

Enhanced Stability of LiCoO_2 Cathodes in Lithium-ion Batteries Using Surface Modification by Atomic Layer Deposition

Yoon S. Jung*, Andrew S. Cavanagh**, Anne C. Dillon***, Markus D. Groner****, Steven M. George*****, and Se-Hee Lee*****†

*Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, CO, USA

**Department of Physics, University of Colorado at Boulder, Boulder, CO, USA

***National Renewable Energy Laboratory, Golden, CO, 80401 USA

**** Department of Chemistry and Biochemistry and Department of Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, CO, USA

*****ALD NanoSolutions Inc., 580 Burbank St., Unit 100 Broomfield, CO, USA

*****WCU Hybrid Materials, Seoul National University, Seoul, Korea

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ABSTRACT

Ultrathin atomic layer deposition (ALD) coatings were found to enhance the performance of lithium-ion batteries (LIBs). Previous studies have demonstrated that LiCoO_2 cathode powders coated with metal oxides with thicknesses of $\sim 100\text{-}1000$ Å grown using wet chemical techniques improved LIB performance. In this study, LiCoO_2 powders were coated with conformal Al_2O_3 ALD films with thicknesses of only $\sim 3\text{-}4$ Å established using 2 ALD cycles. The coated LiCoO_2 powders exhibited a capacity retention of 89% after 120 charge-discharge cycles in the $3.3\text{-}4.5$ V (vs. Li/Li^+) range. In contrast, the bare LiCoO_2 powders displayed only a 45% capacity retention. This dramatic improvement may result from the ultrathin Al_2O_3 ALD film acting to minimize Co dissolution or to reduce surface electrolyte reactions.

Key words: Lithium-ion batteries, Atomic layer deposition, Surface modification, Stability, Cathode

1. Introduction

Efficient and durable electrical energy storage is one of the major limiting factors for wide-spread adoption of renewable energy. Since the Sony Corporation first commercialized lithium ion batteries (LIBs) in the early 1990s, LIBs have been emerging as a major energy storage device for portable electronics.¹⁾ However, greatly improved LIBs are needed for their use in plug-in hybrids or all-electric vehicles.

The construction of nanoscale electrode materials has been a critical issue for LIBs.²⁾ $\text{Li}_{1-x}\text{CoO}_2$ is the most commercialized cathode material. Unfortunately, the practical use of $\text{Li}_{1-x}\text{CoO}_2$ is limited to $x \leq 0.5$, because the stability rapidly deteriorates when potentials higher than $4.2\text{-}4.3$ V (vs. Li/Li^+) are used for $x > 0.5$.^{2,3)} This instability problem can be addressed by coating the LiCoO_2 powders with nanosized metal oxides.^{2,4,5)} Examples of the metal oxides that have been explored include Al_2O_3 , ZrO_2 , TiO_2 , MgO , SnO_2 and ZnO . Metal phosphates^{2,6)} (e.g. AlPO_4) and metal fluorides⁷⁾ (e.g. AlF_3) have also been studied as coatings.

The majority of the coating strategies have been based on

wet-chemical techniques such as the sol-gel method.^{2,4,7)} The wet-chemical coating methods require large amounts of solvent and usually an excessive amount of precursor. A post-heat-treatment is also necessary after the sol-gel coating.^{2,4,7)} In contrast, atomic layer deposition (ALD) is a method of thin film growth using sequential, self limiting surface reactions.⁸⁾ ALD coatings are conformal and offer atomic thickness control. ALD could be a promising alternative method to coat electrode materials for LIBs. Although ALD films have been employed in a variety of application areas,⁹⁾ the use of ALD films for LIB electrodes has not been pursued extensively.¹⁰⁾

In this paper, the electrochemical performance is reported for LiCoO_2 coated with ultrathin conformal Al_2O_3 films by ALD. The experiments examine the effects of coating material and coating thickness on cycle performance and rate capability. The results reveal that ultrathin Al_2O_3 ALD films can dramatically enhance the stability of LiCoO_2 cathodes.

