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Low-Pressure Chemical Vapor Deposition of LiCoO₂ Thin Films: A Systematic Investigation of the Deposition Parameters

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The feasibility of volatile precursor low-pressure chemical vapor deposition (LPCVD) for the production of LiCoO₂ cathodes for all solid-state microbatteries was examined. To test this feasibility, and gain insight into the deposition behavior, the influence of the deposition parameters on the properties of LPCVD grown thin-film LiCoO₂ cathodes was systematically investigated. The deposition temperature, concentration of the various reactants, and duration of thin-film growth were varied. The resulting LiCoO₂ layers were subjected to X-ray diffraction, inductively coupled plasma-atomic emission spectrometry, Rutherford backscattering spectroscopy, and electrochemical analyses. Stoichiometry of the films could be controlled by varying the precursor flows. Samples deposited at high temperatures with the optimum stoichiometry showed a high crystallinity and a high electrochemical activity; a storage capacity corresponding to a reversible Li-content around the theoretical value of 0.55 per Co was reached, and a good cycling stability was obtained when using this electrode in combination with a solid-state electrolyte.
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Autonomous microelectronic devices are becoming more and more important for the electronic industry in, for example, ambient intelligence and medical applications. As increasingly more functionality is added to these devices, their power supply requirements are considerable. Rechargeable batteries are not applied frequently for these devices because only relatively large volume batteries with insufficient cycling capabilities are generally available. The recent development of planar all-solid-state thin-film microbatteries provides a suitable alternative to conventional rechargeable batteries as a power supply for integrated devices.¹ However, the capacity of these solid-state batteries still remains relatively low.

One method to enhance the total capacity of thin-film batteries is the use of a substrate with a highly enlarged surface area. This surface area can, for example, be created by etching features into a silicon wafer, which is a well-developed technology in the semiconductor industry. Trench capacitors have been produced successfully using this method.² Because both capacitors and microbatteries comprise a stack of various active layers, a similar approach has been proposed for thin-film batteries. Using this method, the capacity of a thin-film battery can theoretically be increased by a factor of 25 (without a loss in power delivery and without an increase of footprint area),³ depending on the choice of the etched three-dimensional (3D) structure and the availability of suitable materials for both the anode and cathode. The evaluation of thin silicon anode films deposited by low-pressure chemical vapor deposition (LPCVD) was recently reported by Baggetto et al.⁴

A well-known and commonly used cathode material for these batteries is LiCoO₂, which has been thoroughly investigated over the past few decades. Various methods have been described to deposit electrochemically active LiCoO₂ films. These include sol-gel methods,⁵⁻⁸ radio frequency (rf)-magnetron sputtering,⁹⁻¹⁰ and pulsed laser deposition.¹⁰ Surprisingly few investigations have focused on LPCVD, although it is a well-known technique to deliver very crystalline and well-defined films for various materials.¹¹ Moreover, LPCVD has several advantages: it provides excellent stoichiometry control because separate precursors are used for lithium and cobalt, and it can be used for step conformal deposition in 3D structures. Before LPCVD can be successfully used as a method to produce 3D microbatteries, the process on planar substrates needs to be thoroughly understood.

In the early 1990s, a few preliminary studies on chemical vapor deposition (CVD) of LiCoO₂ using volatile metal organic precursors

were published. The films obtained were compared to sol-gel-deposited¹² and spray-pyrolysis-synthesized films.¹³ Both studies concluded that CVD was not the most favorable method to deposit LiCoO₂ thin films. Sol-gel-deposited films showed a more open structure, which is beneficial for a large contact area between the LiCoO₂ film and a liquid electrolyte, and gives the material a higher power capability.¹² Spray pyrolysis was suggested as a more favorable technique compared to CVD from a hardware point of view, implying that less hardware investments and more simple reagents are required.¹³ However, neither sol-gel nor spray pyrolysis deposition allow step conformal deposition of thin films into 3D structures.

Also by Kenny,¹⁴ volatile precursor LPCVD has been employed to deposit LiCoO₂. Many different analysis techniques were applied to investigate the influence of deposition parameters on the quality of the deposited films. The desired lithium-to-cobalt ratio could be obtained, but the investigations did not provide any evidence of the presence of crystalline LiCoO₂. Moreover, no electrochemical investigation was performed on these samples.

Cho and Yoon^{15,16} used liquid-delivery metalorganic chemical vapor deposition (MOCVD) to deposit LiCoO₂ films on planar substrates and trenches with a depth and a width of ~1 μm. Their initial measurements revealed that CVD is capable of depositing LiCoO₂ films in 3D structures, but that many deposition variables influence the properties of the deposited films.

In this article, the suitability of volatile precursor LPCVD is investigated for the deposition of LiCoO₂ cathodes for thin-film batteries. It is a systematic investigation of the deposition parameters for LiCoO₂ cathode films by volatile precursor LPCVD in which electrochemical, chemical, and crystallographic results are combined. The influence of the ratio of different reactants, susceptor temperature, and deposition time on the chemical composition, structure, and electrochemical properties is determined.

Experimental

Thin-film deposition.—LiCoO₂ thin films were deposited onto circular silicon substrates with a diameter of ~3 cm. The samples prepared for electrochemical measurements were deposited on similar substrates covered with an adhesive layer of TiO₂ and a layer of platinum to create a conductive back contact. Platinum-covered samples were not used for the other analyses, because platinum could interfere with the materials analyses.

