the number of cycles of Al$_2$O$_3$ ALD it was possible to calculate the thickness of the Al$_2$O$_3$ film. Equation 5.5 shows the model used for calculating the thickness of an over layer oxide film with XPS [91, 53]. This model was derived for calculating the thickness of films on flat substrates [91, 53].

$$t = -\lambda \cos(\theta) \ln \left(1 + \frac{I_f/S_f}{I_s/S_s}\right)$$

The thickness of the over layer film ($t$) is measured as a function of the attenuation length for a photoelectron from the underlying substrate in the over layer film ($\lambda$), the angle of emission ($\theta$), the peak area of the film ($I_f$) and substrate ($I_s$) and the relative sensitivity factors for the film ($S_f$) and substrate ($S_s$). Effective attenuation lengths were obtained from the NIST Electron-Effective-Attenuation-Length Database [154].

Powder samples for XPS were prepared by spreading ~0.5 mm of the powder onto Ag foil and then pressing the powder into the malleable Ag film. Composite electrodes were also examined with XPS. For XPS on composite electrodes that had not undergone any charge-discharge cycles, the electrodes were examined as is. For electrodes that underwent charge-discharge cycling in a battery cell, the electrodes were rinsed with dimethyl carbonate to remove excess electrolyte prior to XPS analysis.
5.3.2.2 Electrical Conductivity

The electrical conductivity was measured by pressing a cylindrical pellet into a custom plastic mold equipped with four electrical contacts arranged in a cross around the cap of the cylinder. The measurement was carried out while the pellet inside the plastic mold was pressed to a pressure of 120 MPa. A current in the range of 0.5-5 µA was sourced between two adjacent electrical contacts and the potential was measured across the two remaining electrical contacts. The resistance was obtained from the slope of a five point voltage vs. current curve. The geometric factor was extracted by measuring the samples with different configuration. This technique for determining resistivity was pioneered by van der Pauw [193].

5.3.3 Electrochemical Characterization

In addition to LiCoO$_2$ the battery electrode consisted of a conductive additive, acetylene black (AB) and a polymer binder poly(vinylidene fluoride)(PVDF). AB and PVDF were obtained from Alfa Aesar (Ward Hill, MA). N-methyl pyrrolidinone from Sigma-Aldrich (St. Louis, MO) was used as the solvent to prepare the electrode material. The electrolyte, 1.0 M LiPF$_6$ dissolved in a solution of ethylene carbonate (EC):dimethylcarbonate (DMC) (1:1 by volume), was obtained from Novolyte (Cleveland, OH).

A slurry of LiCoO$_2$, AB and PVDF was prepared using N-methyl pyrrolidinone as the solvent. The weight ratio of electrode components was 83.0:7.5:9.5 (LiCoO$_2$:AB:PVDF). Cathodes were fabricated by spreading the slurry onto Al foil and evaporating the solvent. Lithium metal from Alfa Aesar (Ward Hill, MA) was employed as the counter electrode. The electrode diameters were 0.5”. A polypropylene (PP)/polyethylene (PE) /polypropylene tri-layer film (Celgard, LLC, Charlotte, NC) was used as a separator between the Li metal and the cathode. The separator was porous with a thickness of ~20 µm. Cells were fabricated using 2032-type coin cell in a glove box under an Ar environment (Vacuum Atmosphere’s Inc., Amesbury, MA). The H$_2$O and O$_2$ concentrations in the glove box were typically under 0.1 and 0.5 ppm respectively.
Constant current charge-discharge cycling was performed in the range of 3.3-4.5 V versus Li/Li$^+$ using a galvanostat (Arbin Instrument, College Station, TX). The current density during the first two charge-discharge cycles was 0.1 C-rate (14 mA g$^{-1}$). For subsequent cycles the current density was 1 C-rate (140 mA g$^{-1}$).

Electrochemical impedance spectroscopy (EIS) was performed using a 1280C Solartron instrument (Solartron Analytical, Hampshire, United Kingdom). Spectra were collected at an amplitude of 5 V over the range of 20 kHz-5 mHz. Prior to EIS measurements, the cells were charged to 4.5 V at a current density of 0.1 C-rate. The cells were then rested for 6 hours in order to allow them to stabilize. EIS was recorded at the open circuit voltage of the cells. EIS measurements were modeled via an equivalent circuit with ZView software (version 3.2c, Scribner Associates, Southern Pines, NC).

5.4 Results and Discussion

5.4.1 Al$_2$O$_3$ ALD on LiCoO$_2$ Powders

Figure 5.2 shows X-ray photoelectron spectra for bare LiCoO$_2$ and for LiCoO$_2$ coated with 2,4,6,8 and 10 cycles of Al$_2$O$_3$ by ALD. The atomic fraction of Al and Co as a function of the number ALD cycles, as observed with XPS, is shown in Figure 5.3. The behavior depicted in Figure 5.3 is indicative of Frank-van der Merwe type growth (layer-by-layer) [10]. The rapid attenuation of the Co signal by the increased number of cycles of ALD Al$_2$O$_3$ indicates that the film is conformal. Using Equation 5.5 and the data in Figure 5.3 the growth rate was determined to be 2.2 Å per ALD cycle. This is depicted in Figure 5.4 where the atomic fraction of Al and Co are shown as a function of the Al$_2$O$_3$ film thickness. The solid lines are the fits from Equation 5.5. The growth rate for the Al$_2$O$_3$ ALD was larger than what is typically reported in the literature [84, 149]. This increased growth rate was attributed to the incomplete purging of H$_2$O during the Al$_2$O$_3$ ALD [139, 140].

The resistance of the bare and Al$_2$O$_3$ ALD coated LiCoO$_2$ powders was measured using the
Figure 5.2: XPS spectra of bare and Al$_2$O$_3$ ALD coated LiCoO$_2$
Figure 5.3: Atomic fraction of Al and Co for bare Al₂O₃ coated LiCoO₂ powders as a function of the number of cycles of ALD Al₂O₃.

Figure 5.4: Atomic fraction of Al and Co for bare and Al₂O₃ coated LiCoO₂ powders as a function of the thickness of the ALD Al₂O₃ film. The solid lines are the fits from Equation 5.5.
van der Pauw method [193]. Figure 5.5 show the conductivity of the LiCoO$_2$ as a function of the number of cycles of Al$_2$O$_3$ ALD. Bare LiCoO$_2$ powder has a conductivity of $2 \times 10^{-4}$ S cm$^{-1}$. The electronic conductivity was successively reduced by subsequent cycles of Al$_2$O$_3$ ALD. After 10 cycles ($\sim 22 \, \text{Å}$) of Al$_2$O$_3$ ALD the electronic conductivity was $9.9 \times 10^{-6}$ S cm$^{-1}$. The large increase in the resistance was attributed to the conformality of Al$_2$O$_3$ film and the numerous particle-to-particle contact resistances.

The specific discharge capacity as function of the number of Al$_2$O$_3$ ALD cycles for the third charge-discharge cycle is shown in Figure 5.6. The current density was 1 C-rate (140 mA g$^{-1}$). The capacity is unaffected for films as thick as 4 cycles of Al$_2$O$_3$ ALD ($\sim 8.8 \, \text{Å}$). Beyond 4 cycles of Al$_2$O$_3$ ALD the capacity is dramatically reduced. By the tenth cycle of Al$_2$O$_3$ ALD the capacity for the third charge discharge cycle is only $\sim 20$ mA g$^{-1}$. As the number of cycles Al$_2$O$_3$ ALD was increased the potential at which current began to flow during charging also increased. Similarly, during discharge, the potential dropped rapidly for LiCoO$_2$ with thicker Al$_2$O$_3$ ALD films. These overpotentials are attributed to the insulating nature of Al$_2$O$_3$ [83]. Figure 5.7 show the voltage profiles for the second and third charge-discharge cycle. Figure 5.7 (a) and (b) shows the second charge-discharge cycle at 0.1 C-rate. The overpotential is increased further when the current density was increased to 1 C-rate (Figure 5.7 (c) and (d)).

Discharge capacity as function of the number of charge-discharge cycles is shown in Figure 5.8. During the first two cycles the current density was 0.1 C-rate. After the first two cycles the current density was raised to 1 C-rate. The initial discharge capacity of the bare LiCoO$_2$ is similar to that of the LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD. For the LiCoO$_2$ with 6 cycles of Al$_2$O$_3$ ALD the initial discharge capacity was dramatically reduced when the current density is increased to 1 C-rate. For the LiCoO$_2$ with 10 cycles of Al$_2$O$_3$ ALD the initial discharge capacity it dramatically reduced even at 0.1 C-rate. The dramatic loss in capacity for the LiCoO$_2$ with 6 and 10 cycles of Al$_2$O$_3$ ALD was attributed to losses in the composite materials ability to conduct electrons and Li ions through the thicker Al$_2$O$_3$ films.

As compared with the bare LiCoO$_2$, the LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD was able retain
Figure 5.5: Electronic conductivity of bare and Al$_2$O$_3$ ALD coated LiCoO$_2$ powders.
Figure 5.6: Specific discharge capacity as a function of the number of cycles of Al2O3 ALD.

Figure 5.7: Voltage profiles for the second and third charge-discharge cycles for bare and Al2O3 ALD coated LiCoO2 powders.
Figure 5.8: Discharge capacity as a function the number of charge-discharge cycles for bare LiCoO$_2$ and LiCoO$_2$ with 2, 6 and 10 cycles of Al$_2$O$_3$ ALD.
its capacity with charge-discharge cycling. After 120 charge discharge cycles, the LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD had retained 89% of its initial capacity, with respect to the third charge-discharge cycle. In contrast, the bare LiCoO$_2$ had retained only 45% of its original capacity. The LiCoO$_2$ with 10 cycles of Al$_2$O$_3$ ALD showed excellent stability with charge-discharge cycling. However, since the material had lost most of it capacity due to the thicker ALD film the overall performance is not a practical improvement.

The voltage profiles for bare LiCoO$_2$ and LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD at the 3rd, 10th and 50th charge-discharge cycle are shown in Figure 5.9. For the bare LiCoO$_2$, as the number of charge-discharge cycles increased, the potential at which current began to flow during charging also increased. Similarly, during discharge, the more the cell had been charge-discharge cycled the greater the potential drop. These overpotentials may be attributed to the decomposition of the electrolyte on the LiCoO$_2$ or an electrochemical reaction between the LiCoO$_2$ and the electrolyte. From the voltage profile it is also evident that the capacity of the bare LiCoO$_2$ fades with the increasing number of charge-discharge cycles. In contrast to this behavior, the LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD appears relatively stable with respect both the development of an overpotential and capacity retention.

Figure 5.10 show the Nyquist plots, obtained from electrochemical impedance spectroscopy (EIS), of bare LiCoO$_2$ and LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD. A spectrum is shown for the bare and coated material at the 1st, 10th, 30th and 50 charge-discharge cycle. $Z'$ (Ω g) is the is the magnitude of the real component of the impedance and $Z''$ (Ω g) is the magnitude of the imaginary component of the impedance.

The Nyquist plots for the bare LiCoO$_2$ show the typical behavior for bare LiCoO$_2$ and consist of two semicircles in the high frequency regime followed by a 45° line in the low frequency regime [127, 102, 166]. The higher frequency semicircle was attributed to the formation of a solid electrolyte interphase due to the decomposition of the electrolyte on the LiCoO$_2$ surface [127, 102, 166]. The lower frequency semicircle was attributed to the reactions at the LiCoO$_2$/electrolyte interface [127, 102, 166]. The 45° line in the low frequency region is related to the diffusion of Li ion through
Figure 5.9: Voltage profiles for bare LiCoO$_2$ and LiCoO$_2$ coated with 2 cycles of Al$_2$O$_3$ ALD at the 3rd, 10th and 50th charge-discharge cycle.
the LiCoO$_2$ [102, 166]. Though the various features of the EIS spectra have been identified in the literature by modeling EIS data with equivalent circuits, it is important to note that equivalent circuits are a simple model for a far more complex structure. The key feature of Figure 5.10 is the evolution on the impedance as the LIB cell is cycled. For the bare LiCoO$_2$ the impedance increases with the number of charge-discharge cycles. The increase occurs for both for the real and imaginary components indicating increases in capacitance and resistance.

The Nyquist plots for the LiCoO$_2$ coated with 2 cycle of Al$_2$O$_3$ ALD are also shown in Figure 5.10. There are not two distinct semicircles in the high frequency region as was the case for the bare LiCoO$_2$. Instead there was one asymmetric semicircle. The 45° line in the low frequency region is initially similar to the bare LiCoO$_2$. The EIS spectra from the LiCoO$_2$ coated with 2 cycles of Al$_2$O$_3$ ALD do not evolve much with charge-discharge cycles. There is little indication of increases in either the real or imaginary component of the impedance. This electrode is exceptionally stable.

Nyquist plots can be modeled by determining an equivalent electrical circuit to account for all the elements in the LIB [136, 15, 126, 219]. For example, the circuit can contain capacitors to account for double layer capacitance at the active material surface or capacitance from films formed on the surface during charge-discharge cycling. Resistors in the equivalent circuit may account for the resistance of the electrolyte, interparticle or particle-current-collector resistances, or resistance from films formed on the active material surface during charge-discharge cycling. Wardberg impedance elements in the circuit may account for Li$^+$ diffusion. A LIB half cell is a complex structure with many evolving interfaces, accordingly it is conceivable to make ever increasingly complex equivalent circuits in order to achieve an accurate model of the LIB system. In this work a relatively simple circuit was used to model the Nyquist plots shown in Figure 5.10.

The Nyquist plots shown in figure 5.10 were modeled using the equivalent circuit shown in Figure 5.11 [145, 135, 14] with the ZView software package. $R_{el}$ is the resistance of the electrolyte, $R_f$ and $C_f$ are the proposed resistance and capacitance of the film formed on the LiCoO$_2$ from the decomposition of the electrolyte during charge-discharge cycling, $R_{ct}$ is the charge transfer resistance, $C_{dl}$ is the double layer capacitance and constant phase element combined into a singe
element for ease of use in the ZView software, W is the Wardburg term for the diffusion of Li$^+$ in the bulk LiCoO$_2$. The impedance of C$_{dl}$ and W take the forms shown in Equations 5.6 and 5.7 respectively [14].

\[
Z_{C_{dl}} = \frac{1}{T(i\omega)^P} \tag{5.6}
\]

\[
Z_{W} = R\frac{\tanh (it\omega)^p}{(it\omega)^p} \tag{5.7}
\]

C$_{dl}$ has two fitting parameters, $T$ and $P$. If $P$ is 1 then C$_{dl}$ is a capacitor with a capacitance of $T$. An inhomogeneous sample surface can cause $P$ to deviate from 1 [135, 14], hence the need for constant phase element to model the rough surface of a LIB electrode. The Wardberg element also has to fitting parameters, $t$ and $p$. The parameter $t$ is proportional to the $L^2/D$ where $L$ is the depth into the LiCoO$_2$ particle and $D$ is the effective diffusion coefficient of the Li$^+$ in the bulk LiCoO$_2$ particle [14]. Since the ALD coating should not effect the bulk properties of the LiCoO$_2$ the parameters W-$t$ and W-$p$ were fixed at 1 and 0.5 respectively as suggested by the Zview software.

