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Surface chemistry of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles coated by Al_2O_3 using Atomic Layer Deposition for lithium- ion batteries

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Abstract

The effects of depositing ultrathin (<1 nm) Al_2O_3 coatings on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) particles using atomic layer deposition (ALD) are presented. Promising electrochemical performance of the Al_2O_3 ALD coated LNMO at 30°C is demonstrated in not only significantly improved coulombic efficiency, cycle retention, and rate capability, but also in dramatically suppressed self-discharge and dissolution of transition metals. Combined analyses by electrochemical impedance spectroscopy, ex-situ X-ray photoelectron spectroscopy, and ex-situ time-of-flight secondary ion mass spectrometry reveal that the solid electrolyte interphase layer on the Al_2O_3 ALD coated LNMO is much thinner and contains fewer organic species than the one on the bare LNMO. This difference originates from the suppression of the side reaction at high voltage by the Al_2O_3 ALD protective coating. Also, fluorination of Al_2O_3 ALD layer upon repeated charge–discharge cycling is confirmed, and this can account for the capacity increases during the initial charge–discharge cycles. Finally, it is also demonstrated that a full LNMO/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery incorporating the Al_2O_3 ALD coated LNMO outperforms the one incorporating only bare LNMO.

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Nomenclature

XRD	X-Ray Diffraction
FESEM	Field Emission Secondary Electron Microscope
HR-TEM	High Resolution Transmission Electron Microscope
ALD	Atomic Layer Deposition
TMA	Trimethylaluminum
ICPOES	Inductively Coupled Plasma Optical Emission Spectrometry
LNMO	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
EIS	Electrochemical Impedance spectroscopy
XPS	X-ray Photoelectron Spectrometer
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectroscopy
SEI	Solid Electrolyte Interface

1. Introduction

By virtue of their high energy density, lithium ion batteries (LIBs) are used as the power sources in most portable electronic devices.[1, 2] Of late, LIBs have opened up new opportunities for energy storage in large-format technologies including electric vehicles and smart grids. [1, 2] With these applications in mind, several characteristics such as energy, safety, and cost need to be improved. [1, 2] High energy densities in LIBs can be achieved by increasing either the capacity or the voltage. Efforts to develop high-capacity anode materials, such as silicon,[3] and high-capacity cathode materials, such as sulfur [4] (theoretically, 1675 mA h g^{-1}) and Li-excess transition metal oxides⁵ ($\text{Li}[\text{Li},\text{Ni},\text{Co},\text{Mn}]\text{O}_2$, typically $200\text{--}250 \text{ mA h g}^{-1}$), are in line with the capacity-based approach to increase the energy density. Regarding the voltage: there is little room for further decreasing the voltage of the anode materials because conventional graphite already operates close to 0 V (vs. Li/Li^+) and silicon reacts with Li at low voltages [$0.2\text{--}0.3 \text{ V}$ (vs. Li/Li^+)]. Therefore, development of high-voltage cathode materials is the only one way to increase the overall voltage of batteries.

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is an attractive cathode material because it can operate at higher voltages [$\sim 4.7 \text{ V}$ (vs. Li/Li^+)] than conventional LiCoO_2 . [6-9] Additionally, the energy density of LNMO (650 W h kg^{-1}) is $\sim 20\%$ higher than that of conventional LiCoO_2 . [10] The presence of three-dimensional diffusion channels for Li^+ ions in the spinel structure is an additional advantage of LNMO. Ni in LNMO exists as Ni^{2+} and is oxidized to Ni^{4+} upon Li^+ intercalation/extraction, while Mn^{4+} remains unchanged. [8, 9] This feature prevents structural degradation by disproportionation reactions and Jahn-Teller distortion, both of which are associated with Mn^{3+} .^{8,11} However, the fact that the high energy density of LNMO, enabled by the high operating voltage, is offset by limitations in the thermodynamic-

stability window of conventional organic liquid electrolytes remains a critical issue.[9,11]

Mn dissolution is also a serious problem, not only in LiMn_2O_4 but also LNMO.[8,9,12] The dissolved Mn^{2+} moves toward the anode and disrupts the solid electrolyte interphase (SEI) on the anode, resulting in rapid degradation of the full cells.[13-15] The stability of the electrode-electrolyte interface for LNMO at high voltages can be improved by either developing advanced electrolytes[16] or shielding the bare LNMO with coating materials.[15,17,18]

Atomic layer deposition (ALD) is an attractive thin film deposition technique based on a sequential and self-limiting surface reaction.[19] Compared to the conventional wet methods,[20] ALD offers several advantages such as excellent conformality and atomic-scale thickness control.[21,22] Also, because ALD offers relatively low operating temperatures,[19] reactions between the substrate and the coating materials is not an issue in most cases. To date, Al_2O_3 ALD coatings deposited on various cathode materials including LiCoO_2 , [21,23-25] $\text{Li}[\text{Ni}, \text{Co}, \text{Mn}]\text{O}_2$, [26,27] and Li-excess materials ($\text{Li}[\text{Li}, \text{Ni}, \text{Co}, \text{Mn}]\text{O}_2$) [28] and anode materials including graphite, [7,22,25] silicon, [29] and metal oxides [30,31] have been demonstrated to significantly improve the performance and safety of the cells. Recently, Al_2O_3 and LiAlO_2 ALD coatings deposited on as-formed LNMO composite electrodes have also been reported. [15, 18] However, detailed and in-depth analyses of the behaviors of the ALD-modified LNMO are lacking.

