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Citation for published version (APA):

DOI:
10.1149/2.011305jes

Document status and date:
Published: 01/01/2013

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Atomic Layer Deposition of LiCoO2 Thin-Film Electrodes for All-Solid-State Li-Ion Micro-Batteries

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One of the remaining challenges in the field of portable electronics is the miniaturization of lithium-ion batteries. To prepare all-solid-state batteries with a sufficient high storage capacity it is vital to prepare high quality thin films for battery stacks on 3D-structured substrates. A remote plasma atomic layer deposition (ALD) process has therefore been developed for LiCoO2 which can serve as a cathode material. A combination of CoCp2 as cobalt precursor, LiOtBu as lithium precursor and O2 plasma as oxidant source was used to create super-cycles to deposit LiCoO2 from CoO2 and Li2CO3 cycles. The thin films were deposited at a temperature of 325 °C and showed linear growth with a rate of 0.06 nm/cycle. After annealing the samples at 700 °C for 6 minutes high temperature phase LiCoO2 was obtained, as was demonstrated by XRD and Raman spectroscopy. A new procedure was proposed to obtain the composition of all three chemical elements in the LiCoO2 films. Elastic Backscattering Spectroscopy (EBS) measurements turned out to be very convenient and reliable to obtain the quantities of all chemical elements, including lithium. Moreover, the ALD-deposited LiCoO2 thin film electrodes were electrochemically characterized, revealing good backscattering spectroscopy performance. To the best of our knowledge this paper provides the first evidence that electrochemically active LiCoO2 can be deposited by ALD.

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Manuscript submitted December 31, 2012; revised manuscript received February 21, 2013. Published March 12, 2013. This was in part Paper 1848 presented at the Boston, Massachusetts, Meeting of the Society, October 9–14, 2011. This paper is part of the JES Focus Issue on Interfacial Compounds for Rechargeable Batteries.

During the past decade, portable electronic devices have become considerably more widespread, complex and powerful, and new challenges have been encountered, especially in the field of medical and autonomous devices. To power these future devices, thin-film, all-solid-state, lithium-ion micro-batteries have been prepared.1–4 To facilitate the required energy demand, both a high energy-to-weight and energy-to-volume ratio is essential. Lithium-ion batteries fulfill these demands. As packaging requirements become more dominant at smaller dimensions, one of the remaining challenges is miniaturization of lithium-ion batteries without decreasing the storage capacity. This formed the basis of the integrated batteries concept.1

Step conformal deposition of films onto etched structures in silicon is an excellent method to tackle this challenge and to facilitate the integration of these high capacity energy storage devices into microelectronics.1,2 Chemical vapor deposition (CVD) has been proposed as deposition method.1 However, CVD has a limited step-conformal deposition capability in highly structured geometries due to the delicate interplay between kinetics and diffusion. By using atomic layer deposition (ALD) this effect can be counteracted as this deposition method is based on a reaction-limited surface saturation, opening up numerous possibilities for the use of more complex substrate structures such as nanowires.5

Industrial scale implementation of ALD has already been proven in micro-electronics and this technique is rapidly penetrating new fields, such as solar cells, catalysis and recently also energy storage devices.1,6,7 In the field of battery technology several interesting materials have been prepared which show much promise.3 However, work on lithium-containing solid-state electrolytes and electrode materials is still very exploratory. Even though several lithium-containing compounds have recently been prepared by ALD,9,10 no reports of electrochemical investigations are available to date. An overview of Li-containing compounds prepared by ALD is presented in Table I. This paper demonstrates the electrochemical activity for ALD-prepared LiCoO2, which is, to the best of our knowledge, the first active Li-containing battery material, deposited by ALD, which is electrochemically characterized in detail. Therefore, for reference, also LiCoO2 CVD processes are included in Table I.