2. Experimental

Atomic Layer Deposition on LiCoO_2 : ALD on LiCoO_2 particles was performed using a rotary ALD reactor. The Al_2O_3 ALD reaction sequence was: (1) trimethylaluminum (TMA) dose to 1.0 Torr; (2) TMA reaction time; (3) evacuation of reaction products and excess TMA; (4) N_2 dose to 20.0 Torr;

†Corresponding author : Se-Hee Lee

E-mail : sehee.lee@colorado.edu

Tel : +1-303-492-7889 Fax : +1-303-492-3498

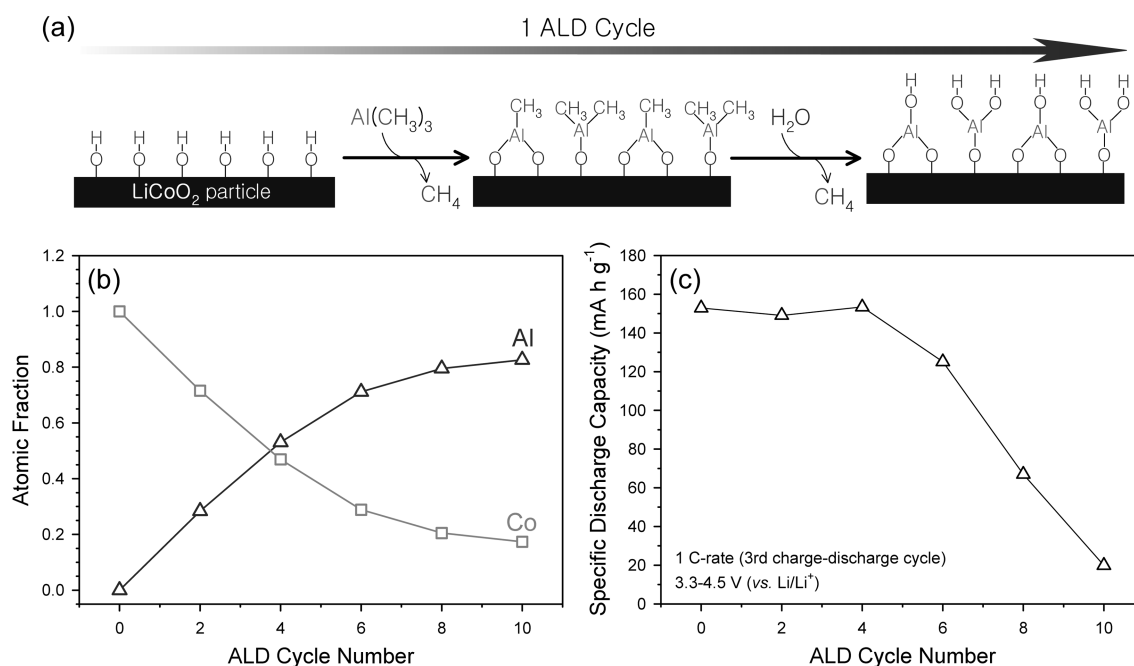


Fig. 1. (a) Schematic representation of atomic layer deposition of Al₂O₃ on LiCoO₂ particles. (b) Atomic fraction of Al and Co for Al₂O₃-coated LiCoO₂ powders as a function of the ALD cycle number. Atomic fraction was determined from XPS spectra (Fig. 2). (c) Specific discharge capacity of Al₂O₃-coated LiCoO₂ electrodes as a function of the ALD cycle number.

(5) N₂ static time; (6) evacuation of N₂ and any entrained gases; (7) H₂O dose to 1.0 Torr, (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 constitutes one AB cycle of Al₂O₃ ALD which is defined in equations (1) and (2). Al₂O₃ ALD was conducted at 180°C.