Here, ultrathin (<1 nm) Al_2O_3 ALD coatings were deposited on LNMO particles. The effects of the Al_2O_3 ALD coating on the electrochemical performance of electrodes fabricated using these materials were examined. The coulombic efficiency, cycle retention, rate capability, self-discharge behavior, and dissolution of transition metals were enhanced. The relationship between the electrochemical performance and the features of the SEI, such as

thickness and composition, for the Al_2O_3 ALD coated LNMO and the bare LNMO materials was also investigated.

2. Theoretical & Mathematical Development

2.1. Principle of lithium ion batteries

Lithium ion batteries consist of two electrodes. Lithium ions can move through the electrolyte as the ionically conductive material. Figure. 1 shows the basic model of operation in practical rechargeable lithium batteries. The major active material for anode and cathode are graphites and LiCoO_2 , respectively. In charge process, Li ions are extracted from the cathode materials and transferred to the anode side through the electrolyte which is electronically insulator and ionic conductor. When Li ions arrive at the anode, they react with electrons. In discharge process, the situation changes reverse. [1]

The situations are summarized by the equations below:

There are two advantages of lithium ion battery system. First of all, lithium ion is lightest metal for available battery materials and lowest standard electrode potential among well-known metal. For these reasons, lithium ion batteries can get high working potential, gravimetric energy density and volumetric energy density. Secondly, lithium ion batteries doesn't have memory effect and have long cycle life.

Figure 1. Scheme description of representative lithium ion battery

2.2. Composition of lithium ion batteries

2.2.1. Cathode materials

The cathode materials can be divided into structures with lithium and without lithium. Most of cathode materials usually used are transition metal oxides. In this chapter, the transition metal oxides for cathode materials are summarized.

Layered Structure

There are three types of different stacking sequence for MO_2 forming the unit cell. [32]

- A. This is the CdI_2 which arrays single blocks stacked upon one another. For example, LiTiS_2 , CoO_2 and TiS_2 shows CdI_2 structure.
- B. It show double blocks stacked upon one another to lithium –containing compounds by ion exchange form a sodium compounds.
- C. Such as LiCoO_2 , this is a cubic close-packed lattice. This structure was found triple blocks which displayed by one the-third in the basal plane. And then, triple blocks stacked on top of one another.

LiCoO₂: The LiCoO_2 as positive electrode materials was suggested for the first time in 1980. [33] Average potential range for the LiCoO_2/Li cell have been known to be 3.9 V in $0.07 < x < 1$. Although, LiCoO_2/Li cell mostly used up to 130 mA h g^{-1} ($0.5 < x < 1$, at 4.3 V), this cell have theoretical capacity to approximately 270 mA h g^{-1} . Because lithiated Li_xCoO_2 which extracted more than $x = 0.72$ from the layered structure suffered from structural instability. Also, lithiated Li_xCoO_2 exposes side reaction with at high voltage. [32, 60, 61]

To solve these problems, first, voltage of LiCoO_2 cuts before extracted lithium ion in $x = 0.5$. Secondly, AlPO_4 coatings on LiCoO_2 powders in the cut-off voltage of $< 4.5 \text{ V}$ as shown by cho et al. [34]

LiNiO₂: LiNiO_2 is attractive cathode materials as post LiCoO_2 because it is cheaper and have higher capacity than LiCoO_2 . However, LiNiO_2 has many problems for being used as

practical cathode material. First, LiNiO_2 is hard to make stoichiometric synthesis. Nickel ions are stabilized when these ions want to the bivalent ion state. [32]

Secondly, Ni^{2+} (0.69 Å) likes to move to lithium layer due to similar size to Li^+ (0.76 Å). So, Ni^{2+} ions reside at lithium layer in the LiNiO_2 . This is cation mixing. Capacity of LiNiO_2 gradually decreases due to Ni^{2+} ions in lithium layer may disrupt lithium ion diffusion.

Finally, side reaction with electrolyte makes oxygen resulting the structural instability, which is dangerous because oxygen may react with organic electrolyte. So, LiNiO_2 is limitation applying commercial battery system. [60]

LiMnO₂: Although, the layered LiMnO_2 is not easy to be synthesized because of its thermodynamic instability at high temperature, alternative methods such as preparation of isostructural NaMnO_2 followed by ion exchange have been applied. [35] LiMnO_2 have high initial capacity to 200 mA h g^{-1} , however, this material occurs irreversible phase transformation to spinel at high State of charge due to instable structure. [36]

The Ni-Mn-Co ternary system emerged to supplement for disadvantage of transition metals used LIBs. $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ have advantages which are thermal stability (manganese), low cost (manganese), stable electrochemical property (cobalt) and high capacity (nickel).

Specially, $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has outstanding charge/discharge property due to no phase transformation ($0.2 < x < 1$), enhanced cycle performance and improved safety issue. [37, 38]

Recently, it was reported that the core-shell structure controlling amount of transition metal oxide shows thermally stable and excellent electrochemical performances. [37]

Spinel structure

For Spinel structure, oxygen ions occupy forming a cubic closed packed (CCP) array. Transition metal ions occupy half of the octahedral sites and one-eighth of the tetrahedral sites. Spinel structural has three-dimension for lithium diffusion channel, which have favorable the power density property. Also, spinel structure is stable structure at high voltage

[60]

LiMnO_4 represents the cathode materials for spinel structure. Manganese is cheaper than other metals due to abundant element in the Earth. Furthermore, various oxidation states of manganese show high capacity during cycle. It is important issues that Jahn-teller distortion and disproportionation reaction by Mn^{3+} at charge process. [39, 40] To solve these problems, researchers reported excess-lithium, aluminum ions and magnesium ions to insert in spinel structure for making higher oxidation state.