Evidently, analyzing the chemical composition of thin films is essential to evaluate the electrochemical properties of the LiCoO2. Although it is most uncommon to use backscattering techniques such as Rutherford backscattering spectroscopy (RBS) for the determination of the Li content in thin films, this has been achieved by making use of non-Rutherford cross sections. The as-obtained results will be verified by Nuclear Reaction Analyzes (NRA).11 This is another novelty within this paper.

Experimental

Film preparation.— The LiCoO2 films were deposited using an open-load thermal and remote plasma ALD reactor as described previously for the deposition of Co3O4.12 An inductively coupled plasma (ICP) source that is operated on O2 is connected to a deposition chamber along with a pump unit through gate valves. The pump unit consists of a rotary and turbo molecular pump, which can reach a base pressure of <10−5 Torr by overnight pumping. The CoCp2 and LiOtBu precursors (both 98%, Strem Chemicals) were heated to 80 °C and 120 °C respectively (Table II) and they were bubbled with Ar at a reactor pressure of 0.2 Torr. The substrate was heated to 325 °C, while the reactor walls, Ar lines, and CoCp2 precursor lines were maintained at a temperature of 105 °C, the LiOtBu precursor lines were kept at 150 °C to prevent precursor condensation. Si(100) with native oxide and Si(100) with 400 nm thermally grown SiO2 were used as substrates for materials analyzes. For the electrochemical characterization, Si/TiO2/Pt substrates were prepared by ALD as described in Ref. 8 and schematically shown in Fig. 1a with thicknesses of 5 and 20 nm for TiO2 and Pt respectively.

The remote plasma ALD process for LiCoO2 consists of the two individual ALD processes for the deposition of CoO2 and Li2CO3 which are combined in a so-called super-cycle (Fig. 2). Here the previously described remote plasma ALD process for CoO2 is combined with a novel ALD process, using a lithium precursor reported recently for the deposition of LLT and Li2CO3.9,10 In this paper a super-cycle is defined as a combination of A cycles of Co3O4 and B cycles Li2CO3 (Fig. 2), resulting in a dosing ratio of A:B (e.g. 4:1), where B is consistently kept as 1 throughout the paper. x is defined as A/B, e.g. for a dosing ratio of 4:1, x equals 4. In both processes a precursor dosing time of 2 s is applied combined with an O2 plasma at 100 W for 5 s
at a pressure of 0.01 Torr. During and after the precursor dosing and plasma exposure, the reaction chamber is purged (3 s and 0.5 s respectively) and evacuated.

**Film analyzes.** The thickness and dielectric function of the films were monitored during the ALD process by in situ spectroscopic ellipsometry (SE) with a J.A. Woollam, Inc. M2000U (0.75–5.0 eV) ellipsometer,\(^1\) The optical range was extended to 6.5 eV after the deposition process, using ex situ variable angle measurements with an optical model employing a Gauss, a Tauc–Lorentz, and two Lorentz oscillators, to account for the absorption bands.\(^2\) The dielectric functions of Li_{2}CO_{3} and LiCoO_{2} were parameterized using a mathematical description in the form of B-splines.\(^3\) This is a method that requires no prior knowledge about the dielectric function of deposited films and enables in situ thickness measurements.

