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Remote Plasma Atomic Layer Deposition of Thin Films of Electrochemically Active LiCoO_2

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One of the remaining challenges in the field of portable electronics is the miniaturization of lithium-ion batteries without decreasing their storage capacity. To tackle this challenge and to effectively integrate battery technology in even a wider variety of applications, it is essential to produce high quality thin films for all-solid-state batteries. A remote plasma ALD process for the positive electrode material LiCoO_2 was developed using the combination of CoCp_2 as the cobalt precursor, LiO^tBu as the lithium precursor and O_2 plasma as the oxidant source. The thin films were deposited at a temperature of $325\text{ }^\circ\text{C}$ with a virtually linear growth rate of 0.06 nm/cycle . After annealing the samples at $700\text{ }^\circ\text{C}$ for 6 minutes the high temperature phase LiCoO_2 was obtained, as demonstrated by XRD and Raman spectroscopy measurements. Electrochemical charge/discharge cycling showed good electrochemical activity with a promising storage capacity.

Introduction

During the past decade, portable electronic devices have become considerably more widespread, complex, and powerful and new challenges have been encountered, especially in terms of energy management. For powering the devices an energy source is required with a high energy-to-weight and high energy-to-volume ratio. Lithium-ion batteries can fulfil these demands and consequently are applied on a large scale. However, one of the remaining challenges in the field is the miniaturization of lithium-ion batteries without decreasing the storage capacity. To tackle this challenge and to effectively integrate battery technology in even a wider variety of applications, 3D-integrated all-solid-state batteries have been proposed in various publications (1-3).

One of the most commonly used positive electrode materials in present-day battery technology is the well-investigated lithium cobalt oxide (LiCoO_2) with a capacity of 155 mAh/g (4). LiCoO_2 has previously been deposited by radio frequency (RF) magnetron sputtering (5,6), sol-gel processing (7), electron beam evaporation (8), spray pyrolysis (6,9), pulsed laser deposition (PLD) (10) and (metal organic) chemical vapor deposition (CVD) (11,12). All these methods can produce high purity LiCoO_2 . However, for the aforementioned application it is essential to produce high quality thin films for all-solid-state batteries. Atomic layer deposition (ALD) presents a (sub) monolayer growth control

by supplying the precursors to the reactor in alternating sequences, rather than simultaneously as in chemical vapor deposition (CVD). Due to the surface chemistry controlled deposition process, ALD is chosen in this work and provides an excellent conformality and thickness control at the atomic level, even in challenging high-aspect-ratio structures. Several lithium compounds have recently been deposited using ALD in the form of LiOH, Li₂CO₃ and lithium lanthanum titanate [(Li, La)_xTi_yO_z (LLT)] films (13,14), however no reports of electrochemical analysis of ALD deposited lithium containing materials are available to date. An overview of Li-based materials deposited by ALD as reported in the literature is shown in Table I. Also CVD processes for LiCoO₂ are listed in the table.

In this paper the ALD process of Co₃O₄ (15) is combined with the process of Li₂CO₃ (13,14) to deposit an electrochemically active battery electrode material (LiCoO₂) for the first time.

TABLE I. Overview of ALD processes for the deposition of lithium-containing compounds and CVD processes for LiCoO₂.

	Deposited material	Lithium precursor	Other Precursor(s)	Reactant(s)	Deposition temperature	Growth rate	References
ALD	Li ₂ CO ₃	LiO ^t Bu	-	H ₂ O	225 °C	0.08 nm/cycle	13,14
	LLT	LiO ^t Bu	La(thd) ₃ TiCl ₄	O ₃ H ₂ O	225 °C	0.05 nm/cycle	14
	LiOH	LiO ^t Bu	-	H ₂ O	225 °C	0.09 nm/cycle	13
	LiCoO ₂	LiO ^t Bu	CoCp ₂	O ₂ plasma	325 °C	0.06 nm/cycle	This work
CVD	LiCoO ₂	^t BuLi	CpCo(CO) ₂	O ₂	300-600 °C	-	11
	LiCoO ₂	Li(TMHD)	Co(TMHD) ₃	O ₂ / N ₂	450-550 °C	-	12

TABLE II. Overview of LiCoO₂ ALD process parameters for the different sub-cycles of the super-cycle.