The other solution is partial exchange ions from manganese to nickel to achieve high energy density and powder density such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Theoretically, Manganese and nickel oxidation state are 4+ and 2+. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is very stable due to tetravalent of manganese ion and has high working voltage at 4.7 V (vs. Li/Li^+) because redox couple is nickel ion. [12, 41] $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ high voltage spinel structure can be made into two types of crystallographic symmetries depending on the synthesis method. One is a primitive simple cubic form Mn^{4+} and Ni^{2+} ions in 12d and 4b the octahedral sites ($P4_332$). The other structure is randomly occupied Ni^{2+} and Mn^{4+} in the 16d octahedral sites forming a face centered cubic. At this time, the disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits better electrochemical performances due to low-energy barriers for Li diffusion. However, it is found to be problem that side reaction with the electrolyte and transition metal dissolution at working voltage. [41-43]

Olivine structure

Cobalt is most commonly used as transition metal in the cathode materials for LIBs. Because the cobalt oxide is very expensive, iron oxide has been researched by the researchers recently. LiFePO_4 is well known as one of olivine structure materials for LIBs. For the LiFePO_4 , working voltage for LiFePO_4 is lower than other cathode materials. But, LiFeO_4 has

high theoretical capacity to 170 mA h g⁻¹. So, LiFePO₄ has quite good energy density.

Furthermore, LiFePO₄ has a little side reaction with the electrolyte because most of organic electrolyte is belong to safety electrochemical window. After charge, LiFePO₄ gradually changes to FePO₄ during charge, FePO₄ is thermally stable at 350°C in N₂ atmosphere.

However, LiFePO₄ has poor electronic conductivity and ionic conductivity because most of poly anion has low electronic conductivity and lithium ion can move only one dimension. [60, 61]

2.2.2. Anode materials

There are four required condition for anode materials.

- A. The anode materials should have low standard reduction potential. If two electrodes are separated and have large potential difference, the cell make the high energy and power density.
- B. The anode materials may have little structural change when lithium ions insert in the negative material.
- C. For lithium ion, the anode materials need reversible reaction.
- D. The negative potential materials have high electronic conductivity and high capacity.

Lithium metal

For lithium ion battery system, lithium metal has high theoretical capacity to 3860 mA h g⁻¹. Also, lithium ion metal can make high energy density and power density because of low standard reduction potential. Many researchers study lithium metal for using next generation lithium ion battery system such as Li-S and Li-air battery. Lithium metal have a problem. This is lithium dendrite. Lithium dendrite may break a hole in the separator and connect to cathode during cycle. This is internal-short-circuit by lithium dendrite. To solve the problem, surface modification and the electrolyte additive are usually used to lithium metal for making

solid electrolyte interface. [44, 45]

Carbon- based material

Carbon can be briefly divided into two classes as graphitic and non-graphitic carbons. [46]

Graphite carbons are carbonaceous materials with a layered structure with or without a number of structural defects. They can be further classified graphite (AB) and rhombohedral graphite (ABC) with regard to the stacking order of grapheme layers although the term “graphite” is often used regardless of stacking order. Graphitic carbons include natural graphite, artificial or synthetic graphite, pyrolytic graphite and, etc.

Non-graphitic carbons which are mostly prepared by pyrolysis of organic polymer or hydro-carbon precursors at temperatures below $\sim 1500^{\circ}\text{C}$ consist of carbon atoms that are mainly arranged in a planar hexagonal network but without long-range crystallographic order in the c-direction. Additionally, Non-graphitic carbons further can be divided into graphitizing and non-graphitizing carbons.

Graphite is widely used as anode material. Lithium ion intercalate between basal planes in the graphite, which amounts as 372 mA h g^{-1} for one lithium per six carbon atoms. Graphite is similar to lithium metal for the negative redox potential (0.1-0.2 (V vs. Li/Li^{+}) and dimensional stability which result in good cycle performance. Intercalation of graphite process below equation.

Lithium ions are resided within the interlayer of the graphite host, which accompanies the increase of inter layer distance. A general feature of intercalation into graphite can be characterized by “staging phenomena”. [46]

Lithium- alloy based materials

Although, the lithium-alloy materials is similar mechanism of graphite, this materials can

get higher capacity than graphite. For example, silicon is representative material as lithium-alloy based materials. Silicon is reported to have the theoretical capacity to approximately 4000 mA h g⁻¹ because 4.4 lithium atoms can react with one silicon atom. The lithium-alloy based materials processed according to equation. [60]

Volume expansion/shrinkage are problem for Li-alloy materials. For example, the silicon suffers from approximately 400% of volume expansion during discharge. This situation may make the crack at lithium-silicon alloy. Also, decomposition of the electrolyte makes SEI from new surface areas, which lead to electrically dead particles that remain as lithiated metallic state on de-lithiation are the origins for capacity decay.

To minimize volume expansion, the several strategies are reported such as lithium-alloy/carbon nano-structure, minimized metal particle which can react with lithium ion etc. [47, 48]

2.2.3. Electrolyte

The electrolyte is the medium for transfer of ions and consist of organic solvents and salt. The basic of electrolyte for lithium ion battery is organic solvent which dissolves lithium salt. The electrolyte should meet the properties as follows: A. To high ionic conductivity. B. To chemical /electrochemical stability for electrodes. C. To have wide working temperature range. D. To have low melting points and high boiling points. E. To be safe, nontoxic, and economical. In general, mixed the electrolyte is used which is composed with linear carbonate and cyclic carbonate such as diethyl carbonate (DEC), dimethyl carbonate (DEC), ethylmethyl carbonate (EMC) and ethylene carbonate (EC). Ethylene carbonate has comparable viscosity and slightly higher dielectric constant than linear carbonates. So, the drawback of EC can be compromised by mixing liner carbonate. Lithium metal or graphite

anodes have lower reduction potential than the electrochemical window for the electrolyte, which causes the first reduction/oxidation from the electrolyte. Fortunately, electronically insulation solid electrolyte inter face layer though which Li^+ ions can transfer is formed by decomposition of electrolytes.