Materials Characterization: XPS measurements were performed on a PHI 5600 X-ray photoelectron spectrometer using a monochromatic Al K_α source (1486.6 eV). The base pressure in the XPS during analysis was 3 × 10⁻¹⁰ Torr. During the data acquisition, the constant analyzer energy mode was employed at pass energies between of 58.7~93.9 eV and a step size between 0.25~0.4 eV. In order to obtain the atomic fraction of Co and Al (Fig. 1(b)) from XPS spectra (Fig. 2), the effective attenuation length was calculated using the "NIST Electron Effective Attenuation Length Database, Version 1.1." The input parameters were the Co 2p_{3/2} kinetic energy, the asymmetry parameter (from the manual to the data base), the over layer film composition (Al₂O₃), the number of valence electrons, the material's band gap and the material's density (specific to ALD Al₂O₃, determined by X-ray reflectivity (XRR)). The effective attenuation length (this is the distance for the Co signal to decrease by a factor of 1/e) was determined to be 16.7 Å. Using this information we fit the curves in Fig. 1(b) to determine the growth rate. We assumed that the LiCoO₂ surface is flat for this modeling. A LiCoO₂-embedded Ag foil for obtaining XPS spectra was prepared by pressing (~1.5 GPa) the LiCoO₂ powders that were spread on a piece of Ag foil with a thickness of 0.5 mm. The composite electrodes were

used for the *ex-situ* XPS analysis. Cells were disassembled and electrodes were rinsed with dimethyl carbonate (DMC) and dried in an Ar-filled dry box.

Electrochemical Characterization: For the galvanostatic charge-discharge cycling, the composite electrode was prepared by spreading a slurry mixture of LiCoO₂ powder (7~10 μm, L106, LICO Technology), AB, and PVDF (83.0 : 7.5 : 9.5 weight ratio) on a piece of Al foil. Cells were assembled in an Ar-filled dry box and tested in a temperature-controlled oven. The galvanostatic charge-discharge cycling was performed with a two-electrode 2032-type coin cell in the potential range of 3.3~4.5 V (*vs.* Li/Li⁺) at a current density of 0.1 C-rate (14 mA g⁻¹) for the first two cycles and 1 C-rate for the subsequent cycles at room temperature.

Li metal foil was used as the counter electrode. 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and DMC (1:1 v/v) was used as the electrolyte. Porous 20 μm thick polypropylene (PP)/poly ethylene (PE)/PP tri-layer film was used as the separator. The EIS study was performed using a 1280C Solartron instrument. The AC impedance measurement was recorded using a signal with an amplitude of 5 mV and frequency range from 20 kHz to 5 mHz. After the LiCoO₂/Li cells were charged to 4.5 V (*vs.* Li/Li⁺) with a current density of 0.1 C-rate (14 mA g⁻¹) and stabilized by resting for 6 h, the AC impedance spectra were recorded at the open circuit voltage.

3. Results and Discussion

Al₂O₃ ALD films were grown directly on the LiCoO₂ particles using a rotary reactor. The precursors utilized for Al₂O₃

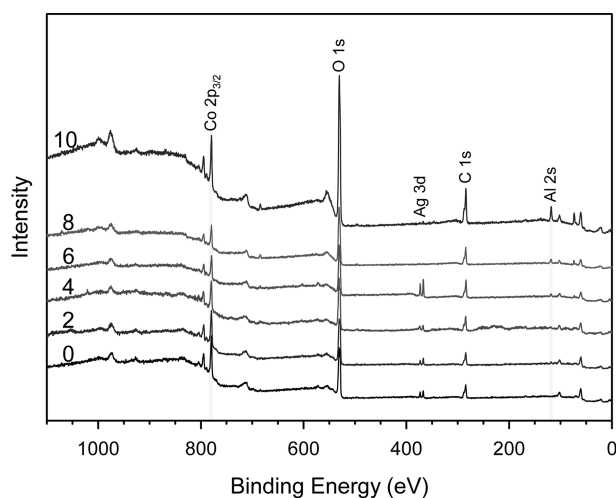
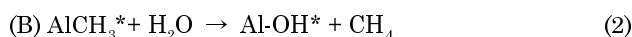


Fig. 2. Series of XPS spectra for bare and Al₂O₃-coated LiCoO₂ powders according to ALD cycle number which is indicated in the inset. Atomic fraction of Al and Co in Fig. 1 was obtained by analyzing the intensities of Al 2s and Co 2p_{3/2} peaks.