	Precursor/ reactant	Dosing time	Pump purge time	Precursor temperature	Precursor line temperature
Co ₃ O ₄	CoCp ₂	2 s	3 s	80 °C	105 °C
	O ₂ plasma	5 s	0.5 s	-	-
Li ₂ CO ₃	LiO ^t Bu	2 s	3 s	120 °C	150 °C
	O ₂ plasma	5 s	0.5 s	-	-

Experimental details

Film preparation

The LiCoO_2 films were deposited using a home-built open-load ALD reactor as described previously for the deposition of Co_3O_4 (15). In this setup an inductively coupled plasma (ICP) source 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^tBu 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 0.02 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 and the LiO^tBu precursor lines 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 analysis. For electrochemical analysis Si/TiO₂/Pt substrates were prepared by ALD as described in an earlier publication and shown in Figure 2 (16).

The remote plasma ALD process for LiCoO_2 consists of two individual ALD processes which are combined in a so-called super-cycle (Fig. 1). Here the previously described remote plasma ALD process for Co_3O_4 is combined with a novel ALD process using a lithium precursor reported recently for the deposition of LLT and Li_2CO_3 (13,14). In both processes a precursor dosing time of 2 s is applied combined with an O_2 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 and then evacuated.

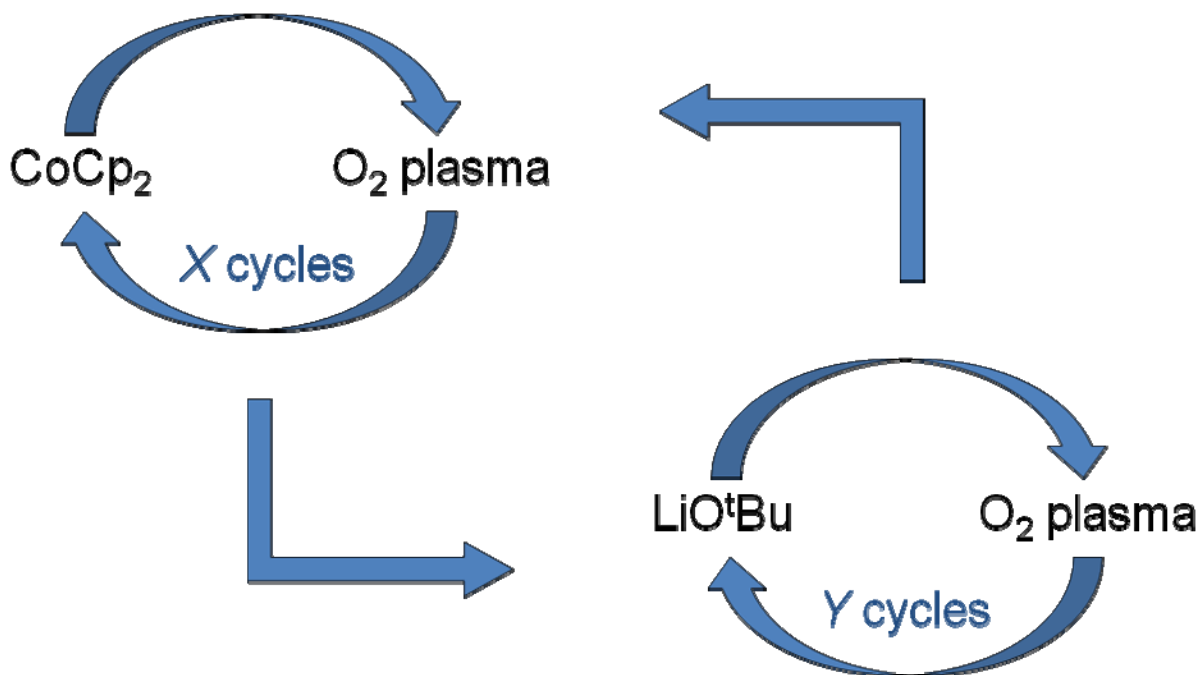


Figure 1: Schematic representation of an ALD super-cycle consisting of the two individual ALD processes for Co_3O_4 and Li_2CO_3 . X cycles of the Co_3O_4 process are alternated with Y cycles of the Li_2CO_3 process.