2.3. Solid Electrolyte Interface (SEI)

New interface layer is made by decomposition of electrolyte when it contacts to metal, graphite and oxide electrodes. This is SEI. Although, SEI layer partially is extracted or dissolved, most of it is coated on the surface as protect layer. This layer has low electric conductivity but high ionic conductivity. So, the film is called solid electrolyte interface as it works like solid electrolyte. It is important to know the generation mechanism and control the SEI after knowing features of it. In this chapter, SEI coated on cathode and anode is summarized.

Electrolyte- anode interface reaction

SEI, made by decomposition of the electrolyte on the surface, differs physical chemistry characteristic depending on surface for the anode, organic solvent and lithium salt. Carbonate electrolyte contacting lithium metal is decomposed and reduced at the same time. The film is composed of LiF , Li_2CO_3 , Li_2O and lithium alkyl carbonate using FTIR, XPS, NMR analysis.

For surface of graphite, interface reaction also is occupied. Graphite anode has high irreversible capacity at first cycle because the electron transfer from the graphite to the electrolyte occurs to make SEI. The formation of SEI by decomposition of the electrolyte in the graphite occurs approximately at 0.5- 1.7 V (V vs. Li/Li^+) and continuously to 0.0 V (V vs. Li/Li^+).

Electrolyte – cathode interface reaction

While there are many researches focused on the electrolyte- anode interface reaction, there

are only few researches on the electrolyte- cathode interface reaction. Because most of the cathode materials are located in the stable electrochemical window for the electrolyte. Recently, researchers have interest about cathode materials having high voltage. So, it is being increased about research that understanding the electrolyte-cathode interface reaction or making good SEI.

SEI layer formation on the cathode is similar to the film which is composed mixed organic and inorganic materials on the anode. LiF is mostly observed in SEI for cathode. LiF may be made by electrolyte decomposition with existence of water or with residence of lithium in the cathode. [40, 41] The inorganic materials such as LiF have been reported to adversely affect the resistance of the electrode or the passivation layer formation. [41]

2.4. Atomic Layer Deposition (ALD)

The history of ALE (transition from ALE (Atomic Layer Epitaxy) to ALD (Atomic Layer Deposition) in the 2000s) started in the 1970s in Finland. The first ALE system developed was ZnS.[49] Specially, Atomic Layer Deposition has used manly the semiconductor industry which needs thin film and precise control such as high dielectric constant gate in the MOSFET, copper diffusion barriers and low electron leakage dielectrics for magnetic read/write heads [19,49]

The advantage of ALD is lower deposition temperature than CVD for growing thin film of single crystal. Also, ALD is able to meet the needs for conformal deposition using sequential reaction, self-limiting reactions. The precursors will react sequentially to the surface areas and produce a very conformal film. As a result, the film remains smooth and conformal on the original substrate.

The advantages of ALD is summarized. [19]

1. ALD can make very thin film layer.
2. ALD processing is also extendible to very large substrates.
3. The coating layer made by ALD processing is pinhole- free.
4. The film can be formed on the powder.

The ALD of Al_2O_3 has developed as well known ALD system. The first report of Al_2O_3 ALD using TMA and H_2O dates back to the 1980s and early 1990s. [50, 51]

The surface reaction of Al_2O_3 ALD is shown below: [19, 52]

The growth rate of $1.1 - 1.2 \text{ \AA}$ per one cycle can be compared to the thickness of one Al_2O_3 “monolayer”. The monolayer thickness is equal to $3.8 \text{ \AA}$ per cycle. The growth per one cycle using ALD is lower than this estimated thickness of the monolayer. The representative ALD chemistries are TiO_2 , ZnO , ZrO_2 , HfO_2 , Ta_2O_5 etc. [19]

3. Experimental

3.1. Atomic layer deposition of Al_2O_3 on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders

Al_2O_3 films were grown by ALD on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders using a custom-made rotary ALD reactor, as described in previous reports. [21, 22] The ALD precursors were trimethylaluminum (TMA) and H_2O . During ALD, a porous stainless-steel cylinder containing the powders in the reaction chamber rotated at 140 rpm. A single cycle of Al_2O_3 ALD sequence was: (1) dose with TMA to 1.0 Torr, (2) wait for the duration of TMA reaction, (3) evacuate chamber to eliminate reaction products (CH_4) and excess TMA, (4) dose with Ar to 20.0 Torr, (5) Ar static time, (6) evacuate chamber to purge Ar and any entrained gases; (7) dose with H_2O to 1.0 Torr, (8) wait for the duration of the H_2O reaction, (9) evacuate chamber to eliminate reaction products (CH_4) and excess H_2O , (10) dose with Ar to 20.0 Torr, (11) Ar static time, and (12) evacuate chamber to purge Ar and any entrained gases. ALD was conducted at 180°C .

3.2. Materials characterization

X-ray diffraction (XRD) measurements were performed using a D8-Bruker Advance diffractometer with Cu K_α radiation ($1.54056\text{ \AA}$). The Al content of the Al_2O_3 ALD coated LNMO powders was determined using inductively coupled plasma optical emission spectrometry (ICPOES, 720-ES, Varian). Field emission scanning electron microscopy (FESEM) images were obtained using a Nanonova 230 microscope (FEI). High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM-2100F microscope (JEOL).