The modeled values of $R_{el}$, $R_f$, $C_f$, $R_{ct}$, C$_{dl}$-$T$ and C$_{dl}$-$P$ for bare and ALD coated LiCoO$_2$ are shown in Tables 5.1 and 5.2 respectively. The most apparent change with charge-discharge cycling is the increase in the $R_{ct}$ from 81.4 $\Omega$ at the 1$^{st}$ charge-discharge cycle to 1511 $\Omega$ at the 50$^{th}$ charge-discharge cycle. For comparison, at the 1$^{st}$ charge-discharge the ALD coated LiCoO$_2$ had a $R_{ct}$ of 71.92 $\Omega$ and a $R_{ct}$ of 138.6 $\Omega$ at the 50$^{th}$ charge-discharge cycle. According to the model equivalent circuit shown in Figure 5.11 large increase in the $R_{ct}$ is the cause of the overall increase in the impedance for the bare LiCoO$_2$.

Figures 5.8, 5.9 and 5.10 clearly illustrate that Al$_2$O$_3$ films on LiCoO$_2$ enhance the charge-discharge stability of the LiCoO$_2$. This phenomenon is not surprising as it has been documented in the literature that Al$_2$O$_3$ films can enhance LiCoO$_2$. Al$_2$O$_3$ may act as scavenger for HF. HF can be produced by reactions between trace amounts of contaminant H$_2$O and LiPF$_6$. The resultant HF can then act to dissolve Co from LiCoO$_2$ [88, 186, 229]. The dissolution of Co results in structural changes in the LiCoO$_2$ and degradation the LIBs capacity [146]. It has been reported that Al$_2$O$_3$ particles can be employed to sacrificially react with the HF to form stable insoluble
Figure 5.10: Impedance spectra for bare LiCoO$_2$ and LiCoO$_2$ coated with 2 cycle of Al$_2$O$_3$ ALD. The spectra were collected at the 1st, 10th, 30th and 50th charge-discharge cycle.

Figure 5.11: Equivalent circuit used to model EIS measurements.
Table 5.1: Modeled values of the parameter in the equivalent circuit shown in Figure 5.11 for the bare LiCoO$_2$ data shown in Figure 5.10.

<table>
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<th>Charge-discharge cycle number</th>
<th>$R_{el}$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$C_f$ (F)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{dl-T}$ (F)</th>
<th>$C_{dl-P}$</th>
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</tr>
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<td>60.02</td>
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<td>1.70 $\times 10^{-3}$</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 5.2: Modeled values of the parameters in the equivalent circuit shown in Figure 5.11 for the ALD coated LiCoO$_2$ data shown in Figure 5.10.

<table>
<thead>
<tr>
<th>Charge-discharge cycle number</th>
<th>$R_{el}$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$C_f$ (F)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{dl-T}$ (F)</th>
<th>$C_{dl-P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.56</td>
<td>52.73</td>
<td>5.22 $\times 10^{-6}$</td>
<td>71.92</td>
<td>2.34 $\times 10^{-3}$</td>
<td>0.59</td>
</tr>
<tr>
<td>10</td>
<td>1.27</td>
<td>43.72</td>
<td>7.17 $\times 10^{-6}$</td>
<td>62.73</td>
<td>3.22 $\times 10^{-4}$</td>
<td>0.57</td>
</tr>
<tr>
<td>30</td>
<td>0.93</td>
<td>31.94</td>
<td>1.33 $\times 10^{-5}$</td>
<td>96.31</td>
<td>1.09 $\times 10^{-4}$</td>
<td>0.66</td>
</tr>
<tr>
<td>50</td>
<td>0.75</td>
<td>63.46</td>
<td>1.32 $\times 10^{-5}$</td>
<td>138.60</td>
<td>4.22 $\times 10^{-4}$</td>
<td>0.44</td>
</tr>
</tbody>
</table>
The Al$_2$O$_3$ film may suppress electrochemical reactions between the LiCoO$_2$ and the electrolyte by acting as a physical protection barrier [129, 76]. This protection barrier may prevent the dissolution of Co by the electrolyte [148]. It may also be possible that the Al$_2$O$_3$ is less reactive with the electrolyte than the LiCoO$_2$ surface. Al$_2$O$_3$ films on LiCoO$_2$ have also demonstrated enhanced electrical conductivity leading to superior battery performance [148].

Figure 5.12 shows XPS spectra of LiCoO$_2$ coated with 4 cycle of Al$_2$O$_3$ ALD, (a) before and (b) after 10 charge-discharge cycles. The region from 250-0 eV has been magnified 10×. As expected Al, C, Co, F and O are observed. P was observed in the electrode that had undergone charge-discharge cycling, Figure 5.12 (b). The presence of P is due to insufficient removal of excess LiPF$_6$, from the electrolyte, prior to XPS.

Prior to charge-discharge cycling the binding energy of the Al 2s peak was observed at 118.7 eV with a full width at half-maximum (fwhm) of 2.2 eV. After 10 charge-discharge cycles the Al 2s peak was broader, the fwhm was 2.8 eV, and shifted to a slightly higher binding energy, 119.2 eV. Literature values for the Al 2s binding energy in Al$_2$O$_3$, range from 116.25 eV [191] to 119.2 eV [27]. The Al 2s peak for AlF$_3$ has been observed at a binding energy of 121.0 eV [141]. The shift in the binding energy and the broadening of the fwhm for Al 2s peak after 10 charge-discharge cycles are indicative of the formation of AlF$_3$.

The Co 2p$_{3/2}$ peak prior to charge-discharge cycling had a binding energy of 779.8 eV and a fwhm of 2.4. Literature values for the binding energy of the Co 2p$_{3/2}$ peak in LiCoO$_2$ are similar, 780.1 eV [134]. After charge discharge cycling the Co 2p$_{3/2}$ the binding energy remained similar at 279.7 eV. The fwhm had broadened to 2.9 eV and a high binding energy shoulded had begun to develop. The broadening at higher binding energy may be indicative of the presence of cobalt oxides [183].

### 5.4.1.1 Annealing Al$_2$O$_3$ Coated LiCoO$_2$

Thicker Al$_2$O$_3$ films reduce the electronic conductivity. It should be expected that thicker Al$_2$O$_3$ films should also reduce Li ion conductivity. It has been reported in the literature that...
Figure 5.12: XPS spectra of LiCoO$_2$ coated with 4 cycle of Al$_2$O$_3$ ALD, (a) before and (b) after 10 charge-discharge cycles. The region from 250-0 eV has been magnified 10×.
Al₂O₃ films on LiCoO₂ results in an alloying of the Al₂O₃ and the LiCoO₂ to form LiCo₁₋ₓAlₓO₂ on the surface of the LiCoO₂ [107, 108]. The LiCo₁₋ₓAlₓO₂ is said to result in faster Li ion diffusion[107, 108]. It has also been demonstrated in the literature that Al₂O₃ films on LiCoO₂, followed by annealing, can lead to the migration of Al atoms into the LiCoO₂ resulting in an increased electronic conductivity of the composite material [148]. Considering that Al₂O₃ is an insulator and that any film should impede Li ion conduction it is surprising that thick (∼100-1000 Å) Al₂O₃ films result increased electron and Li ion conductivity [107, 108, 148].

For the wet chemical techniques used to produce Al₂O₃ films on LiCoO₂ annealing was part of the synthesis [107, 108, 148]. The annealing process can produce an alloy at the Al₂O₃-LiCoO₂ interface resulting in the production of LiCo₁₋ₓAlₓO₂ [45, 115]. Conversely, it has been observed that sol-gel films of Al₂O₃ and SiO₂ on LiCoO₂ do show enhanced capacity retention when compared to untreated LiCoO₂ [39]. However, in this study the same effect was achieved with only the post sol-gel heat treatment and no Al₂O₃ or SiO₂ film.

For comparison, LiCoO₂ that had been coated with 20 cycles of Al₂O₃ ALD was subjected to an anneal at 450 °C for 10 hours in air. The unannealed LiCoO₂ had a discharge capacity of 8 mA h g⁻¹ at 1 C-rate. Annealing the coated powder increased the discharge capacity to 15 mA h g⁻¹. While an improvement was observed for the annealed composite material, it was not close to the performance of bare LiCoO₂ at ∼160 mA h g⁻¹. In comparison to the much thicker Al₂O₃ films on LiCoO₂ that have already been studied [107, 108, 148], films grown with ALD are much more conformal. The inability for annealing to significantly improve the performance of the Al₂O₃ coated LiCoO₂ was attributed to the superior conformality of ALD. It is possible that for films grown with wet chemical techniques conduction pathways were maintained because the films were nonuniform and nonconformal.

5.4.2 ZnO ALD on LiCoO₂ Powders

Stoichiometric ZnO is an n-type semiconductor with carrier densities of ∼10¹⁶ cm⁻³ and resistivities of 0.1-1 Ω cm [96]. ZnO grown with ALD at elevated temperatures can have oxygen
deficiencies leading to lower resistivities[96]. The resistivity of ZnO grown with ALD has been reported as low as \(8 \times 10^{-3} \ \Omega \ cm\) [63]. Similar enhancements to those of Al\(_2\)O\(_3\) have been demonstrated for other metal oxide systems [39], including ZnO [67]. The enhancements are often independent of the metal oxide [39]. The HF scrubbing or physical protective properties of ZnO should be similar to Al\(_2\)O\(_3\) [39]. However, the decreased resistivity of ZnO, with respect to Al\(_2\)O\(_3\) (\(\sim 10^{16} \ \Omega \ cm\) [63]), makes it an interesting candidate to compare with Al\(_2\)O\(_3\).

For comparison, 4 cycles of ZnO were deposited on LiCoO\(_2\) with ALD. Figure 5.13 shows the charge-discharge voltage profiles at the 3rd, 10th and 50 charge-discharge cycle. This behavior is similar to the behavior of the bare LiCoO\(_2\) shown in Figure 5.9. By the 10th charge-discharge cycle the electrode is showing a reduced capacity, the onset of current flow during charge is at a higher potential and the voltage drop during discharge is larger in comparison to the 3rd charge-discharge cycle. These problems are worse by the 50th charge-discharge cycle.

Figure 5.14 shows the discharge capacity as a function the number of charge-discharge cycles for LiCoO\(_2\) with 4 cycles of ZnO ALD. For comparison the data shown in Figure 5.8 for bare LiCoO\(_2\) and LiCoO\(_2\) with 2 cycles of Al\(_2\)O\(_3\) ALD has been added. The LiCoO\(_2\) with 4 cycles of ZnO ALD shows similar stability to bare LiCoO\(_2\), there is a dramatic loss in the capacity as the number of charge-discharge cycles is increased.

Figure 5.15 shows XPS spectra of LiCoO\(_2\) coated with 4 cycle of ZnO ALD, (a) before and (b) after 10 charge-discharge cycles. As expected C, Co, F, O and Zn are observed. Prior to charge-discharge cycling the Zn 2p peak at a binding energy of \(\sim 1021.6\) eV is a dominant feature in Figure 5.15(a). After charge-discharge cycling the Zn 2p is practically gone. From the absence of the Zn 2p peak in Figure 5.15(b) it appears that under the conditions in the LIB during charge-discharge cycling that ZnO is not stable.

In order to quantify the relative stability of ZnO and Al\(_2\)O\(_3\) high resolutions XPS scans were performed on the Zn 2p, Al 2s and Co 2p peaks, these are shown in Figure 5.16. Black lines show the peak before the 10 charge-discharge cycles, blue lines show the peak after the 10 charge-discharge cycles. It was assumed that Co dissolution was minimal during the 10 charge-discharge
Figure 5.13: Voltage profiles for LiCoO$_2$ coated with 4 cycles of ZnO ALD at the 3rd, 10th and 50th charge-discharge cycle.
Figure 5.14: Discharge capacity as a function the number of charge-discharge cycles for bare LiCoO$_2$, LiCoO$_2$ with 2 cycles of Al$_2$O$_3$ ALD and LiCoO$_2$ with 4 cycles of ZnO ALD.
Figure 5.15: XPS spectra of bare LiCoO$_2$ and LiCoO$_2$ coated with 4 cycle of ZnO ALD, (a) before and (b) after 10 charge-discharge cycles.
cycles. For the LiCoO$_2$ coated with 4 cycle of Al$_2$O$_3$, the Co 2p peak intensities were normalized (Figure 5.16(a)) and the Al 2s peaks were scaled accordingly (Figure 5.16(b)). Similarly, for the LiCoO$_2$ coated with 4 cycle of ZnO, the Co 2p peak intensities were normalized (Figure 5.16(c)) and the Zn 2p peaks were scaled accordingly (Figure 5.16(d)).

From Figure 5.16(b) it appears that the intensities of the Al 2s peak are independent of whether the electrode was cycled. In contrast, Figure 5.16(d) illustrates that the amount of ZnO on the electrode is dramatically reduced with just 10 charge-discharge cycles. To examine this further the atomic fractions of the metal with respect to Co (M/(M + Co), where M = Al or Zn), were calculated from the XPS peak areas. The results are summarized in Table 5.3. Before charge-discharge cycling the atomic fraction of Al with respect to Co is 0.55, after cycling it is 0.53. While some Al$_2$O$_3$ may be converted to AlF$_3$ or a solid solution of LiAl$_x$Co$_{1-x}$O$_2$, overall Al is stable in the electrochemical cell. In contrast, prior to charge-discharge cycling, the atomic fraction of Zn with respect to Co was 0.49. After just 10 charge-discharge cycles the atomic fraction was 0.01. The ZnO and any Zn containing products from electrochemical reactions in the LIB are not stable and do not remain on the LiCoO$_2$ surface. It is possible that the Zn diffuses far enough into the LiCoO$_2$ to produce a diminished XPS signal or that the Zn is dissolved away in the electrolyte.

Table 5.3: The atomic fraction of Al and Zn, calculated from XPS, with respect to Co before and after 10 charge-discharge cycles.

<table>
<thead>
<tr>
<th>Atomic Fraction</th>
<th>Before Cycling</th>
<th>After Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.55</td>
<td>0.53</td>
</tr>
<tr>
<td>Zn</td>
<td>0.49</td>
<td>0.01</td>
</tr>
</tbody>
</table>

5.4.3 ALD Films on Composite Electrodes

ALD has been grown on a variety of porous substrates including aerogels [26], photonic crystals [109] and high aspect ratio trench structures [64]. A composite LIB electrode consisting of an assembly of particles held together with a polymer binder can be consider a porous substrate.
Figure 5.16: High resolution XPS spectra of LiCoO\textsubscript{2} coated with 4 cycle of Al\textsubscript{2}O\textsubscript{3} ALD (a) the Co 2p peak before (black line) and after (blue line) 10 charge-discharge cycles and (b) the Al 2s peak before (black line) and after (blue line) 10 charge-discharge cycles. High resolution XPS spectra of LiCoO\textsubscript{2} coated with 4 cycle of ZnO ALD (c) the Co 2p peak before (black line) and after (blue line) 10 charge-discharge cycles and (d) the Zn 2p peak before (black line) and after (blue line) 10 charge-discharge cycles.
Given sufficient time the ALD precursors will be able to diffuse through the tortuous paths in between the particles and uniformly coat the LiCoO$_2$. Furthermore, where the LiCoO$_2$ surface is inaccessible due to PVDF coating, it may be possible for the ALD precursors to diffuse through the PVDF film and reach the LiCoO$_2$ surface [207]. The key differences between coating the particles prior to electrode assembly and coating the assembled electrode are: 1) coating not only the LiCoO$_2$ but also possibly coating the AB and the PVDF that are present in the assembled electrode; 2) the contact points at particle-particle, particle-current collector and particle-AB contacts will not be coated. Issue 2 may offer to improve the electrode electrical conductivity.