The microstructure of the LiCoO_{2} films was studied using Grazing Incidence X-ray diffraction (GI-XRD) with a Philips X’Pert MPD diffractometer equipped with a Cu K\(_{\alpha}\) source (1.54 Å radiation). The Raman spectra of the samples were recorded using an in-via Renishaw micro Raman scattering setup with a wavelength of 514.5 nm, a maximum power density of 105 W/cm\(^2\) and a resolution of 1 ppm. Galvanostatic cycling was performed with a M2300 galvanostat (Maccor, Tulsa, USA), applying a current density of 0.5 \(\mu\)A/cm\(^2\) and a cycling range between 3.0 and 4.1 V. The following definition is adopted throughout the manuscript: charging LiCoO_{2} refers to Li-ion extraction (or delithiation) and discharging to Li-ion insertion (or lithiation). Based on the electrode surface area, the layer thickness as determined by spectroscopic ellipsometry and the density determined by quantitative EBS measurements (Table III), the volumetric and gravimetric capacities were calculated. Cu plate was used as electrical conductor for the working electrode, while pure lithium foils were used as counter and reference electrodes. 1 molar LiClO\(_{4}\) dissolved in Ethyl Carbonate (EC)/Diethyl Carbonate (DEC) was used as liquid electrolyte (Puriel, Techno, Semichem Co., Ltd, Korea). The cells were placed in a stainless steel holder that was thermostatically controlled at room temperature. Contaminants in the glove-box (water and oxygen) were monitored and controlled below 1 ppm. Galvanostatic cycling was performed with a M2300 galvanostat (Maccor, Tulsa, USA), applying a current density of 0.5 \(\mu\)A/cm\(^2\) between 3.0 and 4.1 V. The following definition is adopted throughout the manuscript: charging LiCoO\(_{2}\) refers to Li-ion extraction (or delithiation) and discharging to Li-ion insertion (or lithiation). Based on the electrode surface area, the layer thickness as determined by spectroscopic ellipsometry and the density determined by quantitative EBS measurements (Table III), the volumetric and gravimetric capacities were calculated.

**Electrochemical analyzes.** The electrochemical analyzes were performed in three-electrode cylindrical electrochemical cells with an effective surface area of 2 cm\(^2\) (Fig. 1). The cells were made of Teflon with a volume of about 15 ml. The cells were assembled in an argon-filled glove-box. The Si/TiO\(_{2}\)/Pt substrates are used as working electrode during the electrochemical measurement. Layer thicknesses are 5 and 20 nm for TiO\(_{2}\) and Pt respectively.

![Figure 1](image_url) Schematic representation of the Teflon three-electrode measurement setup. The LiCoO\(_{2}\) films under investigation deposited on Si/TiO\(_{2}\)/Pt substrates are used as working electrode during the electrochemical measurement. Layer thicknesses are 5 and 20 nm for TiO\(_{2}\) and Pt respectively.
Results and Discussion

**ALD growth.** To investigate the ALD process parameters, the self-limiting behavior of the ALD process was investigated for the CoCp₂ and LiO'Bu precursors using a Co:Li dosing ratio of 1:1 for the super-cycle as presented in Fig. 2. This means that one cycle of Co₃O₄ was alternated with one cycle of Li₂CO₃. The plasma exposure time was fixed at 5 seconds for both precursors. The Li precursor dosing time was varied while the Co dosing time remained constant at 2 s, which is the same dosing time used during the deposition of Co₃O₄. Saturation of the Li precursor occurs after about 2 s as can be seen in Fig. 3a. The same procedure was conducted for the Co precursor while the Li dosing time was kept constant at 2 s. Proper saturation is also observed in the Co case (Fig. 3b). Note that the growth rates under saturated conditions are slightly different in Fig. 3a and 3b. This can most likely be attributed to the different film thicknesses employed when generating Fig. 3a and 3b. The growth rate was found to change slightly with film thicknesses (see Fig. 4). Dosing times of 2 s for both precursors were therefore fixed for all deposition experiments described.

Applying a Co:Li dosing ratio of 1:1 lead to a slightly higher growth rate than expected on the basis of the individual growth rates for Co₃O₄ (0.05 nm/cycle) and Li₂CO₃ (0.08 nm/cycle). This could be due to the high growth rate of pure Li₂CO₃ as compared to pure Co₃O₄, but

<table>
<thead>
<tr>
<th>Co/Li dosing ratio (x)</th>
<th>2</th>
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<td>Composition</td>
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<td>Li₁.₂CoO₃.₈</td>
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<td>Average Capacity (% of maximum)</td>
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<td>–</td>
<td>62</td>
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the growth of Li$_2$CO$_3$ could also be catalyzed by the presence of cobalt atoms. Fig. 4 shows that the thickness was almost linearly dependent on the number of ALD cycles at a dosing ratio of Co:Li = 4:1 with an overall growth rate of $\sim 0.06$ nm/cycle. It is not expected that a change in Co:Li dosing ratio will significantly affect the saturation behavior for both precursors in the Co$_3$O$_4$ and Li$_2$CO$_3$ cycles.