3.3. Electrochemical characterization

The LNMO composite electrode was prepared by spreading the LNMO powder (Mitsui Corp.), Super P, and poly(vinylidene fluoride) (PVDF) binder (KF1100, Kureha Inc.) on a piece of Al foil in a weight ratio of LNMO:Super P:PVDF = 90:5:5. The mass of LNMO loaded into the composite electrode was $\sim 5.5 \text{ mg cm}^{-2}$. 2032-type coin cells were assembled in an Ar-filled dry glove box. Galvanostatic charge-discharge cycling was performed over the potential window 3.0–5.0 V (vs. Li/Li⁺) at 30 °C at a current density of 0.1C (14 mA g⁻¹) for the first two cycles and 0.5C for the subsequent cycles. Li metal foil was used as the counter electrode in the half cells. A 1.0 M solution of LiPF₆ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) (3:4:3 v/v) (Panax Inc.) was used as the electrolyte. A porous polypropylene (PP)/polyethylene (PE)/PP tri-layer film (Celgard Inc.) was used as the separator. AC impedance measurements were performed using a signal with amplitude 10 mV over a frequency range from 100 kHz to 5 mHz using an IviumStat (IVIUM Technology Corp.). After the LNMO/Li half cells were discharged to 60 mA h g⁻¹ at 0.1C after the requisite number of cycles and rested for 6 h, AC impedance spectra were recorded at the open circuit voltage, which was $\sim 4.7 \text{ V}$ (vs. Li/Li⁺). For the full-cell tests, Li₄Ti₅O₁₂ (LTO) was used as the anode material. The composite anode included LTO, Super P, and PVDF (80:10:10 by weight). The mass ratio of LNMO/LTO in the LNMO/LTO full cells was ~ 1.4 . The full cells of LNMO/LTO were cycled between 2.00 and 3.45 V at 0.5C. Based on the reversible capacities obtained from the half-cell experiments on LTO/Li ($\sim 160 \text{ mA h g}^{-1}$ at 0.1C between 1.2–2.0 V), the

np ratio of LNMO/LTO was determined to be ~0.9. All of the cells were assembled in an Ar-filled dry box and tested at 30 °C.

3.4. Ex-situ analyses

For the *ex-situ* analyses of the electrodes, the cycled electrodes collected from the disassembled coin cells were rinsed with anhydrous DMC and dried in the Ar-filled dry box. For the *ex-situ* XRD analyses, a specially designed cell was used: the air-sensitive cycled electrodes were placed on a beryllium window and hermetically sealed inside the Ar-filled dry box. The amount of dissolved transition metal was obtained by the following procedure: The dissolved transition metals in the composite electrodes and the electrolytes were collected by rinsing the composite electrode, the separator, and the coin cell components in DMC. The transition metals deposited on the lithium metal counter electrode were collected by dissolving the cycled lithium metal in deionized water. (Caution: The reaction between lithium and water is dangerous.) The total amount of dissolved transition metals was determined using the aforementioned DMC and water solutions by ICPOES measurements. *Ex-situ* characterization with XPS was performed using a K-alpha X-ray photoelectron spectrometer (Thermo Fisher) with a monochromatic Al K $_{\alpha}$ source (1486.6 eV). Time-of-flight secondary ion mass spectrometry (TOFSIMS) analyses were conducted on a TOF SIMS 5 (ION TOF). A 25 kV Bi $^{+}$ and O $^{+}$ source was employed for analysis and sputtering. For the *ex-situ* XPS and TOFSIMS analyses, the LNMO/Li cells were discharged to 3.0 V at 0.1C after the selected cycle.

4. Results & Discussion

The XRD patterns of the bare and Al₂O₃ ALD coated LNMO particles shown in Figure 1a match well with a disordered phase with a space group of $Fd\bar{3}m$. [7] The XRD pattern of the Al₂O₃-coated LNMO is identical to that of the bare LNMO; this indicated that the ALD operation did not affect the bulk structure of LNMO. Figures 1b and 1c show HRTEM images of the bare LNMO particles and the Al₂O₃-coated LNMO particles after 10 ALD cycles. It is apparent that a ~2-nm-thick amorphous layer was deposited on the crystalline substrate in Figure 1c, a situation that is supported by previous reports in which the Al₂O₃ grown by ALD is amorphous and the ALD film growth rate on powders is ~2 Å per cycle.²¹ As an alternative method to estimate the thickness of the Al₂O₃ ALD coating, the Al content of the Al₂O₃-coated LNMO particles was measured by ICPOES after 10 ALD cycles, giving 828 ppm. Given the surface area (0.25 m² g⁻¹) of LNMO as determined by the N₂ adsorption-desorption isotherm method and the specific density of ALD-grown Al₂O₃ (3.0 g cm⁻³), [19] the thickness of the Al₂O₃ ALD film was calculated as 2.1 nm. This value agrees perfectly with the results in Figure 1c and the calculation based on a growth rate of 2 Å per deposition cycle, demonstrating that the Al₂O₃ ALD coating on the LNMO is very conformal.

Figure 1. a) XRD patterns of the bare and Al_2O_3 ALD coated (4 ALD cycles) LNMO powders. HRTEM images of b) the bare LNMO particles and c) the Al_2O_3 ALD coated (10 ALD cycles) LNMO particles.