Material analysis

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 (17). 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 Co_3O_4 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 (15). The dielectric functions of Li_2CO_3 and LiCoO_2 were parameterized using a mathematical description in the form of B-splines (18). 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 lithium cobalt oxide films was studied using Grazing Incidence X-ray diffraction (GI-XRD) with a Philips X'Pert MPD diffractometer equipped with a Cu K_α source (1.54 Å radiation). The Raman spectra of the samples were recorded using a micro Raman scattering setup (In-via Renishaw) with a resolution of 1.6 cm^{-1} .

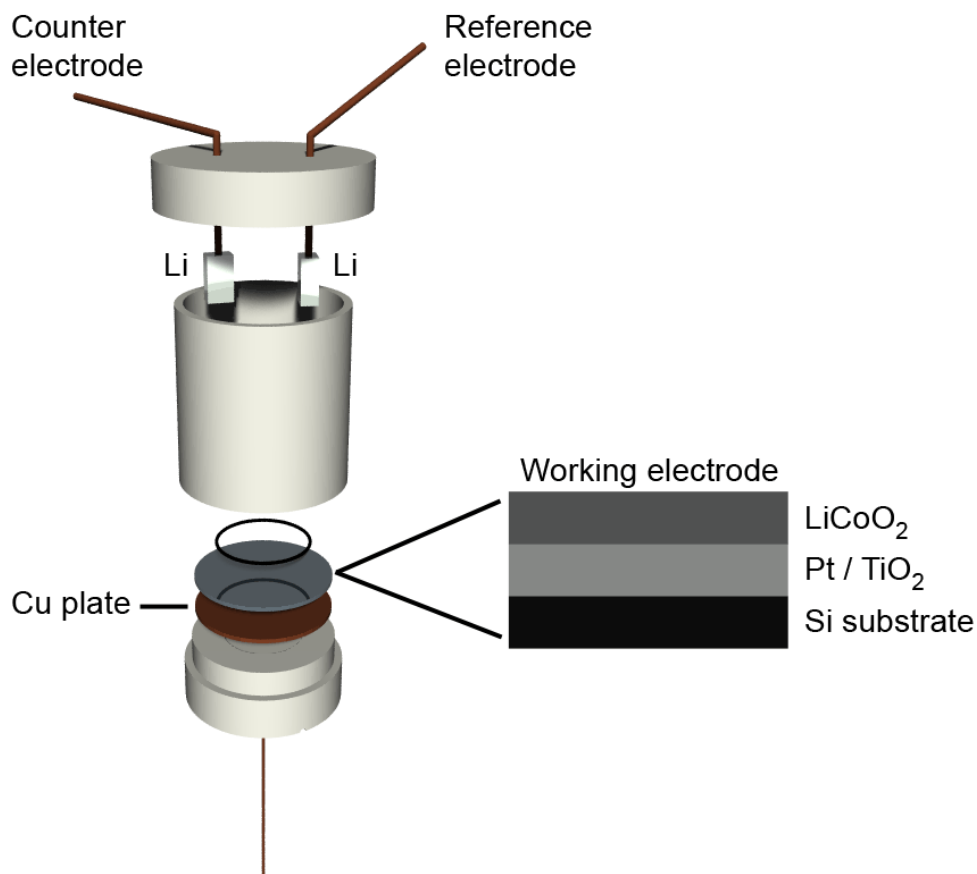


Figure 2: Schematic representation of the Teflon® three-electrode measurement setup in which the LiCoO_2 on $\text{Si/TiO}_2/\text{Pt}$ substrates are used as working electrode for the electrochemical measurements.

Electrochemical analysis

The electrochemical analyses were performed in three-electrode cylindrical electrochemical cells with an effective measurement surface area of 2 cm^2 (Fig. 2). The cells were made of Teflon[®] with a volume of about 15 ml. The cells were assembled in an argon-filled glove-box. The LiCoO_2 electrodes were mounted as working electrodes and back-contacted with silver paint to facilitate a good electrical connection. 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). The following definition is adopted throughout the manuscript: discharging an electrode material refers to Li-ion insertion (or lithiation) and charging to Li-ion extraction (or delithiation).