Figure 5.17 shows the discharge capacity as a function of the number of charge-discharge cycles for electrodes fabricated from bare LiCoO$_2$. One electrode was subsequently coated with 2 cycles of Al$_2$O$_3$ ALD prior to cycling. Coating the composite electrode, as compared with leaving it bare, showed a dramatic improvement in the discharge capacity retention. For the coated electrode the capacity retention after 120 charge-discharge cycles was 78%, with respect to the third charge discharge cycle. This is not as good of an improvement when compared with the LiCoO$_2$ that was coated with 2 cycles of Al$_2$O$_3$ ALD prior electrode assembly, Figure 5.8. The positive result as compared with the bare electrode is a strong indicator that the Al$_2$O$_3$ ALD was able to grow on the LiCoO$_2$ in the fabricated electrode.

Figure 5.18 shows the charge-discharge voltage profile for bare LiCoO$_2$, LiCoO$_2$ that was coated with 20 cycles of Al$_2$O$_3$ ALD prior to electrode fabrication (powder coated), and a LiCoO$_2$ electrode that was coated with 20 cycles of Al$_2$O$_3$ ALD (electrode coated). Figure 5.8 show that 10 cycles of Al$_2$O$_3$ ALD on LiCoO$_2$ powder is too thick and has a detrimental effect on the electrode performance. In this experiment 20 cycles of Al$_2$O$_3$ ALD was used to amplify the effect of coating the powder versus the electrode. For the Al$_2$O$_3$ ALD coated LiCoO$_2$ the potentials at which the current started to flow was greater than for the bare LiCoO$_2$. The powder coated LiCoO$_2$ had a larger overpotential (a) than electrode coated LiCoO$_2$ (b). The difference in the overpotentials between the powder coated LiCoO$_2$ and the electrode coated LiCoO$_2$ may be from the lack of an interparticle and particle-current-collector conduction pathway due to the conformality of the
Figure 5.17: Discharge capacity as a function of the number of charge-discharge cycles for electrodes fabricated from bare LiCoO$_2$. One electrode was left bare the second electrode was coated with 2 cycles of Al$_2$O$_3$ ALD prior to cell cycling.
Al₂O₃ ALD film on the LiCoO₂. The Al₂O₃ ALD film on the LiCoO₂ electrode may preserve electron conduction pathways. A schematic of the possible conduction pathways is shown in Table 5.4.

5.4.4 Discussion

Both Al₂O₃ [44, 39] and ZnO [67], grown with wet chemical techniques, have been demonstrated to enhance the capacity retention of LiCoO₂. It is surprising that thick Al₂O₃ films grown with wet chemical techniques [44, 39] could be successfully scaled down with ALD, and ZnO films [67] could not. It is possible the mechanisms by which the films enhance LiCoO₂ may be different. ZnO may be consumed as an HF scavenger during charge-discharge cycling and as such more ZnO may be required to enhance the LIB performance, while Al₂O₃ may serve as a protective barrier blocking interactions between the LiCoO₂ and the electrolyte.

5.4.4.1 The Importance of Thin Films

Currently the majority of the mass in LIBs designed for automobiles is in the packaging [195]. This is an important consideration when adding a new component, a protective coating, to LIBs. Protective coatings add mass at the cost of the specific energy density. Thin films of Al₂O₃ clearly enhance the capacity retention of LiCoO₂. To achieve similar results as those presented here, films deposited with wet chemical techniques are much thicker and less conformal [44]. Thick protective films will become a large component of the mass as LIB active materials are scaled from micron size particles to nanoparticles [167].

The mass fraction (MF) of a protective Al₂O₃ film is given by Equation 5.8, where \( t \) is the Al₂O₃ thickness, \( \rho_f \) is the Al₂O₃ ALD density, \( r \) is the LiCoO₂ particle radius, and \( \rho_p \) is the LiCoO₂ density. The density of Al₂O₃ ALD is \( \sim 79\% \) of bulk Al₂O₃ [18]. The density of bulk Al₂O₃ is 3.98 g cm\(^{-3} \) [202]. The density of LiCoO₂ is \( \sim 4.9 \) g cm\(^{-3} \) [192].

\[
MF = \frac{t (3r^2 + 3rt + t^2) \rho_f}{t (3r^2 + 3rt + t^2) \rho_f + r^3 \rho_p}
\] (5.8)
Figure 5.18: Charge-discharge voltage profile for bare LiCoO$_2$, LiCoO$_2$ that was coated with 20 cycles of Al$_2$O$_3$ ALD prior to electrode fabrication (powder coated), and a LiCoO$_2$ electrode that was coated with 20 cycles of Al$_2$O$_3$ ALD (electrode coated).
Table 5.5 shows the mass fraction for various sizes of LiCoO$_2$ particles with varying thickness of Al$_2$O$_3$ films. For a large particle (10 µm) a "thick" (100 nm) Al$_2$O$_3$ film contributes 1.9% of the composite mass. This is a significant contribution considering that the active materials are the only portion of the LIB that stores energy and they are already only a fraction of the total mass of the LIB. More importantly, on a 100 nm LiCoO$_2$ particle a "thick" (100 nm) Al$_2$O$_3$ film contributes 81.8% of the composite mass. It is impractical to have the majority of the mass of the active material be a protective coating as this dramatically reduces the specific energy density of the active material. In contrast a 0.2 nm Al$_2$O$_3$ ALD film on a 100 nm LiCoO$_2$ particle contributes only 0.4% of the composite mass. By keeping the mass fraction of the protective Al$_2$O$_3$ lower it will be possible to make lighter, higher energy density LIBs.

5.4.4.2 Advantages of ALD

ALD provides a solvent free method to coat LIB active materials. The efficiency of an ALD process can be tuned to ensure that very little precursor is wasted. The lack of a solvent and the efficiency of ALD processes may make them more environmentally benign than wet chemical techniques.

ALD offers a wealth of chemistries. Many of the chemistries demonstrated by wet chemical techniques to enhance LIB such as ZrO$_2$ [131], SiO$_2$ [13] and TiO$_2$ [132] can also be grown by ALD: ZrO$_2$ [118], SiO$_2$ [31] and TiO$_2$ [71]. It should be possible to follow the wet chemistry LIB literature employing and developing ALD processes to further enhance LIBs.

By employing multiple ALD chemistries it is possible to grow composites or nanolaminates (superlattices) these materials may have applications as protective films for LIBs. ALD chemistries can be combined to tune specific properties. For example the conductivity of ZnO can be tuned by alternating ALD cycles of Al$_2$O$_3$ [63]. It may be similarly possible to tune the stability a ZnO film in an electrochemical cell by the introduction of Al$_2$O$_3$.

Molecular layer deposition (MLD) is analogous to ALD in that it is a self-limiting, gas phase thin film growth technique that relies on sequential gas-surface reactions [80]. However, instead
of depositing a monolayer of atoms, a bifunctional monolayer of molecules is deposited. MLD can be employed to grow organic and hybrid organic-inorganic thin films [80]. MLD films may be grown to form solid state electrolytes with structures similar to polyethylene oxide [52] using TMA and ethylene glycol [55]. MLD films allow for the tuning of the mechanical properties of a hybrid organic-inorganic [143]. Compliant, i.e. low Young’s modulus, films may aid in protecting high volume expansion active materials [160].

It is not possible to coat assembled electrodes with wet chemical techniques. ALD has the advantage of being able to conformally coat tortuous high aspect ratio structures of almost any shape [64, 26, 109]. This attribute makes it well suited for coating composite electrodes. It has be demonstrated that Al₂O₃ ALD on MoO₃ electrodes can assist in maintaining electrical contact between the MoO₃ particles and the conductive additive [160]. This effect was not observed when the MoO₃ particles were coated prior to electrode fabrication [160].

5.5 Conclusions

Al₂O₃ ALD films were grown on LiCoO₂ powders and on fabricated electrodes comprised of LiCoO₂. In both cases the Al₂O₃ ALD films enhanced the capacity retention of the LiCoO₂. With respect to the third charge-discharge cycle, LiCoO₂ coated with 2 cycles of Al₂O₃ ALD had a capacity retention of 89% after the 120 charge-discharge cycles, while the coated electrode had a capacity retention of 78% after the 120 charge-discharge cycles. The stability of the coated LiCoO₂ is remarkable because the cells were cycled beyond 4.2 V, the upper limit for suppressing Co dissolution. Bare LiCoO₂ powders only maintained 45% of the initial capacity after the 120 charge-discharge cycles. Thin films of ZnO ALD did not exhibit any improvements. Though XPS confirmed the presence of ZnO prior to charge-discharge cycling, the ZnO was present only in trace amounts after 10 charge-discharge cycles. The fact that thick films of ZnO deposited with wet chemical techniques improve the performance of LiCoO₂, while thin films do not improve the performance, is crucial to elucidating the mechanisms for the enhancement. The mechanisms for the enhancements observed from Al₂O₃ ALD films on LiCoO₂ may include acting as a physical
barrier to block interactions between the LiCoO$_2$ and the electrolyte, altering the LiCoO$_2$ surface chemistry to change the interactions between the LiCoO$_2$ and the electrolyte, acting as an HF scrubber, and preventing Co dissolution.

5.5.1 A Note on Significance

The material used in this study was commercial grade LiCoO$_2$. It must be emphasized that the cycling the cells beyond 4.2 V dramatically reduces the cell lifetime. In order to realize the performance enhancement offered by the ALD films it was necessary to employ these harsh condition to accelerate cell testing. It is believed that the enhancements in LIB performance from the ALD films will translate to LIB cells that are cycled under normal conditions.

5.6 Acknowledgements

This work was funded by a DOE SBIR subcontract from a grant to ALD NanoSolutions, Inc. (Broomfield, CO). Mr. Andrew S. Cavanagh received additional support from the DARPA Center on Nanoscale Science and Technology for Integrated Micro/Nano-Electromechanical Transducers (iMINT). Dr. Yoon Seok Jung also acknowledges a Korea Research Foundation Grant.
Table 5.4: Electron conduction pathways for bare LiCoO$_2$, ALD on LiCoO$_2$ powder and ALD on assembled LiCoO$_2$ electrode.

<table>
<thead>
<tr>
<th></th>
<th>Surface Protection</th>
<th>Conduction Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>ALD on powder</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>ALD on electrode</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

Table 5.5: Mass fraction of a protective Al$_2$O$_3$ film on LiCoO$_2$. The LiCoO$_2$ particle sizes are 10 $\mu$m, 1 $\mu$m and 100 nm. The Al$_2$O$_3$ film thicknesses are 0.2, 1, 10 and 100 nm.

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Al$_2$O$_3$ Thickness (nm)</th>
<th>Mass fraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 $\mu$m</td>
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<td>trace</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.9</td>
</tr>
<tr>
<td>1 $\mu$m</td>
<td>0.2</td>
<td>.06</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>17.5</td>
</tr>
<tr>
<td>100 nm</td>
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<td>0.4</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>81.8</td>
</tr>
</tbody>
</table>
Chapter 6

Enhanced Performance and Stability of Natural Graphite Anodes with thin films of Al₂O₃ Grown with Atomic Layer Deposition

6.1 Abstract

It has been demonstrated in the literature that metal oxide films grown with wet chemical techniques enhance the performance of LIBs. Films grown with wet chemical techniques typically have thicknesses with the range 50-1000 Å. Here we demonstrate that ultrathin films grown with atomic layer deposition (ALD) enhanced the capacity retention of natural graphite (NG) in lithium-ion battery (LIB) half cells and full cells. With respect to the third charge-discharge cycle, NG electrodes coated with 5 cycles of Al₂O₃ ALD had a capacity retention of 102% (no NO₂/TMA pretreatment) and 103% (with NO₂/TMA pretreatment) after 200 charge-discharge cycles at room temperature. At 50 °C the NG electrodes coated with 5 cycles of Al₂O₃ ALD had a capacity retention of 93% (no NO₂/TMA pretreatment) and 96% (with NO₂/TMA pretreatment) after 200 charge-discharge cycles. Bare NG electrodes had a capacity retention of 80% at room temperature and 26% at 50 °C after 200 charge-discharge cycles.

6.2 Introduction

Lithium ion batteries (LIBs) are in demand for portable electronics [11]. In order to realize LIB in high-power and high-energy density systems such as hybrid electric vehicles (HEVs), new materials must be developed that can accommodate the extreme conditions that come with high-power and high-energy density systems [2]. With its high reversible capacity (372 mA h g⁻¹,
assuming a stoichiometry of LiC$_2$), low cost, moderate volume change, and low and flat voltage range, natural graphite (NG) is a promising anode material [217, 77, 165]. NG suffers from its incompatibility with propylene carbonate (PC) electrolyte and the instability of the solid electrolyte interphase (SEI).

Due to its low melting point (-49 °C) PC based electrolytes are essential to operating LIBs in low temperature conditions [217]. Meeting low temperature requirement is essential to using LIBs in HEVs in cold weather environments. For comparison the melting points of EC and DMC are 35-38 °C and 2-4 °C respectively [169]. Graphite electrodes are exfoliated by PC electrolytes [217, 16]. The exfoliation exposes fresh graphite surfaces which require further electrolyte decomposition to form SEI on the freshly exposed surfaces [217, 16]. The exfoliation process also fractures the graphite particle which reduces the conductivity of the electrode due to the disconnects at the fracture sites [16]. This results in irreversible loss of capacity and a low coulombic efficiency [217]. Furthermore, a reaction byproduct of the decomposition of PC is propylene gas [57, 217]. Propylene gas can be explosive [169].

Thermal vapor deposition has been employed to coat protective carbon films onto NG to prevent interactions between the NG on the PC electrolyte [218, 217, 198]. Increasing the thickness of the protective carbon film increased the battery performance. For example, Yoshio et al. observed that a NG coated with an 8.6 weight % protective carbon coating had a coulombic efficiency on the first charge-discharge of 75.8% [218]. The coulombic efficiency was increased to 92.5% by essentially doubling the weight % of the protective carbon coating to 17.6% [218]. These two experiments used an electrolyte that was only 20% PC (PC:DMC, 1:4 by volume) [218]. If the concentration of the PC in the electrolyte was increased the battery performance suffered. The first cycle coulombic efficiency for a 17.6 weight % protective carbon film in an electrolyte that was 33% PC (PC:DMC, 1:2 by volume) was only 71.0% [218]. This is a dramatic reduction in the first cycle coulombic efficiency, 92.5% → 71.0%, with only a 13% increase in the concentration of the PC in the electrolyte, 20% → 33% [218]. Furthermore, the weight % of protective carbon film used in this study, and others, are a significant portion of the mass of the active material.
Efforts have been made to modify the surface of NG with metal oxides to control the behavior of the SEI. Irreversible capacity loss occurs mainly due to the reductive decomposition of the organic electrolytes to form a SEI on the graphite surface [150, 151, 123, 220]. Al$_2$O$_3$ [104], ZrO$_2$ [117, 116] and AlPO$_4$ [123] films deposited with sol gel methods have displayed good capacity retention and high coulombic efficiency at the first cycle. Decomposition of the SEI at elevated temperatures is exothermic and can lead to catastrophic battery failure [21, 212, 59].

