Atomic Layer Deposition of LiCoO$_2$ Thin-Film Electrodes for All-Solid-State Li-Ion Micro-Batteries

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Abstract

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 LiCoO$_2$ which can serve as a cathode material. A combination of CoCp$_2$ as cobalt precursor, LiO'Bu as lithium precursor and O$_2$ plasma as oxidant source was used to create super-cycles to deposit LiCoO$_2$ from Co$_3$O$_4$ and Li$_2$CO$_3$ 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 LiCoO$_2$ 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 LiCoO$_2$ 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 LiCoO$_2$ thin film electrodes were electrochemically characterized, revealing good 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). This is another novelty within this paper.

Experimental

Film preparation.— The LiCoO$_2$ films were deposited using an open-load thermal and remote plasma ALD reactor as described previously for the deposition of Co$_3$O$_4$. An inductively coupled plasma (ICP) source that is operated on O$_2$ 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 CoCp$_2$ and LiO'Bu precursors (both 98%, Strem Chemicals) were heated to 80 °C and 120 °C respectively (Table I) and they were bubbled with Ar at a reactor pressure of 0.02 Torr. The substrate was heated to 325 °C, while the reactor walls, Ar lines, and CoCp$_2$ precursor lines were maintained at a temperature of 105 °C, the LiO'Bu precursor lines were kept at 150 °C to prevent precursor condensation. Si(100) with native oxide and Si(100) with 400 nm thermally grown SiO$_2$ were used as substrates for materials analyzes. For the electrochemical characterization, Si/TiO$_2$/Pt substrates were prepared by ALD as described in Ref. 8 and schematically shown in Fig. 1b with thicknesses of 5 and 20 nm for TiO$_2$ and Pt respectively.

The remote plasma ALD process for LiCoO$_2$ consists of the two individual ALD processes for the deposition of Co$_3$O$_4$ and Li$_2$CO$_3$ which are combined in a so-called super-cycle (Fig. 2). Here the previously described remote plasma ALD process for Co$_3$O$_4$ is combined with a novel ALD process, using a lithium precursor reported recently for the deposition of LLT and Li$_2$CO$_3$. In this paper a super-cycle is defined as a combination of A cycles of Co$_3$O$_4$ and B cycles of Li$_2$CO$_3$ (Fig. 2), resulting in a dosing ratio of \[ A \text{Co}_3\text{O}_4 : B \text{Li}_2\text{CO}_3 \] 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 O$_2$ plasma at 100 W for 5 s.

This paper demonstrates the electrochemical activity for ALD-prepared LiCoO$_2$ which is, to the best of our knowledge, the first electrochemically active LiCoO$_2$ can be deposited by ALD.
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. The optical range was extended to 6.5 eV after the deposition process, using ex situ variable angle measurements with a J.A. Woollam, Inc. M2000D ellipsometer. The dielectric function of Co3O4 has been extracted from the SE measurements using an optical model employing a Gauss, a Tauc–Lorentz, and two Lorentz oscillators, to account for the absorption bands. The dielectric functions of Li2CO3 and LiCoO2 were parameterized using a mathematical description in the form of B-splines. 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 LiCoO2 films was studied using Grazing Incidence X-ray diffraction (GI-XRD) with a Philips X’Pert MPD diffractometer equipped with a Cu Kα source (1.54 Å radiation). The Raman spectra of the samples were recorded using a (in-via Renishaw) micro Raman scattering setup with a wavelength of 514.5 nm, a maximum power density of 3.2 · 105 W/cm2 and a resolution of 1.6 cm⁻¹.

The overall composition of the layers has been analyzed at AccTec BV with backscattering spectrometry using a 2.09 MeV proton beam delivered and a scattering angle of 172°. Under these circumstances the cross sections of the lighter elements are strongly enhanced with respect to the Rutherford cross sections and strictly spoken the technique should be referred to as Elastic Backscattering (EBS) instead of RBS. The enhancement for the cross sections of 7Li, 12C, 16O with respect to the Rutherford values is about 55, 5 and 4 respectively. The alpha yield was simultaneously measured from one single spectrum. The alpha yield was simultaneously measured from one single spectrum.