Figure 2a shows the initial charge-discharge voltage profiles of bare and Al_2O_3 ALD coated LNMO at 0.1C (14 mA g^{-1}) at 30°C . The plateaus at ~ 4 and ~ 4.7 V are associated with $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reactions, respectively. [8, 9] The occurrence of a plateau at 4 V is typical of a disordered phase. [7-9] Polarization increases with an increasing number of ALD cycles; consequently, the capacity decreases. Figure 2b shows the discharge capacities at 0.1C and 0.5C as a function of the number of ALD cycles. The abrupt capacity decrease at 6 ALD cycles is associated with the impeded transport of both electrons and Li^+ ions through the insulating Al_2O_3 ALD coating layers, which agrees well with previous reports. [21,22]

Figure 2c depicts the cycle performances of bare and Al_2O_3 ALD coated LNMO cells cycled at 30°C at 0.1C for the first two cycles and 0.5C for the subsequent cycles. The capacities of the LNMO electrodes subjected to 4, 6, and 10 ALD cycles increase with the number of charge/discharge cycles. The increases in capacity of the LNMO electrodes after the initial charge/discharge cycles are exceptionally large for the materials fabricated using 4 and 6 ALD cycles (indicated by the arrows). These increases may reflect gradual changes in the Al_2O_3 ALD coating layer, a possibility which will be discussed in detail later. The 4 ALD cycles on LNMO show a significant improvement in capacity retention, while the 2 ALD cycles do not. If the capacity retention after the 150th charge-discharge cycle is compared to the retention after the 20th cycle (where the capacity stabilized), the LNMO with 4 ALD cycles exhibits a value of 98.0% while the bare LNMO gives 94.3%. Figure 2d shows the coulombic efficiency of the bare and Al_2O_3 ALD coated LNMO electrodes. The coulombic efficiency is very important because it reflects the performance of the full cell, in which the Li source is limited. [24] For example, a coulombic efficiency of 99% indicates that the full battery loses 1.0% of its capacity every charge-discharge cycle, even if the half

cell shows no capacity loss. No enhancement in coulombic efficiency by the Al_2O_3 coatings during the initial charge/discharge cycle is observed in Figure 2d. However, at higher numbers of charge-discharge cycles, all the Al_2O_3 ALD coated LNMO electrodes exhibit much higher coulombic efficiencies than the bare LNMO electrodes do. For example, the coulombic efficiency of the coated LNMO after 4 ALD cycles at after the 80th charge-discharge cycle is 99.5%, which contrasted sharply with the value of 97.9% determined for the bare LNMO. Because the LNMO particles subjected to 4 ALD cycles showed optimal performance in terms of capacity, coulombic efficiency, and cycle performance, this material will be extensively compared to the bare LNMO in the following results.

Figure 2. a) Initial charge-discharge voltage profiles, b) discharge capacity as a function of ALD cycle number, c) cycle performance, and d) coulombic efficiency of the bare and Al_2O_3 ALD coated LNMO electrodes. The numerals in (a) indicate the ALD cycle numbers for each sample.

Figure 3 compares the rate performances of bare and Al_2O_3 ALD coated (using 4 ALD cycles) LNMO. Increasing the C-rate gradually from 0.1C to 2C resulted in slightly higher polarization and lower capacities in the Al_2O_3 ALD coated LNMO than in the bare LNMO. After prolonged charge-discharge cycling at 4C, however, the trend reversed. This behavior could have originated from severe degradation of the bare LNMO during charge-discharge cycling. The subsequent cycling at 1C starting from the 28th charge-discharge cycle results in noticeable difference in capacity fade between bare and Al_2O_3 ALD coated LNMO, indicating that accumulated fatigue produced by the side reactions at high C-rates is much more significant for the bare LNMO than the Al_2O_3 ALD coated material.

Figure 3. a) Variation in the discharge capacities vs. charge-discharge cycle number and b) discharge voltage profiles for bare and Al₂O₃ ALD coated (using 4 ALD cycles) LNMO electrodes at different C-rates between 3.0 and 5.0 V.

To compare changes in the resistances of bare and Al_2O_3 ALD coated (using 4 ALD cycles) LNMO, electrochemical impedance spectroscopy (EIS) measurements were conducted, as shown in Figure 4. Figure 4a shows Nyquist plots collected after different numbers of charge-discharge cycles. All spectra are comprised of two semicircles and a low-frequency tail. The high-frequency semicircle is associated with transport of Li^+ ions through the SEI film[53] or the inter-particle contact resistance in the composite electrodes.[54] The mid-frequency semicircle reflects the charge-transfer resistance at the electrode/electrolyte interface.[53,55] The low-frequency tail arises from Li^+ ion diffusion in the bulk LNMO.[53,55] After the spectra in Figure 4a were fitted using the Randles circuit, as shown in Figure 4b,[55] the resistance values were obtained; these are plotted in Figure 4c. Both the R_1 and R_2 values after the 2nd charge-discharge cycle for the Al_2O_3 ALD coated LNMO are higher than those for the bare LNMO, indicating that the transport of Li^+ ions was impeded by the insulating Al_2O_3 film. It should be emphasized that both the R_1 and R_2 values for the Al_2O_3 ALD coated LNMO do not change much during charge-discharge cycling, whereas the R values for the bare LNMO increases sharply. This strongly suggests that the Al_2O_3 ALD coatings suppresses the side reactions successfully during continuous charge-discharge cycling.

Figure 4. EIS results for the bare and Al_2O_3 coated (using 4 ALD cycles) LNMO electrodes: a) Nyquist plots at different numbers of charge-discharge cycles, b) equivalent circuit model for fitting the EIS data in (a), and c) resistance values obtained from the EIS data in (a) using the model in (b).