Results & Discussion

ALD growth

To investigate the ALD process parameters, the self-limiting behavior of the ALD process was investigated for the CoCp_2 and LiO^tBu precursors using a Co:Li dosing ratio of 1:1 for the supercycle as displayed in Fig. 1. 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 2s, which is the same dosing time used during the deposition of Co_3O_4 (15). Saturation of the Li precursor is seen around 2s. The same procedure was conducted for the Co precursor while the Li dosing remained constant at 2s. Proper saturation behavior is observed for both cases as shown in Fig. 3a and 3b, however the obtained growth per cycle is different. The deviation in these measurements could be explained by the different starting thickness of the film, because the growth per cycle slightly changed throughout the growth process (Fig. 4). Dosing times of 2s for both precursors are chosen as baseline conditions to ensure proper ALD conditions for all experiments presented below.

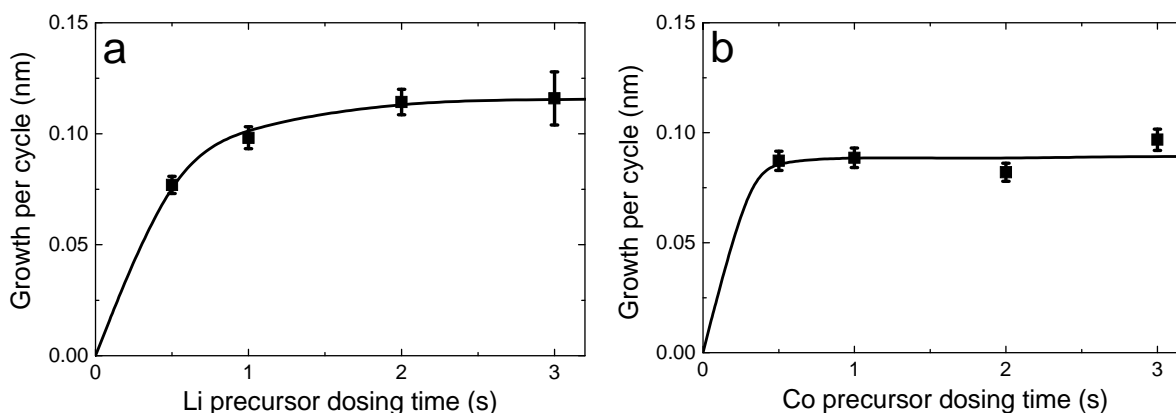


Figure 3: Saturation curves for remote plasma ALD of LiCoO_2 at $325 \text{ }^\circ\text{C}$ (a) Growth rate as a function of LiO^tBu dosing time, while the CoCp_2 dosing time and plasma exposure time are kept constant at 2s and 5s respectively. (b) Growth rate as a function of CoCp_2 dosing time, while the LiO^tBu dosing time and plasma exposure time are kept constant at 2s and 5s respectively. The lines serve as guides to the eye.

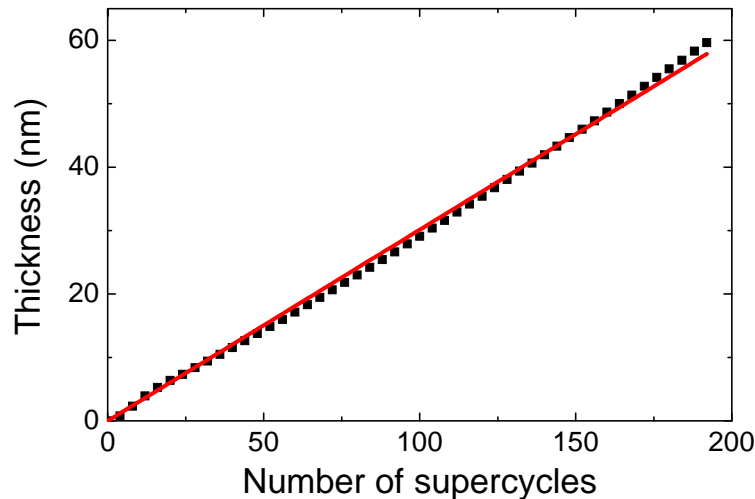


Figure 4. Thickness of LiCoO_2 on $\text{Si}(100)$ as a function of the number of ALD supercycles, as measured with *in situ* spectroscopic ellipsometry. The used Co:Li dosing ratio is 4:1.