Sol-gel methods require large amounts of solvents and post coating heat treatments. Also, sol-gel methods can only apply films to powders as opposed to depositing a film on an assembled electrode. In this study atomic layer deposition (ALD) was used to deposit thin conformal films of Al$_2$O$_3$ on NG powders and electrodes assembled from NG. The electrodes were electrochemically characterized by charge-discharge cycling against Li metal and LiCoO$_2$. ALD does not use the large amount of solvents required for wet-chemical techniques and with ALD the amount of precursor used can be precisely controlled. In these two regards ALD can be seen as more environmentally benign than wet chemical techniques. ALD coated electrodes

6.3 Experimental

6.3.1 Al$_2$O$_3$ ALD on Powders

The natural graphite (NG) used in these experiments was obtained from Asbury Graphite Mills Inc. (Asbury, NJ), manufacture’s product number HPM850. The NG particle size was ~4 $\mu$m. The NG density was 2.6 g cm$^{-3}$. The NG conductivity was 11.4 S cm$^{-1}$. All specifications for the NG were as reported by the manufacturer. For the Al$_2$O$_3$ ALD trimethylaluminum (TMA, Al(CH$_3$)$_3$) (97%) was obtained from Sigma-Aldrich (St. Louis, MO). HPLC (high pressure liquid chromatography) grade H$_2$O was also from obtained from Sigma-Aldrich and was further purified by 5 cycles of freeze-pump-thaw. For the NO$_2$/TMA nucleation pretreatment, commercial purity grade NO$_2$ (99.5%) was acquired from Airgas.
ALD on particles is possible using either fluid bed reactors [201, 200] or rotary reactors [139, 140]. A schematic of the rotary reactor used in this work is shown in Figure 6.1. In order to perform ALD on powders, the powders were placed in a porous stainless steel cylinder (A). The porous stainless steel cylinder was placed in the chamber onto a magnetically coupled axel via an O-ring sealed door (B). A motor rotated the axel and porous stainless steel via a magnetically coupled rotary feed through (Transfer Engineering and Manufacturing, Inc., Fremont, CA)(C). This served to agitate the LiCoO$_2$ during the ALD process. A dual range, 0-10 and 0-100 Torr, Baratron capacitance manometer (MKS Instrument, Andover, MA)(D) was used to measure the pressure in the reaction chamber. Each reactant entered the reaction chamber through a series of pneumatic (E) and needle (F) valves that were attached to 0.25” welded ports on a custom 6.0” to 2.75” Conflat zero length reducer. In order to evacuate the chamber a gate (G) was opened to connect the reactor to an corrosion resistant dual-stage rotary vane pump (Alcatel Vacuum Technology, Annecy, France) (H). A ceramic heater (Watlow Electric Manufacturing Co., St. Louis, MO) (J) on the rotary reactor was employed to heat the reactor. The temperature was monitored with a thermocouple and was controlled via PID loop with a temperature controller (Eurotherm U.S.A., Ashburn, VA).

During the ALD process on particles the porous metal cylinder was rotated in the rotary reactor at $\sim$150 rpm. Given the diameter of the rotating porous cylinder, this rotational frequency is consistent with a centripetal force of $\sim$0.5 g. Reasonable results were obtained using rotational frequencies from 140-180 rpm. Rotational frequencies $<$140 rpm led to less agitation and agglomeration during ALD.

Al$_2$O$_3$ ALD was performed on gram quantities of NG in the rotary reactor. The Al$_2$O$_3$ ALD surface chemistry employs TMA and H$_2$O as the reactants. The sequential, self-limiting reaction sequence during Al$_2$O$_3$ ALD is [58, 84, 149]:

\begin{align*}
\text{A} & \quad \text{AlOH}^* + \text{Al(CH$_3$)$_3$} \rightarrow \text{AlO} - \text{Al(CH$_3$)$_2^*$} + \text{CH}_4 \\
\text{B} & \quad \text{AlCH$_3^*$} + \text{H$_2$O} \rightarrow \text{Al} - \text{OH}^* + \text{CH}_4
\end{align*}
Figure 6.1: Schematic of rotary reactor used to coat gram quantities of LiCoO$_2$ powders.
where the asterisks denote surface species. The Al$_2$O$_3$ ALD reaction sequence was: (1) TMA dose to set pressure; (2) TMA reaction time; (3) evacuation of reaction products and excess TMA; (4) N$_2$ dose; (5) N$_2$ static time; (6) evacuation of N$_2$ and any entrained gases; (7) H$_2$O dose to pressure; (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 any entrained gases. This sequence constituted one AB cycle of Al$_2$O$_3$ ALD. This reaction was carried out at 180 °C.

The typical growth rate for Al$_2$O$_3$ ALD is 1.1-1.2 Å per ALD cycle [84, 149]. During the water dose a hydroxyl terminated surface is generated. The hydroxyl terminated surface will interact with excess H$_2$O in the reactor via hydrogen bonding. Due to the large surface area of the NG powders and the large surface area of the porous stainless steel cylinder, H$_2$O may not be completely purged from the reactor during the evacuation step of the H$_2$O dose. The presence of H$_2$O in the reactor during the TMA half reaction may lead to increased growth per cycle. This behavior is similar to chemical vapor deposition [83, 139].

Al$_2$O$_3$ ALD relies on an initially hydroxyl terminated surface to begin nucleation. The basal planes of graphite are inert and therefore not well suited to nucleating thin film growth. It has been demonstrated that an adsorbed monolayer of NO$_2$/TMA can act to functionalize the surface of carbon nanotubes [69, 35]. With the functionalizaion layer in place, conformal Al$_2$O$_3$ growth can start by reacting the TMA molecules on the surface with H$_2$O. During the NO$_2$ nucleation treatment, an adsorbed functionalization layer was initially formed on the NG surface by alternating exposures of NO$_2$ and TMA [69]:

\[
A \quad \text{NG}^* + \text{NO}_2 \leftrightarrow \text{NG} - \text{NO}_2^* (6.3)
\]

\[
B \quad \text{NG} - \text{NO}_2^* + \text{TMA} \leftrightarrow \text{NG} - \text{NO}_2^* - \text{TMA}^* (6.4)
\]

where the asterisks indicate surface species. In this functionalization process, the nitrogen of the NO$_2$ is attracted to the NG surface and leaves the oxygen atoms accessible. Upon TMA exposure, the oxygen atoms coordinate to the aluminum of the TMA molecule leaving a methyl-terminated surface [69]. The methyl-terminated surface does not interact with subsequent NO$_2$ exposures.
In order to grow conformal films on the basal plane of the NG a NO\textsubscript{2}/TMA pretreatment was employed prior to Al\textsubscript{2}O\textsubscript{3} ALD. The NO\textsubscript{2}/TMA pretreatment reaction sequence was (1) NO\textsubscript{2} dose to a set pressure; (2) NO\textsubscript{2} absorption time; (3) evacuation of excess NO\textsubscript{2}; (1) TMA dose to a set pressure; (2) TMA absorption time; (3) evacuation of excess TMA. This sequence defines one AB cycle of the NO\textsubscript{2}/TMA pretreatment to functionalize the NG surface.

6.3.2 Al\textsubscript{2}O\textsubscript{3} ALD on Electrodes

Al\textsubscript{2}O\textsubscript{3} ALD was also grown on assembled electrodes. The reaction conditions were similar to those described in Section 6.3.1. ALD has been grown on a variety of porous substrates including aerogels [26], photonic crystals [109] and high aspect ratio trench structures [64]. A composite LIB electrode consists of an assembly of particles held together with a polymer binder on metal foil. The space in between the NG particle provides a path for the ALD precursors and reaction byproducts to diffuse in and out of the electrode. Given sufficient time the ALD precursors will be able to diffuse through the tortuous paths in between the particles and uniformly coat the NG particles. NG electrodes were secured to an Al sample holder prior to being placed in the ALD reactor.

6.3.3 Electrical Conductivity

The electrical conductivity was measured by pressing a cylindrical pellet of NG into a custom plastic mold equipped with four electrical contacts arranged in a cross around the cap of the cylinder. The measurement was carried out while the pellet inside the plastic mold was pressed to a pressure of 120 MPa. A current in the range of 0.5-5 \(\mu\)A was sourced between two adjacent electrical contacts and the potential was measured across the two remaining electrical contacts. The resistance was obtained from the slope of a five point voltage vs. current curve. The geometric factor was extracted by measuring the samples with different configuration. This technique for determining resistivity was pioneered by van der Pauw [193].
6.3.4 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

$\text{Al}_2\text{O}_3$ ALD coated NG electrodes were prepared for scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) in two ways. Cross sections of $\text{Al}_2\text{O}_3$ ALD coated NG electrodes were cut for SEM imaging and EDS mapping. Because it is possible to back scatter the material being milled, a hole was drilled through the Cu foil on the electrode to reveal an unperturbed NG/Cu interface. The cross section and the hole were fabricated using focused ion beam (FIB) gallium milling with a NOVA 600i dual beam FIB instrument (FEI, Hillsboro, OR).

A JEOL JSM-6480LV SEM (Peabody, MA) equipped with a Thermo Scientific (West Palm Beach, FL) Noran System Six Microanalysis System X-ray detector was used to image the cross section of the $\text{Al}_2\text{O}_3$ ALD coated NG electrode and map the Al concentration throughout the cross section. EDS was also used to observe the Al concentration at the NG/Cu interface though the hole that had been milled through the Cu. The SEM was run at a pressure of $\sim 10^{-6}$ Torr. Images were collected at an acceleration voltage of 15 kV. EDS spectra and mapping were analyzed using Thermo Scientific’s NSS 2.2 X-ray micro analysis software.

6.3.5 Electrochemical Characterization

N-methyl pyrrolidinone from Sigma-Aldrich (St. Louis, MO) was used as the solvent to prepare the electrode material. Poly(vinylidene fluoride)(PVDF) from Alfa Aesar (Ward Hill, MA) was used as a polymer binder. A slurry of NG and PVDF in N-methyl pyrrolidinone was spread on Cu foil to fabricate the NG electrodes. The NG to PVDF weight ratio was 90:10. The electrolyte, 1.0 M LiPF$_6$ dissolved in a solution ethylene carbonate (EC):dimethylcarbonate (DMC) (1:1 by volume), was obtained from Novolyte (Cleveland, OH). In order to test the stability of propylene carbonate (EC) with ALD coated NG electrodes, some experiments used 1 M LiPF$_6$ in PC.

Lithium metal from Alfa Aesar (Ward Hill, MA) was employed as the counter electrode. The electrode diameters were 0.5". A glass fiber sheet was used as a separator between the Li metal and the NG electrode. Cells were fabricated using 2032-type coin cell (diameter 20 mm, thickness 3.2
mm) in a glove box under an Ar environment (Vacuum Atmosphere’s Inc., Amesbury, MA). The H₂O and O₂ concentrations in the glove box were typically under 0.1 and 0.5 ppm respectively.

Galvanostatic charge-discharge cycling was performed in the range of 0.005-1.5 V versus Li/Li⁺ using a galvanostat (Arbin Instrument, College Station, TX). The current density during the first to charge-discharge cycles was 0.1 C-rate (37 mA g⁻¹). For subsequent cycles the current density was 0.5 C-rate (185 mA g⁻¹). Charge-discharge cycling was carried out at room temperature and at 50 °C.

Full cells were assembled from NG anodes and LiCoO₂ cathodes. The preparation of the LiCoO₂ cathodes is described in Section 5.3.3. The full cells had a porous 20 µm thick polypropylene/polyethylene/polypropylene trilayer separator between the two electrodes. The weight ratio of LiCoO₂ to NG was ~1.4. The full cells were cycled in the range of 3.30-4.45 V. The current density during the first to charge-discharge cycles was 0.1 C-rate (14 mA g⁻¹ of LiCoO₂). For subsequent cycles the current density was 1 C-rate.

### 6.3.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) experiments were conducted using a thermal analysis tool from Perkin-Elmer (Waltham, MA). DSC experiments were conducted on bare NG electrodes and electrodes coated with 5 cycles of Al₂O₃ ALD after having undergone the NO₂/TMA pretreatment. The electrodes were examined over the temperature range 50-350 °C. The scan rate was 10 °C min⁻¹.

Both the bare and the Al₂O₃ ALD coated electrode were lithiated at the time of the DSC measurement. The electrodes were lithiated by cycling the electrodes four times between 0.005 and 1.5 V against Li metal. The current density was 0.063 mA cm⁻². 1 M LiPF₆ in a solution of EC and ethyl methyl carbonate (EMC) was used as the electrolyte. The ratio of EC to EMC was 3:7 by weight. Prior to cell disassembly the electrodes were charged to 0.005 V. Lithiated electrodes were removed from the battery cells. The electrode material was scraped off of the Cu foil current collector into a sealable high pressure stainless steel crucible. All DSC sample preparation was
conducted in an inert Ar environment. An identical, empty, sealed stainless-steel crucible was used as the reference pan for the calorimeter.

6.4 Results and Discussion

Figure 6.2a shows an SEM image of the cross section of an NG electrode that had been coated with 5 cycles of Al$_2$O$_3$ ALD after electrode fabrication. From Figure 6.2a it is clear that the electrode is porous. The line that defines region 1 in Figure 6.2a traces the edge of the trench cut with FIB gallium milling and the top surface of the electrode. Regions 2-6 in Figure 6.2a are the cross section of the electrode and region 7 is the Cu foil current collector. The seven regions shown in Figure 6.2a were analyzed with EDS, the results are shown in Figure 6.2b. Figure 6.2b shows the weight % of Al ($\text{Al}/(C + Cu + Al)$) as a function of the region number. It is clear that there is Al throughout the cross section of the electrode. The concentration of Al throughout the cross section of the electrode is relatively constant until the Cu foil, at which point the Al concentration decreases. The relatively constant Al concentration is indicative of a uniform Al$_2$O$_3$ throughout the cross section of the electrode. The decrease of the Al signal on the Cu foil indicates that the uniformity of the Al is not an artifact of the ion milling process uniformly redistributing the Al. In order to verify that Al$_2$O$_3$ ALD was able to coat the full cross section of the electrode, a hole through the Cu foil was milled to exposes the Cu/NG interface. By approaching the Cu/NG interface from the back side it was not possible to inadvertently redistribute Al$_2$O$_3$ from the electrode surface. EDS confirmed the presence of Al at the Cu/NG interface when approached from the Cu side of the electrode. This conclusively demonstrates that the ALD precursors are able to diffuse through the tortuous paths of the NG electrode.