Fig. 5 shows the in situ measured dielectric function $\varepsilon_2$ for photon energies between 1.24 and 6.5 eV of the as-deposited Co$_3$O$_4$, Li$_2$CO$_3$ and LiCoO$_2$. A clear difference is found between the three films. The dielectric function of Co$_3$O$_4$ has been described in an earlier publication. Unfortunately, from the literature not much is known about the dielectric functions of Li$_2$CO$_3$ and LiCoO$_2$. In order to distinguish between Co$_3$O$_4$, Li$_2$CO$_3$ and LiCoO$_2$ the films of the latter two materials have also been investigate. Fig. 5 clearly shows that Li$_2$CO$_3$ hardly contributes to the LiCoO$_2$ signal and that a typical spectrum for LiCoO$_2$ is obtained.

Material properties.— Knowledge of the overall film composition is essential in order to evaluate ALD-deposited LiCoO$_2$ thin films, especially to properly evaluate the electrochemical results. EBS and NRA are excellent techniques to determine the atomic composition of compounds and can thus be used to reveal the ratio between lithium, cobalt and oxygen in the films (Fig. 6). These analyzes show that materials prepared with a Co:Li dosing ratio $x$ of 4 and higher have more or less the same atomic ratios (Table III). In addition, a Co:Li dosing ratio larger than 4:1 seems to increase the deposition rate of the lithium sub-cycle in the ALD process slightly (Fig. 6), while the deposition rate during the cobalt sub-cycle is unaffected and continues to increase linearly with $x$. This effect is not yet fully understood, but limits the ALD process from obtaining the desired Co/Li = 1 material composition for the range investigated. This illustrates the delicate balance that needs to be taken into account when dealing with the ALD-deposition of ternary compounds.

As-deposited samples were investigated by GI-XRD and Raman spectroscopy and subsequently annealed at 700°C for 6 minutes before being measured again with the same techniques. Fig. 7 shows that a large diffraction peak becomes visible after annealing at a 2$\theta$ angle of 19°, which has also been reported in the literature for metal organic (MO) CVD deposited LiCoO$_2$ at various temperatures. This peak can be assigned to either the (111) reflection of Co$_3$O$_4$ or the (003) reflection of LiCoO$_2$. As both cobalt oxide and lithium cobalt oxide can be present in the deposited thin films it is not possible to unambiguously determine the origin of the diffraction peak and the nature of the film from XRD. Therefore Raman spectroscopy has been used to further investigate these films. Figure 8 shows that the high temperature (HT) hexagonal phase of LiCoO$_2$ is observed with two typical phonon modes at 486 and 596 cm$^{-1}$ which becomes even more defined after annealing. The Raman spectra reveal no significant fraction of Co$_3$O$_4$ in the films as this would lead to a distinct peak at 693 cm$^{-1}$.

Electrochemical analyzes.— It is well-known that a heat-treatment of about 700°C is required to obtain the electrochemically active, crystalline, LiCoO$_2$. The annealed LiCoO$_2$ films were electrochemically characterized in the experimental three-electrode battery set-up using
constant current (dis)charge cycling. The charge transfer reaction of the LiCoO$_2$ electrode can be represented by

$$\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-z}\text{CoO}_2 + z\text{Li}^+ + ze^- \quad (z \leq 0.5) \quad [1]$$

where $z \leq 0.5$. Extracting more than 0.5 lithium atoms per formula unit would irreversibly change the crystal structure of LiCoO$_2$, making the electrode (partly) electrochemically inactive. All electrode films investigated showed electrochemical activity. However, the storage capacity was clearly found to be dependent on the ALD dosing ratio.