Applying a Co:Li dosing ratio of 1:1 lead to a slightly higher growth rate than expected from the individual growth rates of Co_3O_4 and Li_2CO_3 . This could be due to the high growth rate of Li_2CO_3 as compared to Co_3O_4 (13,15), but the growth of Li_2CO_3 could also be catalyzed by the presence of cobalt atoms. At a dosing ratio of Co:Li to 4:1 (Fig. 4) the thickness was virtually linear dependent on the number of ALD cycles and the overall growth rate was ~ 0.06 nm/cycle. It is not expected that the change in Co:Li dosing ratio will significantly affect the saturation of either precursor. Figure 5 shows the dielectric function ϵ_2 of as-deposited Co_3O_4 , Li_2CO_3 and LiCoO_2 between 1.24 eV and 6.5 eV and a clear difference is seen between the three films. The dielectric function of Co_3O_4 has been described in an earlier publication (15), however not much is known in the literature about the dielectric functions of Li_2CO_3 and LiCoO_2 .

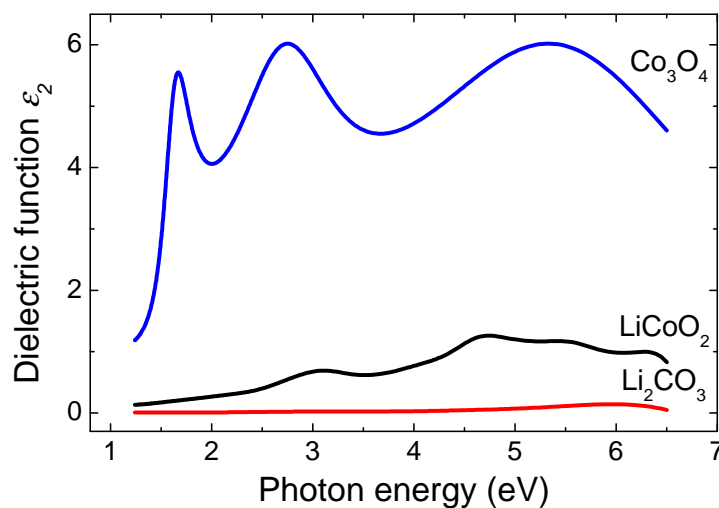


Figure 5. The imaginary part of the dielectric function (ϵ_2) of the Co_3O_4 , Li_2CO_3 and LiCoO_2 films as determined by *in situ* spectroscopic ellipsometry.

Material properties

To ensure a stoichiometric deposition of LiCoO_2 a Co:Li dosing ratio of 2:1 was used to investigate the material properties. The obtained as-deposited samples were investigated by GI-XRD and Raman spectroscopy and subsequently annealed at $700\text{ }^\circ\text{C}$ for 6 minutes before being measured again with the same techniques. In Fig. 6 a large diffraction peak becomes visible after annealing at a 2θ angle of 19° , which has also been reported in the literature for MO-CVD deposited LiCoO_2 at various temperatures (19). This peak can be assigned to both the (111) reflection of Co_3O_4 and 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. Raman spectroscopy has therefore been used as shown in Fig. 7. The high temperature (HT) hexagonal phase LiCoO_2 is observed with two typical phonon modes at 486 and 596 cm^{-1} which becomes even more defined after annealing (12). The Raman spectra reveal no significant fraction of Co_3O_4 in the films as this would lead to a peak at 693 cm^{-1} .