The conformality of the Al$_2$O$_3$ ALD film on the assembled electrode was not confirmed by the SEM/EDS analysis. Measurement of the conductivity of bare NG, Al$_2$O$_3$ ALD coated NG, and Al$_2$O$_3$ ALD coated NG with the NO$_2$/TMA pretreatment revealed the importance of the NO$_2$/TMA pretreatment. The results of the conductivity measurement are shown in Figure 6.3. The bare NG exhibited the highest conductivity at 668.8 S·cm$^{-1}$. The addition of 5 and 10 cycles
Figure 6.2: a) SEM image of the cross section of an NG electrode that had been coated with 5 cycles of Al$_2$O$_3$ ALD after electrode fabrication. Numbers indicate regions in which Al was analyzed with EDS. b) Weight fraction of Al as a function of region number on the SEM.
of Al₂O₃ ALD, without the NO₂/TMA pretreatment, reduced the conductivity to 304.3 and 199.7 S·cm⁻¹ respectively. The reduction of the conductivity by the addition of an insulating Al₂O₃ ALD film was to be expected. The further reduction of the conductivity by the same number of cycles of Al₂O₃ ALD with the NO₂/TMA pretreatment indicates that with the NO₂/TMA pretreatment the Al₂O₃ ALD is more conformal. NG particles with 5 and 10 cycles of Al₂O₃ ALD, with the NO₂/TMA pretreatment, had conductivity of 59.8 and 44.9 S·cm⁻¹ respectively. The same enhancement to the conformality of the Al₂O₃ ALD film from the NO₂/TMA pretreatment on NG particles should translate to Al₂O₃ ALD on assembled NG electrodes.

Electrodes assembled from bare NG and Al₂O₃ ALD on NG powder and electrodes that were coated with Al₂O₃ ALD after assembly were subjected to charge-discharge cycling at 50 °C. Increasing the temperature should accelerate detrimental side reactions on the electrode [21] which allows for more rapid testing of the cells. The discharge capacity as a function of the number of charge-discharge cycles is shown in Figure 6.4. The bare NG rapidly lost its capacity with increasing charge-discharge cycles. The loss of capacity on the bare NG is attributed to the formation of SEI due to the decomposition of the electrolyte [220].

Electrodes assembled from NG particles that were coated with 5 cycles of Al₂O₃ ALD exhibited a dramatically decreased capacity retention as compared to the bare NG. This effect is shown in Figure 6.4. The insulating nature of the Al₂O₃ film was believed to be the cause of the decreased capacity. The Al₂O₃ film may block conduction pathways between both adjacent NG particles and NG particles and the Cu current collector. Table 6.1 shows schematics of the conduction pathways for bare NG, ALD on NG powder and ALD on assembled NG electrode.

As compared to bare NG, electrodes that were assembled prior to coating with 5 cycles of Al₂O₃ ALD displayed a dramatically enhanced capacity retention with respect to the number of charge-discharge cycles. This effect is shown in Figure 6.4. The NO₂/TMA pretreatment did not play a significant role in the capacity enhancement for ALD grown directly on the electrode. The chargedischarge capacity retention for the electrode with the NO₂/TMA pretreatment and 5 cycles Al₂O₃ ALD was 96% after 200 chargedischarge cycles, with respect to the capacity at the third
Figure 6.3: Electrical conductivity of bare and Al$_2$O$_3$ ALD coated NG powders.
Figure 6.4: The discharge capacity as a function of the number of charge-discharge cycles for bare NG and Al₂O₃ ALD on NG powder, and electrodes that were coated with Al₂O₃ ALD after assembly. All charge-discharge cycles were carried out at 50 °C.
chargedischarge cycle. For a similar electrode without the NO$_2$/TMA pretreatment, the capacity retention was 93%. While the conductivity measurement shown in Figure 6.3 seem to indicate that the NO$_2$/TMA pretreatment does produce a less conductive and therefore more conformal film, the enhanced conformality does not appear to dramatically improve the electrode’s electrochemical performance. It may be possible the NG has a sufficient number of defect and edge sites to allow the Al$_2$O$_3$ ALD without the use of NO$_2$/TMA pretreatment.

Table 6.1: Electron conduction pathways for bare NG, ALD on NG powder and ALD on assembled NG electrode.

<table>
<thead>
<tr>
<th></th>
<th>Bare NG</th>
<th>ALD on Powder</th>
<th>ALD on Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conduction Path</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Surface Protection</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

As it is depicted in Table 6.1, it is believed the conduction pathway remains intact when an assembled electrode is coated with Al$_2$O$_3$ ALD. The presence of the protective Al$_2$O$_3$ ALD film and maintaining the conduction pathways between NG adjacent particles, and NG particles and the Cu current collector are both crucial to enhancing the electrode performance. The Al$_2$O$_3$ ALD film may serve as an ”artificial” SEI that blocks the decomposition of the electrolyte on the electrode surface.

Figure 6.5 shows the capacity retention is also improved when the electrodes are subjected
to charge-discharge cycles at room temperature. The results, showing the capacity retention with respect to the third charge-discharge cycles at the 100\textsuperscript{th} and 200\textsuperscript{th} charge-discharge cycle are summarized in Table 6.2. Though it is not evident from Figures 6.4 or 6.5, Table 6.2 show that thicker, more conformal (NO\textsubscript{2}/TMA pretreatment) films have larger capacity retention. For comparison Table 6.3 shows the capacity retention for NG coated with a variety of materials [104, 117, 123].

Table 6.2: Capacity retention of Al\textsubscript{2}O\textsubscript{3} coated NG electrodes at the 100\textsuperscript{th} and 200\textsuperscript{th} charge-discharge cycle with respect to the 3\textsuperscript{rd} charge-discharge cycle.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Al\textsubscript{2}O\textsubscript{3} ALD</th>
<th>NO\textsubscript{2}/TMA Pretreatment</th>
<th>Capacity Retention 100\textsuperscript{th} Cycle (%)</th>
<th>Capacity Retention 200\textsuperscript{th} Cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>Bare</td>
<td></td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>RT</td>
<td>2</td>
<td>No</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>RT</td>
<td>5</td>
<td>No</td>
<td>104</td>
<td>102</td>
</tr>
<tr>
<td>RT</td>
<td>5</td>
<td>Yes</td>
<td>104</td>
<td>103</td>
</tr>
<tr>
<td>50 °C</td>
<td>Bare</td>
<td></td>
<td>53</td>
<td>26</td>
</tr>
<tr>
<td>50 °C</td>
<td>2</td>
<td>No</td>
<td>96</td>
<td>88</td>
</tr>
<tr>
<td>50 °C</td>
<td>5</td>
<td>No</td>
<td>97</td>
<td>93</td>
</tr>
<tr>
<td>50 °C</td>
<td>5</td>
<td>Yes</td>
<td>99</td>
<td>96</td>
</tr>
</tbody>
</table>

The capacity retention is referenced to the third charge-discharge cycle due to SEI formation during the first two charge discharge cycles [150, 151, 220, 74, 16]. SEI formation irreversibly consumes Li from the cathode which reduces the capacity of the cell. The SEI is a high impedance film on the electrode surface. The increased impedance may also reduce the performance of the cell. SEI films of thicknesses varying from 4.5-980 nm have been reported in the literature [113, 214, 74, 22, 220]. Table 6.4 shows several SEI thicknesses, the material on which they were observed and the analysis technique used to determine the SEI film thickness. Controlling how the SEI forms, thickness and materials composition, is critical to determining the performance of the electrode.

Figure 6.6 shows the first charge for bare NG and NG electrodes coated with 5 cycles of Al\textsubscript{2}O\textsubscript{3} ALD, with and without the NO\textsubscript{2}/TMA pretreatment. The small plateau at around 0.7 V (versus Li/Li\textsuperscript{+}) corresponds to the reductive decomposition of the electrolyte to form the SEI.
Figure 6.5: The discharge capacity as a function of the number of charge-discharge cycles for bare NG and Al₂O₃ ALD on NG powder, and electrodes that were coated with Al₂O₃ ALD after assembly. All charge-discharge cycles were carried out at room temperature.
Table 6.3: Capacity retention of coated-NG powders by wet chemical techniques [104, 117, 123]

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>Temperature</th>
<th>Electrode Composition</th>
<th>Current (mA g(^{-1}))</th>
<th>Sample</th>
<th>Capacity Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>RT</td>
<td>80:10:10</td>
<td>175</td>
<td>Bare</td>
<td>76% (100(^{th}) cycle)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Coated</td>
<td>93% (100(^{th}) cycle)</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>30 °C</td>
<td>80:10:10</td>
<td>1050</td>
<td>Bare</td>
<td>65% (100(^{th}) cycle)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Coated</td>
<td>88% (100(^{th}) cycle)</td>
</tr>
<tr>
<td>AlPO(_4)</td>
<td>NA</td>
<td>96:4</td>
<td>350</td>
<td>Bare</td>
<td>36% (50(^{th}) cycle)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Coated</td>
<td>79% (50(^{th}) cycle)</td>
</tr>
</tbody>
</table>

[155]. The effect is more obvious in a plot of the derivative of the specific capacity with respect to voltage (\(dQ/dV\)), this plot is shown in Figure 6.7. The magnitude of the differential charge peaks in Figure 6.7 corresponds to the amount of SEI formed on the electrode surface from the reductive decomposition of the electrolyte. The largest SEI film was observed on the bare NG electrode. With 5 cycles of Al\(_2\)O\(_3\) ALD, the magnitude of the differential voltage profile peak was reduced. This indicates that the Al\(_2\)O\(_3\) films act to prevent the formation of the SEI. However, with 5 cycles of Al\(_2\)O\(_3\) ALD and the NO\(_2\)/TMA pretreatment, the magnitude of the differential voltage profile peak was even further reduced. The least SEI was formed when the Al\(_2\)O\(_3\) film was more conformal due to the NO\(_2\)/TMA pretreatment.

The coulombic efficiency is a ratio of the discharge capacity to the charge capacity, in an ideal battery it would be unity. Due to losses incurred in the formation of the SEI the coulombic efficiency is less than unity. Figure 6.8 shows the coulombic efficiency for the first charge-discharge cycle of a bare NG electrode and NG electrodes coated with 2 and 5 cycles of Al\(_2\)O\(_3\) ALD, with and without the NO\(_2\)/TMA pretreatment. The coulombic efficiency was measured at room temperature and at 50 °C. The worst coulombic efficiency was displayed by the bare NG electrode at cycled at 50 °C. General trends in the performance were observed. Reducing the temperature increased the coulombic efficiency, which stems from the higher rates of electrolyte decomposition at elevated temperatures [21]. Thicker and more conformal Al\(_2\)O\(_3\) ALD films further increased the coulombic efficiency. 2 and 5 cycles of Al\(_2\)O\(_3\) ALD showed improved coulombic efficiency as compared to the
Figure 6.6: Voltage profiles for the first charge of a bare NG electrode and NG electrodes coated with 5 cycles of Al$_2$O$_3$ ALD, with and without the NO$_2$/TMA pretreatment.
Figure 6.7: Differential voltage profiles for the first charge of a bare NG electrode and NG electrodes coated with 5 cycles of $\text{Al}_2\text{O}_3$ ALD, with and without the NO$_2$/TMA pretreatment.
Table 6.4: Thicknesses of SEI films on various graphitic surfaces.

<table>
<thead>
<tr>
<th>Material</th>
<th>Measurement Technique</th>
<th>SEI Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>Spectroscopic ellipsometry</td>
<td>36 nm [113]</td>
</tr>
<tr>
<td>Graphite fiber</td>
<td>SEM</td>
<td>200 nm [214]</td>
</tr>
<tr>
<td>Petroleum coke</td>
<td>Calculated</td>
<td>4.5 nm [74]</td>
</tr>
<tr>
<td>HOPG Edge</td>
<td>XPS Depth Profiling</td>
<td>35 nm [22]</td>
</tr>
<tr>
<td>HOPG basal plane</td>
<td>XPS Depth Profiling</td>
<td>7 nm [22]</td>
</tr>
<tr>
<td>NG</td>
<td>FIB and EDS</td>
<td>450-980 nm [220]</td>
</tr>
</tbody>
</table>

bare NG electrode. This result was improved upon by doing the NO$_2$/TMA pretreatment followed by 2 and 5 cycles of Al$_2$O$_3$ ALD. These results concur with the intensities of the differential charge peaks (Figure 6.7) to indicate that the Al$_2$O$_3$ ALD films suppress the formation of an SEI film during the first charge-discharge cycle.

Previous studies have revealed that SEI formation on highly ordered pyrolytic graphite (HOPG) occurs at different rates on the basal planes and at the graphite edges [22]. This is shown in Table 6.4. The varying degree of improvement from the Al$_2$O$_3$ ALD with and without the NO$_2$/TMA pretreatment may result from the ALD chemistry nucleates on the NG surface. Without the NO$_2$/TMA pretreatment the Al$_2$O$_3$ ALD may only nucleate on the edges or defects of the graphite, while with the NO$_2$/TMA pretreatment the Al$_2$O$_3$ ALD may be able to nucleate on all surfaces of the graphite. The more conformal film may better serve to protect the NG and help explain the improved performance with the NO$_2$/TMA pretreatment.

Figure 6.9 shows the differential scanning calorimetry plots for a lithiated bare NG electrode (6.9a) and an NG electrode that was coated with 5 cycles of Al$_2$O$_3$ ALD after the NO$_2$/TMA pretreatment (6.9b). At temperatures below 150 °C the ALD coated NG electrode did not generate as much heat as the bare NG electrode. The generation of heat by the bare NG electrode was attributed to the exothermic decay of an unstable SEI and further decomposition of the electrolyte. The reduced amount of heat generation below 150 °C by the NG electrode with an Al$_2$O$_3$ film was attributed to the enhanced stability and reduced amount of the SEI film generated in the presence
Figure 6.8: Coulombic efficiency for the first charge-discharge cycles of a bare NG electrode and NG electrodes coated with 2 and 5 cycles of Al₂O₃ ALD, with and without the NO₂/TMA pretreatment.
of the Al$_2$O$_3$ film. These results are consistent with the results shown in Figures 6.7 and 6.8.

6.4.1 Propylene Carbonate Electrolyte

Figure 6.10 shows the charge-discharge voltage profile of bare NG and an NG electrode coated with 5 cycles of Al$_2$O$_3$ ALD after the NO$_2$/TMA pretreatment. The electrolyte for this experiment was 1 M LiPF$_6$ in PC. This experiment was conducted at room temperature. Voltage plateaus in the range of 0.6-0.9 have been observed for the electrochemical decomposition of PC and the exfoliation of graphite [57, 9, 74, 218]. Figure 6.10 shows a similar plateau, at 0.8 V, for the bare NG electrode. In contrast, for NG electrode coated with 5 cycles of Al$_2$O$_3$ ALD after the NO$_2$/TMA pretreatment Figure 6.10 shows reversible Li ion insertion and extraction with no sign of the plateau at 0.8 V associated with the electrochemical decomposition of PC and the exfoliation of graphite. Figure 6.11 show the charge and discharge capacity for an NG electrode coated with 5 cycles of Al$_2$O$_3$ ALD after the NO$_2$/TMA pretreatment as a function of the number of charge-discharge cycles. The capacity is of Al$_2$O$_3$ ALD coated electrode is very stable, even in a PC based electrolyte. The near overlap of the charge and discharge capacity indicates the coulombic efficiency is near unity and very stable. It should be noted that the weight % of a 5 Å Al$_2$O$_3$ on a 4 µm NG particle is 0.05% as compared to 5-20 weight % used for a protective carbon film.