Fig. 9a shows the (dis)charge behavior of the LiCoO$_2$ electrode for the Co:Li dosing ratio $x$ of 4 which revealed the highest storage capacity. By taking the derivative of the storage capacity with respect to the electrode potential (Fig. 9b), the plateaus in Fig. 9a are transformed into either broad or sharp peaks dependent on the slope of the voltage curves. A clear charge transfer reaction is now visible at 3.9 V as expected for LiCoO$_2$. Also a 12% capacity loss between the charge and discharge reactions is found (Fig. 9a). A similar effect has been reported before and this has been attributed to irreversible side reactions (e.g., oxidation of the liquid electrolyte, the formation of the less electrochemically active spinel Li$_2$Co$_3$O$_4$ phase or mechanical strain-induced degradation of the LiCoO$_2$ film, but also the (electro)chemical stability of the impurities found in ALD LiCoO$_2$ with respect to the liquid electrolyte could play a role.

The electrochemical storage capacity is, however, lower than the theoretically expected for LiCoO$_2$ (155 mAh/g), but remained fairly stable upon cycling as shown in Fig. 9c. Over 60% of the maximum theoretical storage capacity has been obtained with the ALD deposited ($x = 4$) thin film electrode (Fig. 9c). This lower capacity can be explained by the presence of Li$_2$CO$_3$ within the thin film as indicated by the increased oxygen over cobalt (O/Co) and decreased cobalt over lithium (Co/Li) ratios and the presence of carbon (Table III). Moreover Table III shows an abundance of lithium and oxygen which could also indicate the formation of inactive Li$_2$O during the ALD process. These two effects may contribute to the reduced capacity compared to the theoretical maximum. Referring to Table III it is clear that the impurity level of the $x = 2$ material is significantly higher than the $x = 4$ material. This is in line with the reduced capacity of the $x = 2$ material compared to $x = 4$. It is expected that further process optimization will yield a higher chemical purity and improved storage capacity.

Conclusions

A remote plasma ALD process for the preparation of LiCoO$_2$ thin films was developed using the combination of CoCp$_2$ as cobalt precursor, LiO’Bu as lithium precursor and a O$_2$ plasma as the oxidant source. To the best of our knowledge this paper provides the first evidence that electrochemically active LiCoO$_2$ can be deposited by ALD. It was shown that LiCoO$_2$ films could be deposited by ALD with the Li/Co ratio depending on the Co:Li dosing ratio. Moreover elastic backscattering spectrometry was shown to be an accurate method to analyze the Li-content in this type of films, which simplifies the analysis significantly. After heat treatment the high temperature phase of LiCoO$_2$ was obtained as shown by XRD and Raman measurements.

Figure 8. Raman measurements for LiCoO$_2$ annealed at 700°C for 6 minutes compared to as-deposited LiCoO$_2$ and the theoretical spectrum of Co$_3$O$_4$. The used Co:Li dosing ratio was 2:1 ($x = 2$).

Figure 9. Constant current (CC) (dis)charge cycling between 3.0 V and 4.1 V (0.35 C-rate) for an ALD-deposited LiCoO$_2$ ($x = 4$) film on Si/TiO$_2$/Pt, using LiClO$_4$ in ethylene carbonate/diethyl carbonate (EC/DEC 1/1) as liquid electrolyte. (a) (dis)charge of LiCoO$_2$, (b) the derivative of the storage capacity with respect to the electrode potential and (c) the electrochemical storage capacity upon cycling showing data for $x = 2$ and $x = 4$. 
Electrochemical charge/discharge cycling experiments showed good reversible electrochemical performance with a significant fraction (60%) of active material for the annealed LiCoO\textsubscript{2} films, revealing that ALD is a promising method to deposit active lithium-containing electrode materials.

**Acknowledgments**

This research was carried out under the project number MC3.06278 in the framework of the Research Program of the Materials innovation institute M2i (www.m2i.nl).

**References**