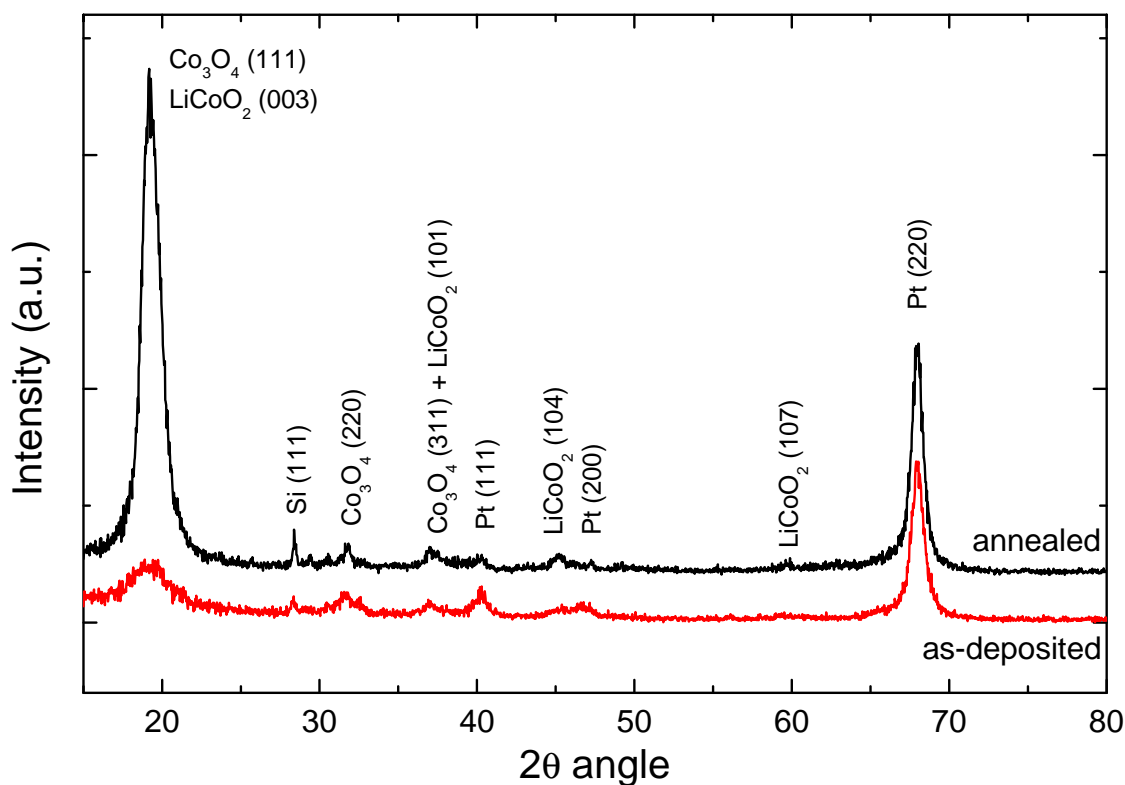


Figure 6: X-ray diffraction measurements ($\lambda = 1.54\text{ \AA}$) revealing overlapping peaks for Co_3O_4 with a preferential (111) orientation and crystalline LiCoO_2 after annealing at $700\text{ }^\circ\text{C}$ for 6 minutes. The spectra have been offset vertically for clarity. The Co:Li dosing ratio was 2:1.