6.4.2 Full Cells

In most of the LIB literature electrochemical tests are performed on half cells (i.e. anode/Li or cathode/Li). Li metal is not a practical electrode outside of the laboratory due to reasons of safety. During charging-discharge cycling with a Li metal electrode dendrite formation on the Li electrode can eventually lead to an electrical short across the two electrodes [81, 194]. In the presence of a short circuit and the flammable organic electrolyte solvents currently in use, there is a risk of heat generation and fire [21, 213]. Using Li metal as the counter electrode simplifies electrochemical experiments because it does not introduce more complex cross reactions from an electrochemically more complex counter electrode. A Li metal counter electrode is the simplest
Figure 6.9: DSC plots of a) a bare NG electrode and b) an NG electrode that was coated with 5 cycles of Al$_2$O$_3$ ALD after the NO$_2$/TMA pretreatment.
Figure 6.10: Voltage profiles of bare NG and an NG electrode coated with 5 cycles of Al$_2$O$_3$ ALD after the NO$_2$/TMA pretreatment.
Figure 6.11: The charge and discharge capacity as a function of the number of charge-discharge cycles for an NG electrode that was coated with 5 cycles of Al\textsubscript{2}O\textsubscript{3} ALD after an NO\textsubscript{2}/TMA pretreatment. All charge-discharge cycles were carried out at room temperature. The electrolyte was 1 M LiPF\textsubscript{6} in PC.
configuration to effectively evaluate the performance of a new LIB material.

Once a material has been proven in a half cell it is necessary to evaluate it in a full cell. Unexpected complications can arise when Li metal is no longer used as the counter electrode. Amatucci et al. successfully demonstrated that LiMn$_2$O$_4$/Li and graphite/Li work well [6]. When the two half cells were combined to make a full cell (LiMn$_2$O$_4$/graphite) the battery performance suffered [6]. It is well known that LiMn$_2$O$_4$ can undergo Mn$^{2+}$ dissolution in an electrochemical cell [6, 112, 41]. In a full cell dissolved Mn$^{2+}$ can destabilize the SEI on the graphite surface and/or become a detrimental constituent of the SEI, leading to capacity loss [6, 112, 41].

The voltage profiles for bare LiCoO$_2$/NG full cells and LiCoO$_2$/NG full cells with 2 cycles of Al$_2$O$_3$ ALD are shown in Figure 6.12. The Al$_2$O$_3$ ALD was done on the LiCoO$_2$ powder prior to electrode assembly and on the NG electrode after electrode assembly. Voltage profiles are shown at the 3$^{rd}$, 50$^{th}$, 100$^{th}$ and 200$^{th}$ charge-discharge cycle. For the bare LiCoO$_2$/NG full cell, as the number of charge-discharge cycles increased the potential at which current began to flow during charging also increased. Similarly, during discharge, the more the cell had been charge-discharge cycled the greater the potential drop. These overpotentials may be attributed to the decomposition of the electrolyte on the either the LiCoO$_2$ or the NG. Or the overpotentials may be from electrochemical reactions between the LiCoO$_2$ or the NG and the electrolyte. From the voltage profile it is evident the capacity of the bare LiCoO$_2$/NG full cell fades with the increasing number of charge-discharge cycles. In contrast to this behavior, the LiCoO$_2$/NG full cell with 2 cycles of Al$_2$O$_3$ ALD appears comparatively stable with respect both to the development of an overpotential and capacity retention.

The discharge capacity retention as function of the number of charge-discharge cycles is shown in Figure 6.13. During the first two cycles the current density was 0.1 C-rate. After the first two cycles the current density was raised to 1 C-rate. The initial discharge capacity of the bare LiCoO$_2$/NG full cell was similar to that of the LiCoO$_2$/NG full cell with 2 cycles of Al$_2$O$_3$ ALD. After 200 charge-discharge cycles the bare LiCoO$_2$/NG full cell had retained only 13.6% of its initial capacity. In sharp contrast the LiCoO$_2$/NG full cell with 2 cycles of Al$_2$O$_3$ ALD had
Figure 6.12: Voltage profiles for 3\textsuperscript{rd}, 50\textsuperscript{th}, 100\textsuperscript{th} and 200\textsuperscript{th} charge-discharge cycle of a bare NG/LiCoO\textsubscript{2} full cell and a Al\textsubscript{2}O\textsubscript{3} ALD coated NG/LiCoO\textsubscript{2} full cell.
6.5 Conclusions

$\text{Al}_2\text{O}_3$ ALD films were grown on NG powders and on fabricated electrodes comprised of NG. The ability of the ALD precursors to penetrate a fabricated electrode was demonstrated with an EDS of a FIB cross section of the electrode and the superior performance of the coated electrode in PC electrolyte. The $\text{Al}_2\text{O}_3$ ALD on the NG particles dramatically reduced the discharge capacity, this may arise from the $\text{Al}_2\text{O}_3$ ALD film insulating the interparticle conduction pathways. ALD deposited directly onto fabricated NG electrodes protects the NG particle surfaces from undesirable interactions with the electrolyte while maintaining an electronically conductive pathway between both adjacent particles, and particles and the current collector. With respect to the third charge-discharge cycle, NG electrodes coated with 5 cycles of $\text{Al}_2\text{O}_3$ ALD had a capacity retention of 102% (no NO$_2$/TMA pretreatment) and 103% (with NO$_2$/TMA pretreatment) after 200 charge-discharge cycles at room temperature. At 50 °C the NG electrodes coated with 5 cycles of $\text{Al}_2\text{O}_3$ ALD had a capacity retention of 93% (no NO$_2$/TMA pretreatment) and 96% (with NO$_2$/TMA pretreatment) after 200 charge-discharge cycles. Bare NG electrodes had a capacity retention of 80% at room temperature and 26% at 50 °C after 200 charge-discharge cycles. As evidenced by the electrical conductivity, the first cycle differential charge profile, and the first cycle coulombic efficiency the NO$_2$/TMA pretreatment provides for a more conformal $\text{Al}_2\text{O}_3$ film. DSC measurement and the excellent charge-discharge capacity retention at 50 °C indicated the ALD coated NG electrodes were safer. The ability to use PC as the electrolyte is a promising result for the possibility to use NG in LIBs for HEVs.

6.5.1 A Note on Significance

Commercial battery grade graphite shows good charge-discharge cycle performance even at 50 °C. In order to demonstrate the enhancement that an ALD film can provide a low grade graphite was employed in this study to accelerate LIB cell testing. It is believed that these enhancement
Figure 6.13: Capacity retention as a function of charge-discharge cycles of a bare NG/LiCoO$_2$ full cell and a Al$_2$O$_3$ ALD coated NG/LiCoO$_2$ full cell.
provided by the ALD film will translate to battery grade graphite.

6.6 Acknowledgements

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Chapter 7

Atomic Layer Deposition on Gram Quantities of Multiwalled Carbon Nanotubes

7.1 Abstract

Atomic layer deposition (ALD) was employed to grow coaxial thin films of Al$_2$O$_3$ and Al$_2$O$_3$/W bilayers on multiwalled carbon nanotubes (MWCNTs). Although the MWCNTs have an extremely high surface area, a rotary ALD reactor was successfully employed to perform ALD on gram quantities of MWCNTs. The uncoated and ALD-coated MWCNTs were characterized with transmission electron microscopy and x-ray photoelectron spectroscopy. Al$_2$O$_3$ ALD on untreated MWCNTs was characterized by nucleation difficulties that resulted in the growth of isolated Al$_2$O$_3$ nanospheres on the MWCNT surface. The formation of a physisorbed NO$_2$ monolayer provided an adhesion layer for the nucleation and growth of Al$_2$O$_3$ ALD films. The NO$_2$ monolayer facilitated the growth of extremely conformal coaxial Al$_2$O$_3$ ALD coatings on the MWCNTs. Cracks were also observed in the coaxial Al$_2$O$_3$ ALD films on the MWCNTs. After cracking, the coaxial Al$_2$O$_3$ ALD films were observed to slide on the surface of the MWCNTs and expose regions of bare MWCNTs. The Al$_2$O$_3$ ALD film also served as a seed layer for the growth of W ALD on the MWCNTs. The W ALD films can significantly reduce the resistance of the W/Al$_2$O$_3$/MWCNT wire. The results demonstrate the potential for ALD films to tune the properties of gram quantities of very high surface area MWCNTs.
7.2 Introduction

Carbon nanotubes (CNTs) have exceptional properties including low electrical resistance [75, 184], high mechanical strength [190, 210] and high thermal conductivity [25, 104]. CNTs can be used as building blocks for the fabrication of nanodevices including chemical sensors [114] and field effect transistors [137]. CNTs can also be employed for many purposes such as field-emission electron sources [56] and nanoprobes for scanning probe microscopy [54]. There are many other emerging applications for both individual CNTs and dispersions of CNTs in composite materials [23, 189]. Many of these applications require thin films deposited on the CNTs to insulate, protect or functionalize the CNTs.

CNTs may also serve as a mechanically robust, electronically conductive scaffolding. Lithium ion battery (LIB) active materials such as TiO$_2$ or MoO$_3$ could be deposited onto CNTs. The insulating nature of TiO$_2$ and MoO$_3$ make the interface with between the active material and the LIB conductive additive crucial to maintaining a good electronic conduction pathway [160]. The intimate contact between a thin film of the active material and the CNT may provide for enhanced electrical conductivity and superior LIB performance. Metal oxide anodes undergo a large volume expansion when they are in the charged (lithiated) state [124]. The volume expansion can lead to fracturing of individual particles and a loss of electronic conductivity [160, 124]. By keeping the films of the active materials thin and by growing them on CNTs with high mechanical strength it may be possible avoid fracturing if the CNTs are flexible enough to be compliant with the expansion of the anode material.

Atomic layer deposition (ALD) methods are preferred to obtain film deposition that is conformal and controlled film deposition at the atomic level. ALD is based on sequential, self limiting surface reactions [79, 181] and has been reported for many materials [156, 161]. ALD can be applied to CNTs because ALD has been demonstrated on very high aspect ratio structures [64] and nanoparticles [70]. Al$_2$O$_3$ ALD growth has been reported on individual single-walled carbon nanotubes (SWCNTs) [68, 69] and multiwalled carbon nanotubes (MWCNTs) [90, 122]. The nucle-
The nucleation of Al₂O₃ ALD was identified as a significant problem for ALD on SWCNT surfaces [68, 69]. Fortunately, a functionalization procedure based on the adsorption of NO₂ and trimethylaluminum (TMA) has been shown to yield an adhesion layer on SWCNTs [69]. This adhesion layer facilitates the nucleation of Al₂O₃ ALD and produces very conformal Al₂O₃ ALD films using TMA and H₂O as the reactants [69]. ALD on CNTs has been developed for CNT nanotube transistors and logic gates [95]. ZrO₂ ALD has been employed to deposit high dielectric constant insulating layers on CNTs to fabricate field-effect transistors [95]. HfO₂ ALD on SWNTs has also been achieved to fabricate high performance thin-film transistors [32]. Nucleation difficulties for ZnO ALD on MWCNTs has been shown to lead to bead-shaped crystalline particles on the surface of the MWCNT that enhance electron field-emission [82]. In contrast, coaxial ZnO/Al₂O₃ heterostructures were fabricated on CNTs after depositing an Al₂O₃ adhesion layer on CNTs [106]. Vanadium oxide ALD has also been employed to fabricate gas sensors from CNTs [205]. Most of the previous applications for ALD on CNTs have been demonstrated using single CNTs. Single individual CNTs avoid the many difficulties that are encountered when attempting ALD on large quantities of CNTs. Gram quantities of CNTs have an extremely high surface area of 200-300 m²/g and can be entangled to form CNT aggregates. ALD on large quantities of CNTs has the same problems as ALD on particles in particle beds. The CNTs must be agitated to enhance gas conductance of the ALD reactants to the individual CNTs. Likewise, the CNTs must be displaced relative to each other during ALD to prevent the CNTs from being glued together by the ALD film. Enhanced gas conductance and constant CNT motion in the bed of CNTs can be accomplished using fluidized bed reactors [201, 200] or rotary reactors [139, 140]. ALD on large quantities of CNTs would be useful for preparing CNTs for CNT/polymer composites. CNT/polymer composites should have high mechanical strength, high thermal conductivity and high electrical conductivity. Possible applications for these CNT/polymer composites include transparent conductive coatings, electromagnetic interference shielding and flexible electrostatic dissipation films. There are many previously reported examples of CNT/polymer composites [157, 189, 49, 121, 28]. However, dispersion of CNTs in the polymer composite is a difficulty and may limit the properties of the CNT/polymer com-
posite. ALD on the CNTs may help to improve the dispersion and coupling of CNTs in polymers. The inertness of the surface of the CNT is the cause for the insolubility of CNTs in water and organic solvents [187] and the lack of dispersion of CNTs in polymers. Covalent functionalization can enhance CNT solubility [187] and provide coupling between CNTs and polymers [28]. Unfortunately, covalent functionalization of the CNT surface damages the inherent properties of the CNT [19]. Surfactants can also noncovalently functionalize the surface of CNTs without perturbing the underlying CNT properties [85, 130]. However, covalent and noncovalent functionalization of CNTs both require wet chemical treatment. ALD can deposit ultrathin coatings on CNTs using gas phase procedures that will facilitate CNT dispersion without requiring a solution process. In this paper, ALD on large quantities of high surface area MWCNTs is demonstrated using a rotary ALD reactor. The nucleation of Al\textsubscript{2}O\textsubscript{3} ALD on gram quantities of MWCNTs is achieved using NO\textsubscript{2} and TMA to form an adhesion layer. Without the NO\textsubscript{2} nucleation procedure, the Al\textsubscript{2}O\textsubscript{3} ALD grew nanospheres on the MWCNT surface. With the NO\textsubscript{2} nucleation procedure, the Al\textsubscript{2}O\textsubscript{3} ALD grew very conformally on the MWCNTs. The ALD-coated MWCNTs were examined using transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) versus the number of Al\textsubscript{2}O\textsubscript{3} ALD reaction cycles. The Al\textsubscript{2}O\textsubscript{3} ALD coating was also used as a foundation for the subsequent growth of W ALD films on the MWCNTs.