The severe side reaction of LNMO at high operating voltage also leads to negative effects related to self-discharge. [12] Figure 5 compares the results of self-discharge of bare and Al₂O₃ ALD coated (using 4 ALD cycles) LNMO. Figures 5a and 5b show the discharge voltage curves measured after the LNMO/Li cells were fully charged to 5 V (vs. Li/Li⁺) and kept at 30 °C for various lengths of time. It is evident that the discharge capacities of the bare LNMO decreases significantly as the storage time increases whereas the Al₂O₃ ALD coated LNMO do not lose much capacity. The lowered discharge capacity after storage reflects the fact that the charged LNMO could self-discharge *via* the reaction [12]

The lithiation of fully charged LNMO by self-discharge is also confirmed by the *ex-situ* XRD results shown in Figure 5c. The smaller negative shift of the peaks associated with the Al₂O₃ ALD coated LNMO compared to those of the bare LNMO directly indicates a smaller amount of inserted Li.[7] In other words, there was less self-discharge.

Figure 5. Results of the self-discharge tests of bare and Al_2O_3 coated LNMO (using 4 ALD cycles) electrodes. Discharge voltage profiles of a) bare and b) Al_2O_3 ALD coated LNMO electrodes after the LNMO/Li cells were fully charged to 5 V at 0.1C and subsequently kept at 30 °C for different times. c) Corresponding *ex-situ* XRD results of the LNMO electrodes.

The degrees of the dissolution of transition metals in bare and Al_2O_3 -coated LNMO were also compared using ICPOES, as shown in Figure 6. The overall amount of dissolved transition metal was obtained by collecting residuals not only from the used electrolytes and coin cell components, but also the cycled Li metal. The fully charged LNMO/Li cells kept at 30 °C for 7 days were used. The Al_2O_3 ALD coated LNMO exhibited significantly less dissolved transition metals. In particular, the amount of dissolved Mn recovered from the Al_2O_3 ALD coated LNMO cell is 6.6 times less than that recovered from the bare LNMO cell. Enhanced dissolution of Mn is related to the evolution of the soluble Mn^{2+} . [40] First, the disproportionation of Mn^{3+} can generate the Mn^{2+} . [56] Second, the severe side reaction in LNMO at high voltages also promotes the dissolution of Mn. [12] It has been reported that higher state of charge results in increased dissolution of Mn and Ni from LNMO. [12] At high voltages, anion oxidation can be accompanied by the reduction of Mn^{4+} to Mn^{3+} , which in turn leads to disproportionation and the generation of soluble Mn^{2+} . [40] Alternatively, the severe side reaction at high voltage is also known to produce more HF, which likely promotes the dissolution of transition metals. [12,40]

Figure 6. Weight fraction of dissolved transition metals from the bare and Al_2O_3 ALD coated (4 ALD cycles) LNMO electrodes after the LNMO/Li cells were fully charged to 5 V at 0.1C and subsequently kept at 30 °C for 1 week.

From the extensive comparative analyses of coulombic efficiency, cycle performance, rate capability, EIS spectra, self-discharge behavior, and transition-metal dissolution measurements, it was confirmed that the Al_2O_3 ALD coating significantly suppressed the undesirable side reaction at LNMO surfaces. To understand the aforementioned behaviors in-depth, surface analyses were carried out. Figure 7 shows the surface morphologies of bare and Al_2O_3 ALD coated (using 4 ALD cycles) LNMO electrodes before and after charge-discharge cycling. The pristine electrodes (Figures 7a and 7c) have similar morphologies. After charge-discharge cycling, however, the surfaces of the electrodes look quite different. The bare LNMO electrode exhibits smooth surfaces, indicating a thick SEI layer was deposited. In contrast, the surface morphology of the Al_2O_3 ALD coated LNMO electrode does not change significantly. This suggests that the SEI layer on the Al_2O_3 ALD coated LNMO is much thinner than that on the bare LNMO, which in turn reflects a smaller degree of side reaction.

Figure 7. FESEM images of bare and Al_2O_3 coated (4 ALD cycles) LNMO electrodes before and after 50 charge-discharge cycles.

In order to collect in-depth information about the SEI layers, *ex-situ* XPS signals of for the C 1s, O 1s, F 1s, and Al 2p were collected for bare and Al₂O₃ ALD coated (using 4 ALD cycles) LNMO electrodes both before and after 50 charge-discharge cycles at 30 °C, as shown in Figure 8. The peak assignments and deconvolution method were based on previous reports. [24,57,58] Comparing the signals after the 50 charge-discharge cycles, four features are notable. First, the relative intensity of the C–C peak at 285.0 eV in Figure 8a is smaller for the bare LNMO electrode than the Al₂O₃ ALD coated LNMO electrode, which supports the assessment that there was a thicker SEI layer on the bare LNMO electrode. This behavior also agrees with the smaller intensity of the O 1s peak from Ni^(II)O at 530.3 eV for the bare LNMO after charge-discharge cycling compared to the Al₂O₃ ALD coated LNMO, as shown in Figure 8b. Second, much higher intensities related to organic species, including alkyl carbonates and Li₂CO₃, as well as inorganic species, such as LiPF_xO_y, are observed for the bare LNMO electrode compared to the Al₂O₃ ALD coated LNMO electrode, as indicated by the arrows in Figure 8a and 8b. Third, a much higher intensity of the LiF peak at 685.6 eV is observed for the Al₂O₃ ALD coated LNMO compared to the bare LNMO, as shown in Figure 8c. This behavior can be interpreted as the result of much thinner organic SEI components on the Al₂O₃ ALD coated LNMO electrode than on the bare LNMO electrode. However, a definite explanation is prohibited because the contribution of AlF₃ or AlO_xF_y may be superimposed on the LiF peak. Fourth, the Al 2p peak of the Al₂O₃ ALD coated LNMO shown in Figure 8d becomes broadened and positively shifted after charge-discharge cycling. This result is a direct evidence of fluorination of the Al₂O₃ ALD coating layer by HF upon repeated charge-discharge cycles. The final composition of the Al₂O₃ ALD coating is somewhere in between Al₂O₃ and AlF₃. The chemically or electrochemically driven transformation of Al₂O₃ into AlO_xF_y should be accompanied by