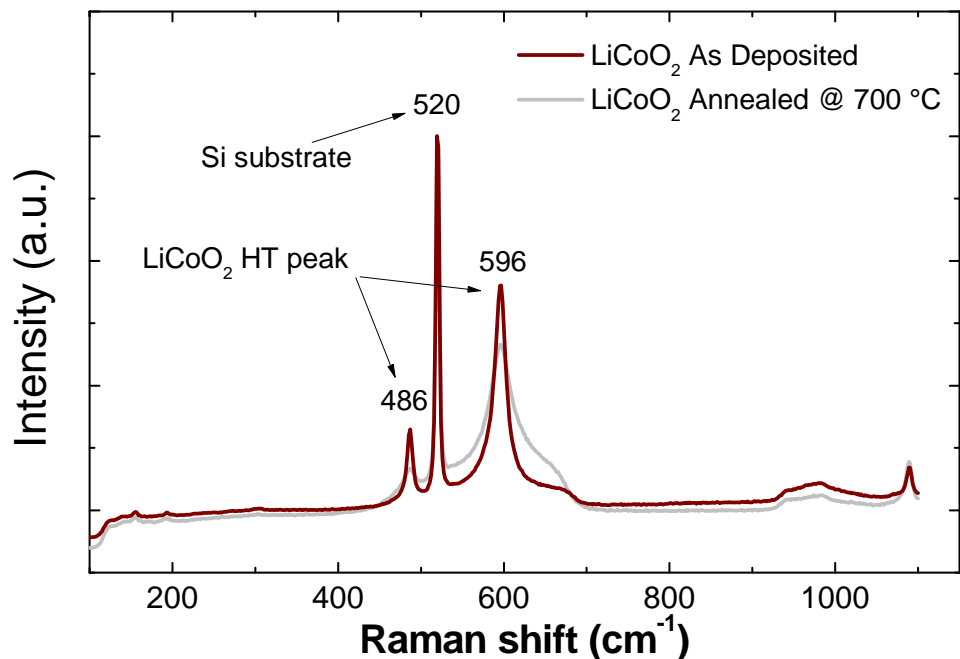


Figure 7: Raman measurements for LiCoO₂ annealed at 700 °C for 6 minutes compared to as-deposited LiCoO₂. The used Co:Li dosing ratio was 2:1.

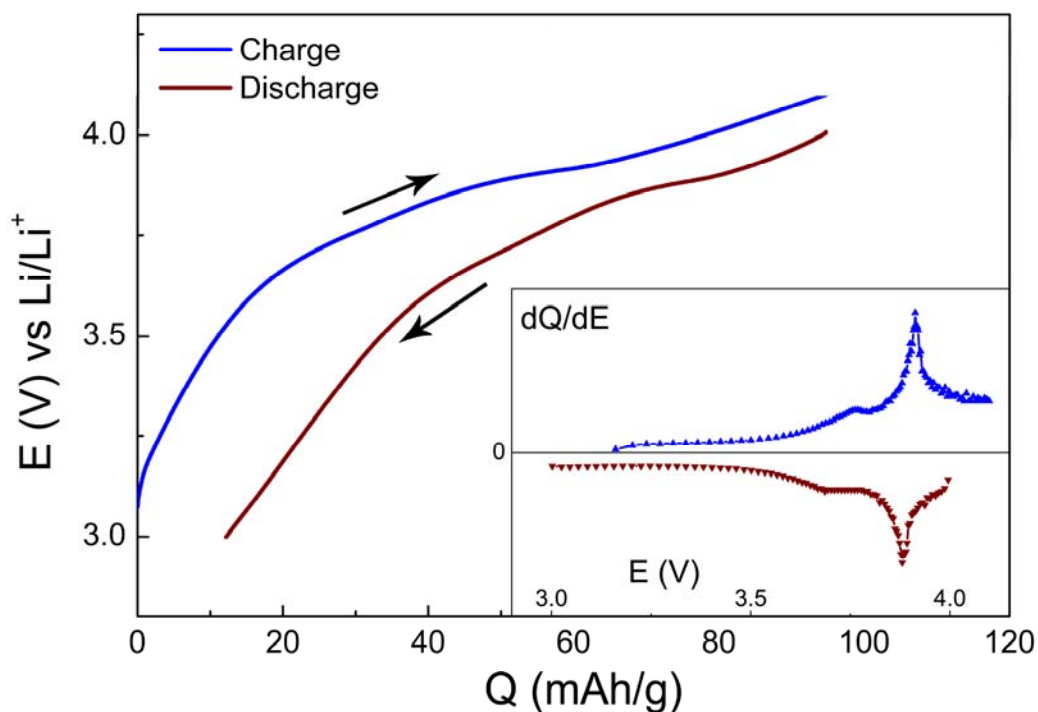


Figure 8: Constant current (CC) (dis)charge cycling between 3.0 V and 4.2 V (1 μA , 0.35 C-rate) for an ALD LiCoO₂ film deposited on Si/TiO₂/Pt. LiClO₄ in ethylene carbonate/diethyl carbonate (EC/DEC 1/1) was used as liquid electrolyte. The graph displays a 12% capacity loss between charge and discharge. The used Co:Li dosing ratio was 4:1. The inset shows the derivative of the capacity with respect to the potential.

Electrochemical analysis

For the electrochemical analysis, ~50 nm LiCoO₂ was deposited on a Si substrate covered with an ALD synthesized TiO₂/Pt stack which acts as a current collector (surface area of 2 cm²). The obtained LiCoO₂ films were annealed at 700 °C for 6 minutes and analyzed using constant current (CC) (dis)charge cycling applying a current of 1 μA, i.e. 0.35 C-rate. The positive electrode reaction for LiCoO₂ is shown below, in which the maximum amount of lithium that can be extracted from one LiCoO₂ unit is 0.5. Extracting more than 0.5 would irreversibly change the crystal structure of LiCoO₂ (20).