Cu plate was used as electrical conductor for the working electrode, while pure lithium foils were used as counter and reference electrodes. 1 mol LiClO4 dissolved in Ethyl Carbonate (EC)/Diethyl Carbonate (DEC) was used as liquid electrolyte (Purile, 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 μA/cm². The cells were 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 μA/cm². 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 μA/cm².

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Figure 2. Schematic representation of an ALD super-cycle consisting of the two individual ALD processes for Co\textsubscript{3}O\textsubscript{4} and Li\textsubscript{2}CO\textsubscript{3}. A cycles of the Co\textsubscript{3}O\textsubscript{4} process are combined with B cycles of the Li\textsubscript{2}CO\textsubscript{3} process. The film-substrate stack is also shown.

Results and Discussion

**ALD growth.**—To investigate the ALD process parameters, the self-limiting behavior of the ALD process was investigated for the CoC\textsubscript{p}\textsubscript{2} and LiO\textsubscript{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 Co\textsubscript{3}O\textsubscript{4} was alternated with one cycle of Li\textsubscript{2}CO\textsubscript{3}. 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 Co\textsubscript{3}O\textsubscript{4}.\textsuperscript{12} 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 the 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 Co\textsubscript{3}O\textsubscript{4} (0.05 nm/cycle) and Li\textsubscript{2}CO\textsubscript{3} (0.08 nm/cycle). This could be due to the high growth rate of pure Li\textsubscript{2}CO\textsubscript{3} as compared to pure Co\textsubscript{3}O\textsubscript{4},\textsuperscript{9,12} but

![Figure 3](image)

Table III. Material properties and electrochemical results for LiCoO\textsubscript{2} thin films prepared for various Co/Li dosing ratios. Compositions are measured by EBS. The Co/Li dosing ratio (x) for the ALD process is defined as the number of Co\textsubscript{3}O\textsubscript{4} sub-cycles divided by the number of Li\textsubscript{2}CO\textsubscript{3} sub-cycles. For the lithium concentration an average is taken of the EBS and NRA measurements. Typical experimental errors are: Co (3%), Li (5%), O (5%) and C (7%).

<table>
<thead>
<tr>
<th>Co/Li dosing ratio (x)</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td><strong>ALD process</strong></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Super-cycles</td>
<td>300</td>
<td>200</td>
<td>200</td>
<td>169</td>
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<tr>
<td>Cycles (total)</td>
<td>900</td>
<td>800</td>
<td>1000</td>
<td>1014</td>
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<tr>
<td>Thickness (nm) (± 0.5 nm)</td>
<td>54</td>
<td>48</td>
<td>60</td>
<td>61</td>
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<tr>
<td><strong>Composition</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Co (10\textsuperscript{15} atom/cm\textsuperscript{2})</td>
<td>45.3</td>
<td>51.6</td>
<td>79.0</td>
<td>83.6</td>
</tr>
<tr>
<td>Li (10\textsuperscript{15} atom/cm\textsuperscript{2})</td>
<td>149</td>
<td>98.7</td>
<td>91.6</td>
<td>101</td>
</tr>
<tr>
<td>O (10\textsuperscript{15} atom/cm\textsuperscript{2})</td>
<td>353</td>
<td>210</td>
<td>266</td>
<td>315</td>
</tr>
<tr>
<td>C (10\textsuperscript{15} atom/cm\textsuperscript{2})</td>
<td>86</td>
<td>41</td>
<td>30</td>
<td>37</td>
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<tr>
<td>Average Co/Li ratio</td>
<td>0.30</td>
<td>0.52</td>
<td>0.86</td>
<td>0.83</td>
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<tr>
<td>Average O/Co ratio</td>
<td>7.9</td>
<td>4.1</td>
<td>3.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Composition Li\textsubscript{1.3}Co\textsubscript{0.7}O\textsubscript{3.9}</td>
<td>Li\textsubscript{1.9}Co\textsubscript{0.1}O\textsubscript{4.4}</td>
<td>Li\textsubscript{1.2}Co\textsubscript{0.8}O\textsubscript{3.5}</td>
<td>Li\textsubscript{1.2}Co\textsubscript{0.8}O\textsubscript{3.5}</td>
<td></td>
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<tr>
<td>Density (g · cm\textsuperscript{-3})</td>
<td>3.2</td>
<td>2.6</td>
<td>2.8</td>
<td>3.0</td>
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<td><strong>Electrochemical results</strong></td>
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<tr>
<td>Average Capacity (\textmu Ah · \textmu m\textsuperscript{-1} · cm\textsuperscript{-2})</td>
<td>12.1</td>
<td>–</td>
<td>27.0</td>
<td>–</td>
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<tr>
<td>Average Capacity (% of maximum)</td>
<td>28</td>
<td>–</td>
<td>62</td>
<td>–</td>
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</table>
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 investigated. 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 of 2:1 (x = 2) 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 2θ 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 a Li as counter electrode and a Pt as auxiliary electrode. A 2-electrode configuration was used with a Li as reference electrode. The electrolyte was 1M LiPF$_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC). A Li foil was used as counter and reference electrode and a Pt wire as auxiliary electrode. The electrochemical performance of the as-deposited LiCoO$_2$ film and the film annealed at 700 °C were measured in a three electrode battery configuration using a charge/discharge cycle with a current density of 5 mA cm$^{-2}$ between 2.5 and 4.8 V vs Li/Li$^+$. Both electrodes showed a stable and reversible electrochemical stability up to 4.8 V. The Coulombic efficiency was close to 100% for both samples. However, the as-deposited sample showed a lower capacity of 145 mAh g$^{-1}$ compared to the annealed sample with 185 mAh g$^{-1}$. This could be attributed to the different crystalline structures of the two samples.