7.3 Experimental

7.3.1 MWCNTs and Rotary Reactor

The MWCNTs used in these experiments were 7000 series MWCNTs from Nanocyl (Sambreville, Belgium). For the Al\textsubscript{2}O\textsubscript{3} ALD and W ALD, trimethylaluminum (97%) and WF\textsubscript{6} were obtained from Sigma-Aldrich (St. Louis, MO). HPLC grade H\textsubscript{2}O was also from Sigma-Aldrich and was further purified by 5 cycles of freeze-pump-thaw. For the NO\textsubscript{2} nucleation treatment, commercial purity grade NO\textsubscript{2} (99.5%) was acquired from Airgas (Radnor, PA). The Si\textsubscript{2}H\textsubscript{6} used for W ALD was from Voltaix Inc. (Branchburg, NJ). The specific surface areas of MWCNTs are on the order
of hundreds of m²/g [89, 215, 162]. From Brunauer, Emmett and Teller (BET) measurements, the manufacturer reports a specific surface area of 250-300 m²/g for the 7000 series MWCNTs. This surface area is approximately an order of magnitude larger than the nanopowders previously coated with ALD [139]. For equivalent masses of material, larger reactant exposures and purge times are required for the MWCNTs compared with typical nanopowders. BET measurements may also probe the inner surfaces of the MWCNT if the MWCNTs have open ends. ALD on particles is possible using either fluid bed reactors [201, 200] or rotary reactors [139, 140]. Rotary reactors have an advantage when performing ALD on nanoparticles because the rotary reactors can provide for static reactant exposures [139]. These static reactant exposures can minimize the amount of reactant that is lost to the vacuum pump. Recent work has demonstrated the feasibility of ALD on gram quantities of nanopowders in a rotary reactor [139]. The rotary reactor employed in this study was similar to the rotary reactor employed in the previous work [139, 140]. A schematic of the rotary reactor is shown in figure 7.1. Each reactant entered the reaction chamber (A) through a needle and pneumatic valve (B) that were attached to 0.25” welded ports on a custom 6.0” Con-flat cap (C). During the reaction, the MWCNTs were mechanically agitated in a rotating porous cylinder (D). The rotation was achieved via a magnetically coupled rotary feedthrough (E). The pressure was monitored with 10 and 1000 Torr capacitance manometers (F). A gate valve (G) was opened to exhaust product gases and any excess precursor to the pump (H). Before coating the MWCNTs in the rotary reactor, MWCNTs quantities from 20 mg to 2 g were placed in the porous stainless steel cylinder with pore size of 10 µm. The porous metal cylinder was then attached to the magnetically-coupled rotary feedthrough (E). This feedthrough with the porous metal cylinder was then enclosed in the vacuum chamber of the rotary reactor and left to outgas under vacuum for 24 hours. Vacuum was obtained using a dual-stage rotary vane pump. Pressure was monitored with a Baratron capacitance manometer (MKS, Andover, MA). For the larger quantities of MWCNTs, the reactant exposures were scaled linearly according to the sample mass. For 1-2 g samples of MWCNTs, multiple doses of precursors were required to achieve the desired reactant exposure [140].
Figure 7.1: Schematic of rotary reactor used to coat gram quantities of MWCNTs.
A ceramic heater (Watlow Electric Manufacturing Co., St. Louis, MO) on the rotary reactor was employed for reactions performed at elevated temperatures. The temperature was monitored with a thermocouple and was manually controlled by applying a constant voltage to the resistive heating element. During the NO\textsubscript{2} functionalization treatment and ALD processing, the porous metal cylinder was rotated in the rotary reactor at 150 rpm. Given the diameter of the rotating porous cylinder, this rotational frequency is consistent with a centripetal force of 0.5g. Reasonable results were obtained using rotational frequencies from 140-180 rpm. Rotational frequencies <140 rpm led to less agitation and agglomeration during ALD. Rotational frequencies >180 rpm led to agglomeration resulting from the CNTs staying on the walls of the porous cylinder.

### 7.3.2 \textit{Al}_{2}\textit{O}_{3} ALD and Surface Nucleation Chemistry

\textit{Al}_{2}\textit{O}_{3} ALD was performed on gram quantities of MWCNTs in the rotary reactor. The \textit{Al}_{2}\textit{O}_{3} ALD surface chemistry employs \textit{Al(\text{CH}_3)_3} (TMA) and \textit{H}_2\textit{O} as the reactants. The sequential, self-limiting reaction sequence during \textit{Al}_{2}\textit{O}_{3} ALD is [58, 84, 149]:

\begin{align*}
A & \quad \text{AlOH}^* + \text{Al(\text{CH}_3)_3} \rightarrow \text{AlO} - \text{Al(\text{CH}_3)_2}^* + \text{CH}_4 \\
B & \quad \text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al} - \text{OH}^* + \text{CH}_4
\end{align*}

(7.1) (7.2)

where the asterisks denote surface species. The \textit{Al}_{2}\textit{O}_{3} ALD reaction sequence was: (1) TMA dose to set pressure; (2) TMA reaction time; (3) evacuation of reaction products and excess TMA; (4) \textit{N}_2 dose; (5) \textit{N}_2 static time; (6) evacuation of \textit{N}_2 and any entrained gases; (7) \textit{H}_2\textit{O} dose to pressure, (8) \textit{H}_2\textit{O} reaction time; (9) evacuation of reaction products and excess \textit{H}_2\textit{O}; (10) dose \textit{N}_2; (11) \textit{N}_2 static time; and (12) evacuation of \textit{N}_2 and any entrained gases. This sequence constituted one \textit{AB} cycle of \textit{Al}_{2}\textit{O}_{3} ALD.

During the NO\textsubscript{2} nucleation treatment, an adsorbed functionalization layer was initially formed on the MWCNTs by alternating exposures of NO\textsubscript{2} and TMA [69]:

\begin{align*}
A & \quad \text{MWCNT}^* + \text{NO}_2 \leftrightarrow \text{MWCNT} - \text{NO}_2
\end{align*}

(7.3)
where the asterisks indicate surface species. In this functionalization process, the nitrogen of the NO\textsubscript{2} is attracted to the CNT surface and leaves the oxygen atoms accessible. Upon TMA exposure, the oxygen atoms coordinate to the aluminum of the TMA molecule leaving a methyl-terminated surface \[69\]. The methyl-terminated surface does not interact with subsequent NO\textsubscript{2} exposures. Following the previous nucleation procedure \[69\], 50 cycles of NO\textsubscript{2}/TMA were used to functionalize the MWCNTs at room temperature. This NO\textsubscript{2} treatment was performed with the following sequence: (1) exposure to NO\textsubscript{2} to set pressure; (2) NO\textsubscript{2} static reaction time; (3) evacuation of excess NO\textsubscript{2}; (4) exposure to TMA to set pressure; (5) TMA static reaction time; and (6) evacuation of excess TMA. This sequence defines one AB cycle of the NO\textsubscript{2}/TMA functionalization layer. For 20 mg of MWCNTs, the dose pressures were 300 mTorr for both NO\textsubscript{2} and TMA. The static reaction times for NO\textsubscript{2} and TMA were 10 s. The NO\textsubscript{2} and TMA purge times were 7 s and 30 s, respectively. The NO\textsubscript{2}/TMA functionalization layer will desorb at elevated temperatures. Consequently, the adsorbed NO\textsubscript{2}/TMA layer was stabilized with 5 AB cycles of Al\textsubscript{2}O\textsubscript{3} ALD at room temperature. Al\textsubscript{2}O\textsubscript{3} ALD growth could then be continued at higher reaction temperatures. For the Al\textsubscript{2}O\textsubscript{3} ALD on the untreated MWCNTs and on the NO\textsubscript{2}/TMA functionalized MWCNTs, the Al\textsubscript{2}O\textsubscript{3} ALD reaction sequence was employed at 180 °C. For 20 mg of MWCNTs, the dose pressures were 1.0 Torr for TMA and H\textsubscript{2}O and 20 Torr for N\textsubscript{2}. The reaction times for the TMA and H\textsubscript{2}O were both 60 s. The N\textsubscript{2} static time was 5 s. All purge times were 60 s. Figure 7.2 displays the ALD reactor pressure versus time for one AB cycle of Al\textsubscript{2}O\textsubscript{3} ALD for (a) untreated MWCNTs and (b) NO\textsubscript{2}/TMA functionalized MWCNTs.

For both the untreated MWCNTs and the NO\textsubscript{2}/TMA functionalized MWCNTs, the pressure responses during the TMA doses shown in figures 7.2a and 7.2b are similar. The pressure responses during the H\textsubscript{2}O doses were different for the untreated MWCNTs and NO\textsubscript{2}/TMA functionalized MWCNTs. For the untreated MWCNTs, figure 7.2a reveals that the pressure dropped following the H\textsubscript{2}O dose of 1 Torr. For the NO\textsubscript{2}/TMA functionalized MWCNTs, figure 7.2b shows that the
Figure 7.2: Reactor pressure versus time for one AB cycle during Al₂O₃ ALD for (a) untreated MWCNTs and (b) NO₂/TMA functionalized MWCNTs.
pressure dipped briefly and then returned to 1 Torr.

The difference in behavior for H$_2$O on the untreated MWCNTs and the NO$_2$/TMA functionalized MWCNTS is accounted for by the difference in reactive surface areas. The conformally coated MWCNTs have a larger Al$_2$O$_3$ surface area. The H$_2$O reacts nearly completely on this surface area and little extra H$_2$O is available for reabsorption. The pressure stays close to 1 Torr because H$_2$O is converted to CH$_4$ reaction product. For the untreated MWCNTs and an equivalent H$_2$O exposure, the growth of Al$_2$O$_3$ nanospheres only consumes a fraction of the H$_2$O. The excess H$_2$O molecules then slowly adsorb on the Al$_2$O$_3$ surface.

After depositing an Al$_2$O$_3$ ALD layer on the MWCNTs, other ALD coatings can be applied such as W ALD. W ALD was accomplished using WF$_6$ and Si$_2$H$_6$ as the reactants. The sequential, self-limiting reaction sequence for W ALD is [110, 87]:

\[
A \quad WF_3^* + Si_2H_6 \rightarrow W - SiH^* + SiHF_3 + 2H_2 \tag{7.5}
\]

\[
B \quad WSiH^* + WF_6 \rightarrow W - WF_3^* + SiHF_3 \tag{7.6}
\]

The W ALD chemistry is not a truly self-limiting process. W ALD is dependent on the Si$_2$H$_6$ exposure and the substrate temperature [61]. A typical growth rate for W ALD is 5 Å/cycle [65].

For W ALD on the MWCNTs, the W ALD reaction sequence was: (1) dose Si$_2$H$_6$ to set pressure; (2) Si$_2$H$_6$ reaction time; (3) evacuation of reaction products and excess Si$_2$H$_6$; (4) N$_2$ dose; (5) N$_2$ static time; (6) evacuation of N$_2$ and any entrained gases; (7) dose WF$_6$ to set pressure; (8) WF$_6$ reaction time; (9) evacuation of reaction products and excess WF$_6$; (10) dose N$_2$; (11) N$_2$ static time; and (12) evacuation of N$_2$ and any entrained gases. This sequence constituted one AB cycle of W ALD. The W ALD reaction sequence was employed at 180 °C. For 20 mg of MWCNTs, the dose pressures were 1.0 Torr for the Si$_2$H$_6$ and WF$_6$ and 20 Torr for the N$_2$. The reaction times for the Si$_2$H$_6$ and WF$_6$ were 200 s and the purge times were both 50 s. The N$_2$ static time was 20 s and the purge time was 200 s.
7.3.3 TEM and XPS Analysis

Transmission electron microscopy (TEM) images of the MWNCTs and ALD-coated MWCNTs were collected on a Philips CM10 electron microscope (Mahwah, NJ). A Gatan digital camera (Gatan, Pleasanton, CA) was used to record the images. Measurements of the micrographs were made in Deneba Canvas 9 (ACD Systems, Victoria, British Columbia, Canada). These measurements were used to determine the film thickness.

A PHI 5600 X-ray photoelectron spectrometer was used to obtain X-ray photoelectron spectra (XPS) of the ALD-coated MWCNTs. The powder samples were pressed into pellets with a thickness of 0.7 mm and a diameter of 5.5 mm and affixed to the sample puck with carbon tape. Monochromatic Al Kα x-rays (1486.6 eV) were used for the XPS analysis. The pass energy was 58.7-93.9 eV and the step size was 0.250-0.400 eV. An electron beam neutralizer was employed at 17.8 mA. Data was collected with Auger Scan (RBD Enterprises, Inc., Bend, OR). XPS data was analyzed in CASA XPS (Casa Software Ltd., U.K.). Peak fits for the W-4f peaks were obtained using a linear background and a 70:30 Gaussian: Lorentzian peak.

7.4 Results and Discussion

7.4.1 Entangled MWCNT Clusters

Transmission electron microscopy (TEM) images were used to characterize the MWCNTs and the ALD film growth on the MWCNTs. The uncoated MWCNTs were a fine powder. These uncoated MWCNTs displayed a range of tube diameters as observed by TEM. The manufacturer reported an average tube diameter of 10 nm. The nanotubes were also agglomerated in entangled clusters prior to the ALD coating. A TEM image of these uncoated entangled clusters of MWCNTs is displayed in figure 7.3. The diameter of these entangled clusters was ∼2-3 µm.

TEM images of the coated MWCNTs were typically imaged on the edge of a µm-scale entangled cluster. Further agglomeration of the MWCNTs during ALD was prevented by performing the ALD in the rotary reactor under agitation by rotation [139]. There were still µm-scale agglomerates
Figure 7.3: TEM image of an uncoated entangled cluster of MWCNTs.
of MWCNTs after ALD processing. Some of these agglomerates were mechanically crushed prior to TEM analysis to obtain MWCNTs from the center of the entangled clusters. MWCNTs from the edge and center of the entangled clusters were all found to be coated with Al$_2$O$_3$ ALD.

### 7.4.2 Al$_2$O$_3$ ALD Nanospheres on Untreated MWCNTs

ALD Al$_2$O$_3$ on untreated MWCNTs resulted in the growth of Al$_2$O$_3$ nanospheres. A TEM micrograph of these nanospheres after 50 AB cycles is shown in figure 7.4. The nanospheres are fairly spherical and monodisperse. The radii of the nanospheres are in the range of 11-13 nm. The TEM images suggest that Al$_2$O$_3$ ALD growth nucleates at specific sites on the MWCNT surface during the initial Al$_2$O$_3$ ALD cycles. The nanospheres then grow isotropically versus the number of AB cycles to yield fairly monodisperse sphere diameters. Very similar Al$_2$O$_3$ nanospheres were observed earlier after Al$_2$O$_3$ ALD on individual SWCNTs [68].

Figure 7.5 shows TEM images of the Al$_2$O$_3$ nanospheres after 100 AB cycles. There is an increase in the nanosphere diameter and the number of nanospheres after 100 AB cycles. However, the nanospheres are not as monodisperse compared with the nanospheres after 50 ALD cycles. The radii of the nanospheres range from 11-20 nm. This finite range indicates that the Al$_2$O$_3$ ALD nanospheres do not all nucleate at the same time. Sites that nucleate later should experience fewer Al$_2$O$_3$ ALD cycles and produce nanospheres with smaller radii. For adjacent nanospheres, the spheres eventually begin to coalesce to form a rough, pseudo-continuous Al$_2$O$_3$ film. Previous studies of Al$_2$O$_3$ ALD on individual MWCNTs have observed conformal growth on nanotube surfaces that were not intentionally functionalized [90, 122]. In contrast, figures 7.4 and 7.5 reveal that the Al$_2$O$_3$ ALD growth was not conformal in this study. Distinct nanospheres are observed that are similar to the Al$_2$O$_3$ nanospheres observed after Al$_2$O$_3$ ALD on unfunctionalized SWCNTs [68]. A possible explanation for this difference in growth involves the presence of defects or inadvertent chemical functionalization on the earlier MWCNT surfaces.