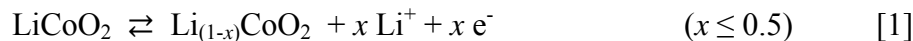


Figure 8 shows the (dis)charge of LiCoO₂ and the inset presents the curve of the derivative of the capacity with respect to the potential. This type of plot emphasizes the reactions by transforming the plateaus into broad or sharp peaks. Using this transformation a clear reaction is made visible around 3.9 V for LiCoO₂ as is expected from the literature (4,7). Also a 12% loss in capacity between the charge and discharge reactions is found, which can be explained by the formation of a solid electrolyte interface (SEI) related to the use of a liquid electrolyte in these measurements. The lifetime of the LiCoO₂ electrode was evaluated using the same constant current method and is presented in Figure 9. The electrochemical activity is lower than expected theoretically for LiCoO₂ (155 mAh/g, 46.5 μAh μm⁻¹ cm⁻²) (4), but remained fairly stable. After changing the Co:Li dosing ratio from 2:1 to 4:1 the amount of active material was increased significantly from ~26% to ~58% of the expected maximum storage capacity. Optimization of the LiCoO₂ process is expected to further improve the storage capacity.

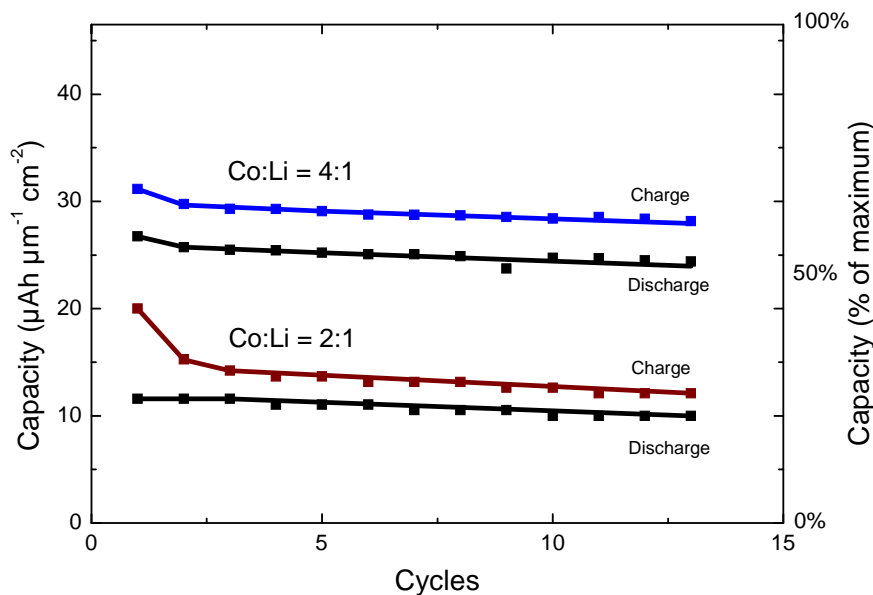


Figure 9: Capacity of a LiCoO₂ electrode versus cycle number. The electrode was cycled between 3.0 V and 4.2 V at 1 μA (0.35 C) with a half hour resting period in between the cycles. LiClO₄ in ethylene carbonate/diethyl carbonate (EC/DEC 1/1) was used as liquid electrolyte. The Co:Li dosing ratio were 2:1 and 4:1.

Preliminary attempts to determine the lithium concentration using ion beam analysis revealed a good correlation with the electrochemical results and could be an important new tool for the characterization of lithium-containing thin films (21).

Conclusions

A remote plasma ALD process (0.06 nm/cycle at 325 °C) for LiCoO₂ has been developed for the first time using the combination of CoCp₂ as cobalt precursor, LiO^tBu as lithium precursor and O₂ plasma as the oxidant source. After annealing the samples for 6 minutes at 700 °C the high temperature phase LiCoO₂ is obtained as shown by XRD and Raman spectroscopy measurements. Electrochemical charge/discharge cycling experiments showed good electrochemical performance with a promising storage capacity.

Acknowledgements

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