microstructural changes as well. Assuming the specific density of AlF_3 is $\sim 3.0 \text{ g cm}^{-3}$, based on the crystallographic data for AlF_3 (JCPDS no. 43-0435: 2.82 g cm^{-3} , no. 44-0231: 3.13 g cm^{-3} , no. 47-1659: 3.02 g cm^{-3}) and considering the specific density of amorphous Al_2O_3 ($\sim 3.0 \text{ g cm}^{-3}$), the volume change produced by complete fluorination of Al_2O_3 to 2AlF_3 is

$$\frac{(2 \times \text{molar volume of AlF}_3) - \text{molar volume of Al}_2\text{O}_3}{\text{molar volume of Al}_2\text{O}_3} \times 100 = 64\% \quad (5-2)$$

which is comparable to the values obtained when the conversion-type transition metal oxides react with Li. [59] In this regard, the possibility of cracks developing in the ALD coating layer during fluorination is not surprising. The microstructural changes induced by fluorination thus can lead to an increased rate of Li^+ ion transport, and consequently account for the dramatic increase in capacity during the initial charge-discharge cycles shown in Figure 2c. However, the microstructural change in the ALD coating layer is not desirable in terms of conformality of the protective coatings. In this regard, further improvement of electrochemical performance of LNMO is believed to be possible by directly coating with AlF_3 by ALD.

Figure 8. *Ex-situ* XPS results of bare and Al_2O_3 ALD coated LNMO electrodes before and after 50 charge-discharge cycles. The signals for C 1s, O 1s, F 1s, and Al 2p are shown in (a), (b), (c), and (d), respectively.

Figure 9 shows the depth profiles of cationic fragments obtained by *ex-situ* TOFSIMS experiments for the bare and Al₂O₃-coated LNMO electrodes after 50 charge-discharge cycles at 30 °C. The LiF⁺ signals suggest that the Al₂O₃ ALD coated LNMO electrode is coated with slightly thinner F-bearing SEI species than the bare LNMO electrode. The CH₃⁺ signals, which represent the organic SEI components, however, demonstrates the huge impact of the Al₂O₃ ALD coating. The etching time at which the intensity decreases to half of its original is 7.4 and 2.5 s for the bare LNMO electrode and the Al₂O₃ ALD coated LNMO electrode, respectively. This clearly indicates a much thinner organic SEI component on the Al₂O₃ ALD coated LNMO than on the bare LNMO, which is nicely supported by the *ex-situ* XPS results in Figure 8.

Figure 9. *Ex-situ* TOFSIMS depth profiles of bare and Al₂O₃ ALD coated LNMO electrodes after 50 charge-discharge cycles for a) LiF⁺, b) CH₃⁺, and c) Al⁺.

Based on the *ex-situ* surface analyses by XPS and TOFSIMS, a schematic diagram representing the SEI layers on bare and Al_2O_3 ALD coated LNMO particles after charge-discharge cycles was constructed; this is shown in Figure 10. Compared to the bare LNMO particles, the Al_2O_3 ALD coated LNMO particles have much thinner SEI layers and the amount of organic species is lower. The Al_2O_3 ALD layer also became fluorinated.

Figure 10. Schematic diagram of a) bare and b) Al_2O_3 ALD coated LNMO electrodes after charge-discharge cycling, showing different features in the SEI layers.

Finally, full cells of LNMO/Li₄Ti₅O₁₂ incorporating bare and Al₂O₃ ALD coated LNMO were cycled between 2.00 and 3.45 V at 0.5C at 30 °C, as shown in Figure 11. The full cell with the Al₂O₃ ALD coated LNMO appears to outperform the one with bare LNMO. The improved performance of the LNMO particles with the Al₂O₃ ALD coating can be explained by the enhanced stability of LNMO and the higher coulombic efficiency (or lower irreversible Li consumption), as demonstrated by the half-cell results.

Figure 11. Cycle performance of LNMO/LTO full cells cycled between 2.00 and 3.45 V at 0.5C at 30 °C. Bare (*b*) and Al₂O₃ ALD coated (*c*, 4 ALD cycles on powders) LNMO electrodes were used.

5. Conclusions

Ultrathin (< 1 nm) Al_2O_3 films were grown using ALD on LNMO particles.

Significantly improved performance at 30 °C associated with the Al_2O_3 ALD coating was demonstrated not only in the coulombic efficiency, cycle retention, and rate capability, but also in the self-discharge behavior and the dissolution of transition metals. The combined *ex-situ* surface analyses using XPS and TOFSIMS revealed that the SEI layer on the Al_2O_3 ALD coated LNMO was much thinner and contained fewer organic species than the layer on the bare LNMO. This difference is the result of suppression of the side reaction at high voltages. Also, fluorination of the Al_2O_3 ALD layer was confirmed, shedding light on strategies for further improvement. Finally, the full LNMO/LTO battery incorporating the Al_2O_3 ALD coated LNMO was demonstrated to outperform the one incorporating bare LNMO.

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