ALD are trimethylaluminum (TMA) and H₂O as shown in Fig. 1(a). The two self-limiting surface reactions that define Al₂O₃ ALD growth are¹¹:



The typical growth rate for this chemistry is 1.1~1.2 Å per ALD cycle.¹¹ However, due to the large surface of the LiCoO₂ powders, H₂O may not be completely purged from the reactor. The presence of H₂O in the reactor during the TMA reaction may lead to slightly larger growth per cycle resulting from some chemical vapor deposition (CVD).¹²

Fig. 1(b) shows the Al and Co atomic fraction as determined by X-ray photoelectron spectroscopy (XPS) (Fig. 2). The rapid attenuation of the Al signal is evidence that the Al₂O₃ ALD is conformally coating the LiCoO₂ particles. If the attenuation of the Co signal is modeled as Al₂O₃ grown on a wafer of LiCoO₂, XPS analysis indicates a growth rate of 2.2 Å per ALD cycle.

Fig. 1(c) plots the specific discharge capacity for a current density of 1 C-rate (140 mA g⁻¹) as a function of the number of Al₂O₃ ALD cycles deposited on the LiCoO₂ particles. The capacity does not change considerably for up to 4 ALD cycles. After 6 ALD cycles, the capacity starts to decrease significantly and shows a negligible value of ~20 mA h g⁻¹ after the 10th ALD cycle. This loss of capacity is attributed to the large overpotential required for particles with more than 6 ALD cycles.

The loss of capacity shown in Fig. 1(c) could result from the electronically insulating character of Al₂O₃ ALD film. The bare LiCoO₂ powders have an electronic conductivity of 2 × 10⁻⁴ S cm⁻¹. After only two ALD cycles, the electronic conductivity is significantly reduced to 5 × 10⁻⁵ S cm⁻¹. The con-

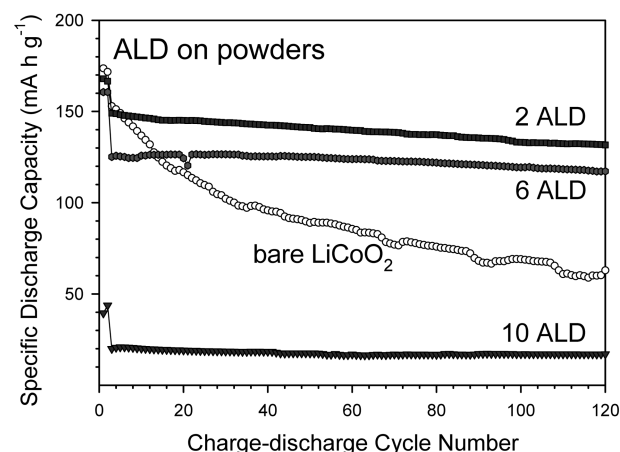


Fig. 3. Charge-discharge cycle performance of Al₂O₃-coated LiCoO₂ electrodes. ALD was performed on the LiCoO₂ powders (2, 6, and 10 ALD cycles).

ductivity continuously decreases with increasing ALD cycle. The slow transport of Li⁺ ions through the Al₂O₃ film could also restrict the charge-discharge kinetics.

An Al₂O₃ ALD film with a thickness of only >10 Å can significantly reduce the electronic and/or ionic conductivity and slow the charge/discharge kinetics. This behavior is surprising because kinetic problems have not been reported for LiCoO₂ powders coated using wet-chemical routes.^{2,4-7,13} These LiCoO₂ powders have been claimed to be uniformly coated with several or tens of nanometer-thick materials.^{5,7} In many wet-chemical procedures the samples are prepared by a final post-heat-treatment. This may lead to inter-diffusion between Al₂O₃ layer and LiCoO₂ core and seems to result in LiAl_xCo_{1-x}O₂ solid-solution.⁴ This alloy, LiAl_xCo_{1-x}O₂, may show enhanced Li⁺ ion transport properties and/or increased electronic conductivity.