As can be seen from Figure 9, the electrochemical performance of the as-deposited LiCoO$_2$ film is inferior to that of the annealed sample. The as-deposited sample shows a lower capacity and a lower coulombic efficiency, which is likely due to the presence of Li$_2$CO$_3$ and Co$_3$O$_4$. This is confirmed by the XRD and Raman measurements. The annealed sample shows a higher capacity and a higher coulombic efficiency, which is consistent with the XRD and Raman measurements. The annealing process results in a more crystalline and defect-free LiCoO$_2$ film, which is responsible for the improved electrochemical performance.

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Figure 8. Raman measurements for LiCoO₂ annealed at 700 °C for 6 minutes compared to as-deposited LiCoO₂ and the theoretical spectrum of Co₃O₄. The used Co:Li dosing ratio was 2:1 (x = 2).

Constant current (dis)charge cycling. The charge transfer reaction of the LiCoO₂ electrode can be represented by

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

where \( z \leq 0.5 \). Extracting more than 0.5 lithium atoms per formula unit would irreversibly change the crystal structure of LiCoO₂, 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 LiCoO₂ electrode for the Co:Li dosing ratio \( x \) of 4 which revealed the highest storage capacity. By taking the derivate 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 LiCoO₂. 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 LiCo₂O₄ phase or mechanical strain-induced degradation of the LiCoO₂ film, but also the (electro)chemical stability of the impurities found in ALD LiCoO₂ with respect to the liquid electrolyte could play a role. The electrochemical storage capacity is, however, lower than the theoretically expected for LiCoO₂ (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 Li₂CO₃ 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 Li₂O 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 LiCoO₂ thin films was developed using the combination of CoCp₂ as cobalt precursor, LiO’Bu as lithium precursor and a O₂ plasma as the oxidant source. To the best of our knowledge this paper provides the first evidence that electrochemically active LiCoO₂ can be deposited by ALD. It was shown that LiCoO₂ 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 LiCoO₂ was obtained as shown by XRD and Raman measurements.
Electrochemical charge/discharge cycling experiments showed good reversible electrochemical performance with a significant fraction (60%) of active material for the annealed LiCoO₂ films, revealing that ALD is a promising method to deposit active lithium-containing electrode materials.

Acknowledgments
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References