The density of defects and chemical functional groups on the MWCNT surface may be related to the method of MWCNT synthesis and subsequent cleaning and purification methods [4]. The
Figure 7.4: TEM image of untreated MWCNTs after 50 AB cycles of Al₂O₃ ALD.
Figure 7.5: TEM image of untreated MWCNTs after 100 AB cycles of Al$_2$O$_3$ ALD.
growth of nanospheres may be expected for a low density of defects or active chemical species on the MWCNT surface. If the density of defects or active chemical species is much higher, the larger density could lead to a conformal Al$_2$O$_3$ ALD film. The defect density may have been significantly lower for the MWCNTs utilized in this study compared with MWCNTs used in previous studies [90, 122].

7.4.3 Conformal Al$_2$O$_3$ ALD Growth on NO$_2$/TMA Functionalized MWCNTs

To grow conformal Al$_2$O$_3$ ALD coatings on gram quantities of MWCNTs, a functionalization layer of adsorbed NO$_2$ and TMA was initially formed at room temperature. This adsorbed layer is not stable at the elevated temperatures typically used to grow Al$_2$O$_3$ ALD. However, this adsorbed layer can be stabilized with an Al$_2$O$_3$ passivation layer consisting of 5 AB cycles of Al$_2$O$_3$ ALD at room temperature. The Al$_2$O$_3$ ALD chemistry readily nucleated and grew conformally on this adsorbed layer.

Additional Al$_2$O$_3$ ALD cycles were performed at 180 °C to achieve the desired Al$_2$O$_3$ ALD film thickness. Figure 7.6 displays a TEM image after 50 AB cycles of Al$_2$O$_3$ ALD on the NO$_2$/TMA functionalized MWCNTs. In contrast to the nanospheres observed in figure 7.4 after 50 AB cycles, the Al$_2$O$_3$ films are smooth and conformal after 50 AB cycles on the NO$_2$/TMA functionalized MWCNTs. A second TEM image showing a larger portion of the entangled MWCNT cluster at a reduced magnification is presented in figure 7.7. A conformal Al$_2$O$_3$ ALD coating is observed on all the MWCNTs.

Figure 7.8 shows an enlargement of a coated MWCNT after 40 AB cycles. The Al$_2$O$_3$ ALD film is extremely conformal on the MWCNT. TEM images were performed after 25, 40, 50 and 60 AB cycles. TEM analysis of the film thickness was consistent with Al$_2$O$_3$ ALD growth that was linear with number of AB cycles. The Al$_2$O$_3$ ALD growth per cycle was 1.7 Å/cycle. This Al$_2$O$_3$ ALD growth per cycle is slightly larger than the growth per cycle of 1.1-1.2 Å/cycle reported for Al$_2$O$_3$ ALD on flat substrates [84, 149]. However, this Al$_2$O$_3$ ALD growth rate is in agreement with the growth rates reported for Al$_2$O$_3$ ALD on nanopowders of 1.8-2.0 Å/cycle [70, 139]. The larger
Figure 7.6: TEM image of NO$_2$/TMA functionalized MWCNTs after 50 AB cycles of Al$_2$O$_3$ ALD.
Figure 7.7: TEM image of NO$_2$/TMA functionalized MWCNTs after 50 AB cycles of Al$_2$O$_3$ ALD at lower magnification.
growths per cycle may result from the inability to purge H₂O completely from very high surface area samples.

7.4.4 "Macaroni" on MWCNT String

According to the proposed NO₂ nucleation mechanism, the Al₂O₃ ALD films are grown on an adsorbed layer of NO₂/TMA on the CNTs [69]. This adsorbed layer is not covalently attached to the surface of the CNT. Consequently, the coaxial Al₂O₃ ALD film on the CNT should be free to slide along the CNT. TEM images reveal this "sliding" behavior. Locations where the Al₂O₃ ALD film has broken on the MWCNT show evidence for the sliding of the Al₂O₃ ALD film along the MWCNT. Broken Al₂O₃ ALD films that have moved to reveal bare MWCNTs are indicated by the arrows in figures 7.6 and 7.7.

These broken sections of coaxial Al₂O₃ ALD film on the MWCNT are like "macaroni" on a MWCNT string. A TEM image that captures a segment of an Al₂O₃ ALD film on the MWCNT is displayed in figure 7.9. This Al₂O₃ ALD film was deposited using 60 AB cycles. The mechanical tumbling of the entangled clusters of MWCNTs may facilitate the breaking of the Al₂O₃ ALD films at the ends of MWCNTs. These Al₂O₃ ALD segments may then slide off the MWCNTs to reveal bare MWCNTs at the edge of an entangled cluster. Figure 7.10 shows a TEM image that reveals a number of bare MWCNTs dangling at the perimeter of an entangled MWCNT cluster.

7.4.5 Bilayers of W ALD/Al₂O₃ ALD on MWCNT

The conformal coaxial Al₂O₃ ALD coating on MWCNTs can serve as a substrate for the subsequent growth of another ALD material. W ALD was performed on the Al₂O₃ ALD coating to deposit a W/Al₂O₃ bilayer on the MWCNTs. The initial Al₂O₃ ALD film was prepared using the NO₂/TMA nucleation procedure and then 50 cycles of Al₂O₃ ALD. Subsequently, W ALD was grown on the Al₂O₃ ALD surface. Figure 7.11 displays a TEM image after 60 cycles of W ALD using WF₆ and Si₂H₆. The W ALD leads to an increase in diameter of the coated MWCNTs. Bare MWCNTs where the W/Al₂O₃ bilayer has slipped off the ends of MWCNTs are also indicated by
Figure 7.8: TEM image of NO$_2$/TMA functionalized MWCNT after 40 AB cycles of Al$_2$O$_3$ ALD at higher magnification.
Figure 7.9: TEM image of NO$_2$/TMA functionalized MWCNTs after 60 AB cycles of Al$_2$O$_3$ ALD showing evidence for Al$_2$O$_3$ ALD film cracking and sliding on MWCNT.
Figure 7.10: TEM image of NO$_2$/TMA functionalized MWCNTs after 60 AB cycles of Al$_2$O$_3$ ALD showing bare MWCNTs at the perimeter of entangled MWCNTs. These bare MWCNTs result from the Al$_2$O$_3$ ALD film cracking and sliding off the MWCNTs.
the arrows.

The surface of the W/Al₂O₃ bilayer film is rougher and more granular than the Al₂O₃ ALD film on MWCNTs. The surface roughness may be caused by the polycrystal W ALD film or difficulties for the W ALD nucleating on the Al₂O₃ ALD surface [86, 168, 208]. Both of these factors are believed to affect the roughness of W ALD layers in W/ Al₂O₃ nanolaminates [168, 66]. In spite of the increased roughness, the W/Al₂O₃ bilayer film is still conformal to the MWCNTs. TEM measurements of the W ALD film thickness were difficult because of the lack of a distinct boundary between the Al₂O₃ ALD film and the W ALD film. While the density disparity between Al₂O₃ ALD and W ALD should be evident, the geometry of the two coaxial nested cylinders prevented this distinction.

X-ray photoelectron spectroscopy (XPS) was used to analyze: (a) the uncoated MWCNTs; (b) the Al₂O₃ ALD on the untreated MWCNTs; (c) the Al₂O₃ ALD on the NO₂/TMA functionalized MWCNTs; and (d) the W ALD on the Al₂O₃ ALD on the NO₂/TMA functionalized MWCNTs. The XPS spectrum of uncoated MWCNTs shown in figure 7.12a displayed a distinct C-1s peak with a full width half maximum (FWHM) of 1.5 eV. The XPS spectrum of Al₂O₃ ALD on untreated MWCNTs shown in figure 7.12b also displayed peaks for Al, C, and O. All of these peaks had a broader FWHM of ~2.6 eV. This slight broadening may result from charging effects attributed to the presence of Al₂O₃ on the MWCNTs. The typical ratio for Al:O was 2:2.6 determined from the Al 2p and O 1s XPS signals. The XPS spectrum of Al₂O₃ ALD on the NO₂/TMA functionalized MWCNTs is displayed in figure 7.12c. The Al, C, and O peaks had an average FWHM of ~2.5 eV. The typical ratio of Al:O was 2:2.7. The presence of C in the XPS spectrum exceeded the level of expected adventitious C on the surface of the Al₂O₃ film. The extra C content may result from locations where the Al₂O₃ ALD film had cracked on the MWCNTs during sample preparation.

The XPS analysis of the NO₂/TMA functionalized MWCNTs did not detect N. No N was observed for samples before or after argon sputtering. For a monolayer of NO₂ on the MWCNT surface, the expected N signal should be approximately at the XPS detection limit. However, the
Figure 7.11: TEM image after 60 cycles of W ALD on Al₂O₃ surface prepared by NO₂/TMA functionalization and 50 AB cycles of Al₂O₃ ALD on MWCNTs.
Figure 7.12: XPS scans of: (a) untreated MWCNTs; (b) Untreated MWCNT after 100 AB cycles of Al₂O₃ ALD; (c) MWCNTs after NO₂/TMA functionalization and 100 AB cycles of Al₂O₃ ALD; and (d) MWCNTs after NO₂/TMA functionalization and 50 AB cycles of Al₂O₃ ALD and 60 AB cycles of W ALD.
NO₂ molecules may also desorb from the surface of the MWCNTs. This NO₂ desorption may occur after the Al₂O₃ ALD films crack on the MWCNTs during mechanical agitation in the rotary reactor at 180 °C.

The XPS spectrum of the W/Al₂O₃ bilayers on the MWCNTs is shown in figure 7.12d. This spectrum reveals Al, C, O and W and trace quantities of F and Si. F was present at less than 2 at.% and Si was observed in trace amounts at the noise limit. The W 4f⁵/₂ and W 4f⁷/₂ XPS signals were also examined in more detail at 30-40 eV as displayed in figure 7.13. The presence of a quadruplet instead of a doublet for W 4f⁵/₂ and W 4f⁷/₂ indicates the existence of a WOₓ film in combination with metallic W.

The WOₓ layer on the W ALD film occurs because tungsten metal is not stable in air. When the W/Al₂O₃/MWCNT samples were removed from the rotary reactor and exposed to atmosphere, a tungsten oxide layer forms on the surface of the W ALD film. After accounting for O bonded to Al, the W:O ratio of 1:3.1 was determined from the WO₃ 4f and O 1s XPS signals. This ratio is consistent with tungsten oxidizing to WO₃. An Al₂O₃ ALD coating on top of the W ALD could serve to passivate the W ALD film and prevent the W film oxidation in atmosphere.

Models for determining film thickness from XPS analysis rely on smooth, flat samples for accurate measurements [53]. The entangled cluster agglomerates of coated MWCNTs are more like a powder sample. Models can be employed that were developed for analyzing the XPS signals from powder samples. Based on these models [53], the thickness of the WO₃ from XPS measurements is estimated to be ~10-25 Å. This thickness is close to previously reported values for the thickness of WO₃ on W ALD surfaces [207, 206].

A schematic of a W/Al₂O₃ bilayer on a CNT is shown in figure 7.14. An additional insulating Al₂O₃ ALD film on this W/Al₂O₃ bilayer would produce a nanocoaxial cable [90]. The CNT is the center conductor, the Al₂O₃ ALD layers are insulators and the W ALD layer is the metallic shield. These nanocoaxial cables may be useful as electrical nanoprobes. Similar nanocoaxial cables have been fabricated by sputtering Al₂O₃ and Cr on vertically-aligned MWCNTs and then coating with spin-on glass [164]. The W ALD film thickness in the W/Al₂O₃ bilayer can also be increased to
Figure 7.13: XPS scan of the W 4f peak after 60 AB cycles of W ALD on NO$_2$/TMA functionalized MWCNTs with 50 AB cycles of Al$_2$O$_3$ ALD.
decrease the resistance of a W/Al$_2$O$_3$/CNT wire. The W ALD thickness can tune the resistance of the CNT over a wide range.

Using a four point probe technique, the resistivity of individual single-walled CNTs (SWCNT) was $< 10^{-4}$ $\Omega \cdot$cm for nanotubes with a diameter of $13.8 \pm 2$ Å [188]. From these measurements, the resistance per unit length is $R/L < 167$ $\Omega \cdot$nm$^{-1}$. In comparison, W metal has a resistivity of $5.44 \times 10^{-6}$ $\Omega \cdot$cm [202]. Assuming a SWCNT with a diameter of $13.8$ Å and $R/L = 167$ $\Omega \cdot$nm$^{-1}$, figure 7.15 compares the resistance per unit length for a bare SWCNT and a SWCNT coated with various W thicknesses. For the W-coated SWCNT, the resistance per unit length is progressively reduced versus W thickness. The resistance per unit length is reduced by almost two orders of magnitude with a W thickness of only $\sim 10$ Å. Note that the calculations did not account for W oxidation or electron scattering at the surface or grain-boundaries [163, 222]. Figure 7.15 serves to illustrate the ability of thin metal films to reduce significantly the resistance of CNTs.

7.5 Conclusions

Atomic layer deposition (ALD) was performed on quantities of multiwalled carbon nanotubes (MWCNTs) in a rotary reactor. The uncoated and ALD-coated MWCNTs were characterized with transmission electron microscopy and X-ray photoelectron spectroscopy. Al$_2$O$_3$ ALD grew as nanospheres on quantities of untreated MWCNTs because of nucleation difficulties. After the NO$_2$/TMA nucleation treatment, the Al$_2$O$_3$ ALD film grew conformally on the MWCNTs. In addition, the coaxial Al$_2$O$_3$ ALD growth on the MWCNTs was approximately linear versus the number of Al$_2$O$_3$ ALD reaction cycles.

The Al$_2$O$_3$ ALD films were observed to crack on the MWCNTs. More cracking was monitored after crushing and increased mechanical agitation. The coaxial Al$_2$O$_3$ ALD films were observed to slide on the surface of the MWCNTs and expose regions of bare MWCNTs. This ease in sliding after cracking of the Al$_2$O$_3$ ALD film is consistent with a noncovalently bonded Al$_2$O$_3$ ALD film. The Al$_2$O$_3$ ALD film also served as a foundation for coaxial W ALD film growth on the MWCNTs. XPS analysis indicated that the W/Al$_2$O$_3$ bilayer on the MWCNTs was covered with a native
Figure 7.14: Schematic of coaxial W/Al$_2$O$_3$ bilayer on CNT.
Figure 7.15: Resistance per unit length for W-coated SWCNT versus W thickness and bare SWCNT.
WO$_3$ layer. This WO$_3$ layer results from the exposure of the W ALD film to atmosphere. The coaxial W ALD film growth on the MWCNTs should significantly reduce the resistance of the W/Al$_2$O$_3$/MWCNT wire.

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