Fig. 3 compares the cycle performance for several electrodes when cycled in the range of 3.3~4.5 V (*vs.* Li/Li⁺) with a current density of 0.1 C-rate (14 mA g⁻¹) for the first two cycles and 1 C-rate for the subsequent cycles. The initial capacity of LiCoO₂ powders coated with Al₂O₃ ALD using 2 ALD cycles is similar to the initial capacity of bare LiCoO₂ powders. The capacity decreases for 6 and 10 ALD cycles. This reduction in capacity is attributed to restricted electron transport and slow Li⁺ diffusion kinetics in the Al₂O₃ ALD layer. However, the LiCoO₂ powders coated with Al₂O₃ ALD show dramatically improved retention of capacity versus charge/discharge cycle number regardless of the ALD coating thickness.

Fig. 4(a) shows the charge/discharge voltage profiles for electrodes fabricated with bare LiCoO₂ powders or ALD-coated LiCoO₂ powders using 2 ALD cycles. The polarization increases fast and the specific capacity drops rapidly versus charge/discharge cycle number for the electrodes prepared using the bare LiCoO₂ powders. In contrast, the voltage profile and specific capacity do not change significantly for the electrodes made using the ALD-coated LiCoO₂ powders.

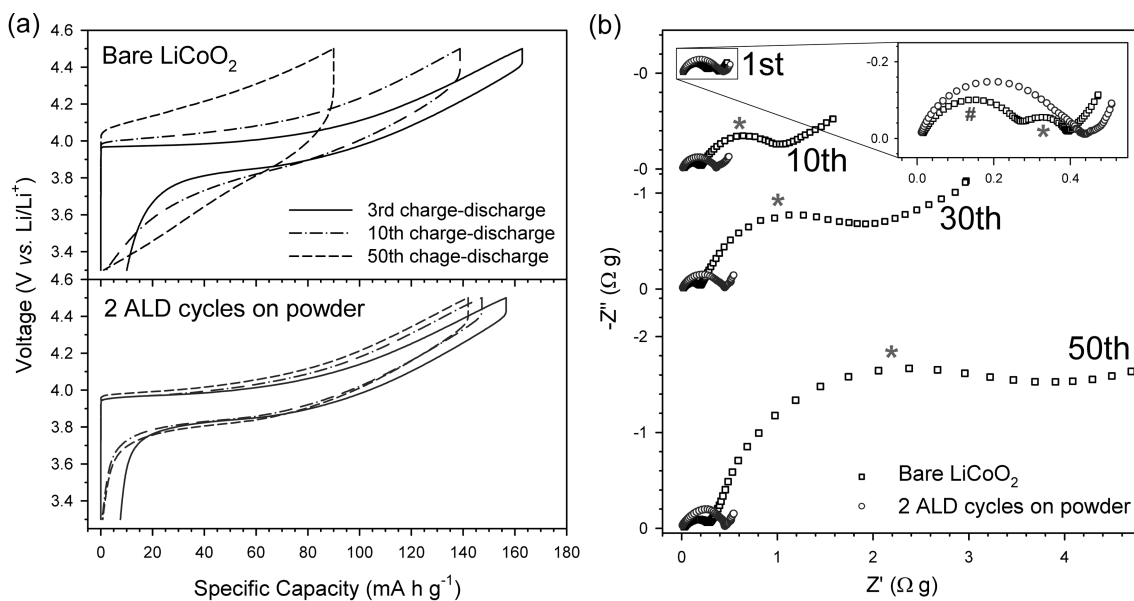


Fig. 4. (a) Charge-discharge voltage profiles of bare and Al_2O_3 ALD-coated LiCoO_2 electrodes at the 3rd, 10th, and 50th cycle when cycled at a current density of 1 C-rate (140 mA g^{-1}). (b) Series of mass-normalized impedance spectra for bare and Al_2O_3 ALD-coated LiCoO_2 electrodes for various charge-discharge cycle numbers.

Electrochemical impedance spectroscopy (EIS) analyses was also utilized to evaluate the performance of electrodes prepared using bare LiCoO_2 powders and Al_2O_3 ALD-coated LiCoO_2 powders prepared using 2 ALD cycles. Results versus number of charge-discharge cycles are shown in Fig. 4(b). The impedance spectra for bare LiCoO_2 powders follow the typical spectra of LiCoO_2 which comprises two semicircles and a 45° -inclined line.¹⁴

The semicircle in the higher frequency zone (#) is related to the solid-electrolyte interphase (SEI) while the semicircle in the lower frequency zone (*) is a charge-transfer reaction at the electrolyte/electrode interface.¹⁴ The charge-transfer resistance at the $\text{Al}_2\text{O}_3/\text{LiCoO}_2$ interface may also contribute to the overall charge-transfer.¹⁴ Although one superficial semicircle is observed for $\text{Al}_2\text{O}_3\text{-LiCoO}_2$, the shape of semicircle is not symmetric. One semicircle for $\text{Al}_2\text{O}_3\text{-LiCoO}_2$ includes a small charge transfer resistance at the $\text{Al}_2\text{O}_3/\text{LiCoO}_2$ and/or electrolyte/electrode interfaces.

For the electrodes prepared using bare LiCoO_2 powders, the first semicircle (#) does not change much during cycling. In contrast, the radius of the second semicircle (*) increases dramatically with the number of charge-discharge cycles. For the electrode prepared using Al_2O_3 ALD-coated LiCoO_2 powders, the interface with the electrolyte is very stable and the semicircle holds its overall radius and shape even after 50 cycles.

There are two possible mechanisms for the enhancement caused by Al_2O_3 ALD. First, the Al_2O_3 ALD film can serve as a scavenger for HF ¹⁵ that results from the reaction of trace amounts of water and LiPF_6 in the electrolyte.¹⁶ HF can attack the LiCoO_2 surface and dissolve Co and cause other complex decomposition reactions.^{4,6,17} Insulating films formed by these reactions can then electrically isolate the

LiCoO_2 particle from other particles, conducting aids and current collectors. The XPS spectra of Al 2s for the electrode coated with Al_2O_3 ALD using 4 ALD cycles before charge-discharge cycling and after 10 charge-discharge cycles were obtained: before charge-discharge cycling the Al 2s peak was 118.7 eV (FWHM = 2.2 eV), after 10 charge-discharge cycles the Al 2s peak was at 119.2 eV (FWHM = 2.8 eV). The Al 2s peak for Al_2O_3 should fall in the range of 116.25~119.5 eV and that for AlF_3 should be 121.0 eV.¹⁸ The shift and broadening of Al 2s after 10 charge-discharge cycles might be the indication of the formation of some AlF_3 . Considering the thickness of Al_2O_3 using 4 ALD cycles, however, the amount of Al_2O_3 is too small to scavenge all HF. Second, the Al_2O_3 ALD-covered surface may be less of a catalyst for electrolyte decomposition at higher potential ($>4.3 \text{ V (vs. Li/Li}^+)$) compared with a bare LiCoO_2 surface. Even if Al_2O_3 is converted to the AlF_3 , AlF_3 could also act as protecting layer against further attack of HF.^{7,15} Overall, a conformal Al_2O_3 ALD film will keep the bare LiCoO_2 surface from direct contact with electrolyte.^{5,6,13}

In summary, Al_2O_3 ALD films were grown on LiCoO_2 particles. The ALD coatings dramatically improved the performance of electrodes fabricated with the Al_2O_3 ALD-coated LiCoO_2 particles. The Al_2O_3 ALD-coated LiCoO_2 particles using 2 ALD cycles showed a capacity retention of 89% after 100 charge-discharge cycles with respect to the reversible capacity at the 3rd charge-discharge cycle. This behavior was observed when cycling in the range of 3.3~4.5 V (vs. Li/Li^+). In contrast, the bare LiCoO_2 maintained only 45% of the initial capacity after the 100 charge-discharge cycles. The underlying enhancement mechanism is believed to originate from chemically protective and electrochemically stable Al_2O_3 ALD film on the LiCoO_2 surface. The promising

results of ALD-Al₂O₃ on LiCoO₂ shown here will offer enormous opportunities to apply ALD to many electrode materials for LIBs.

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