To deposit LiCoO₂ thin films, a horizontal cold-walled LPCVD reactor was used (a modified Aixtron 200RF system). The substrate was positioned on a graphite susceptor that was heated via rf. The temperature was monitored using a thermocouple inside this suscep-

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Figure 1. Schematic representation of the LPCVD reactor setup.

tor. To increase homogeneity of the deposited films, the sample placed on the susceptor was rotated at 10 rpm during deposition. Growth rates were regulated by the choice of reactor pressure, flow of reactants, and susceptor temperature. It was possible to vary the deposition temperature between 300 and 1000°C and the reactor pressure between atmospheric pressure and 6 mbar.

The vapor supply system (Fig. 1) consisted of two precursor bubblers, one of which was placed in a thermostatic bath and the other was positioned in a furnace, to control low and high temperatures, respectively. These bubblers were fed with argon to evaporate the precursors and an extra pusher flow of argon was added further downstream to increase the gas flow and to prevent condensation of the precursor in the transport lines. The precursor evaporation rate was adjusted by varying the argon flow through the bubbler as well as the pressure and temperature of the bubbler. These variables could be regulated independently for both precursors. To prevent condensation, the vapor generated at elevated temperatures (i.e., from the bubbler positioned in the furnace) was led to the reactor through heated lines and valves (indicated as dashed lines in Fig. 1). Oxygen, mixed with argon, was fed into the reactor via a system completely separated from the precursor bubblers. The oxygen and precursor gas flows were allowed to mix in the deposition chamber.

The starting materials were cobalt dicarbonyl cyclopentadienyl [$\text{CpCo}(\text{CO})_2$] and tert-butyllithium [t-BuLi], both acquired from SAFC-Hitech (United Kingdom). These materials were delivered in stainless steel bubblers. After the bubblers were connected, the system was tested for leaks. Argon was supplied via a purifier to assure oxygen- and water-free gas flows. The settings of the vapor supply system and the deposition chamber are summarized in Table I. Four series of samples were deposited, with variations in the lithium-to-

Table I. Vapor supply system settings. The flows indicated for tert-butyllithium and $\text{CpCo}(\text{CO})_2$ are argon flows led through the bubblers in sccm. The total gas flow indicated is the total of the argon flow through the transport lines, the argon flow through the bubblers, and the oxygen flow.

Precursor	Temperature (°C)	Pressure (Pa)	Flow (sccm)
tert-butyllithium	50	4.0×10^4	400
$\text{CpCo}(\text{CO})_2$	18	2.5×10^4	13.8–55.2
Oxygen	Room temperature		1–50
Total gas flow	Room temperature		1550

cobalt ratio (series A), oxygen flow (series B), susceptor temperature during deposition (series C), and deposition time (series D). Two extra samples were deposited for cycling stability experiments, both containing a LiCoO_2 film deposited for 2 h at 500°C. On one of the samples, a thin protective layer of a solid-state electrolyte (SSE), lithium phosphate, was added.

Sample analyses.—Samples were analyzed by means of X-ray diffraction (XRD) using a Panalytical X'Pert PRO MPD diffractometer equipped with a $\text{Cu K}\alpha$ X-ray source. To suppress the diffraction peaks of the single-crystalline Si substrate, an ω offset of 3° was applied. Scanning electron microscopy (SEM) was performed using a Philips/FEI XL 40 FEG instrument, and Rutherford backscattering spectroscopy (RBS) measurements were done using the singletron radiation facilities of Eindhoven University of Technology. The lithium-to-cobalt ratio was determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Electrochemical analyses.—All electrochemical measurements were performed in an argon-filled glove box (O_2 and $\text{H}_2\text{O} < 1$ ppm). The samples were positioned in Teflon cells and used as working electrodes. Lithium metal foils were utilized as reference and counter electrodes.⁴ The cell was filled with a commercial-grade liquid electrolyte consisting of 1 M LiClO_4 in propylene carbonate (Puriel, Techno, Semichem Co., Ltd., Korea). This three-electrode setup was connected to an Autolab PGSTAT 30 potentiostat/galvanostat (Ecochemie B.V., The Netherlands) to perform cyclic voltammetry (CV) and constant current charge/discharge tests at room temperature. The samples were cycled at 1 mV/s, and all potentials are given vs a Li/Li^+ reference electrode couple. The constant current experiments were performed at $8.3 \mu\text{A cm}^{-2}$.

Results and Discussion

Precursor and oxygen flows.—To determine the correct ratio of flows through the precursor bubblers, a series of samples was prepared. First, the flow through the cobalt bubbler was varied, while the other flows were kept constant (series A). The process conditions of these deposition runs are listed in Table II. Three different argon flows through the cobalt precursor bubbler (F_{Co}) were chosen: 13.8, 27.6, and 55.2 (sccm). The pusher flow of argon was matched to obtain an equal total flow through the reactor in all cases. The active layers were deposited on planar silicon. The expected phases formed

Table II. Process parameters for deposition of LiCoO_2 samples. Listed are the oxygen flow (F_{O_2}), argon flow through the cobalt bubbler (F_{Co}), total gas flow through the reactor (F_{tot}), and the susceptor temperature (T_{dep}).

Series	F_{O_2} (sccm)	F_{Co} (sccm)	F_{tot} (sccm)	T_{dep} (°C)
A	50	13.8–55.2	1550	500
B	1–50	13.8	1550	500
C	1	13.8	1550	300–600

Figure 2. (Color online) XRD patterns of series A: deposited with different argon flows through the cobalt precursor bubbler ($=F_{Co}$).

are $LiCoO_2$ and Co_3O_4 in the case of an excess of cobalt precursor, and $LiCoO_2$ and Li_2O when using an excess of lithium precursor. The sensitivity of XRD for Li_2O is generally very low, and this species could therefore not be observed in the diffractograms. XRD was only used as a tool to distinguish between the Co_3O_4 and $LiCoO_2$ phases, while the formation of Li_2O was assumed because most organolithium compounds are known to react with oxygen.

The XRD results (Fig. 2) clearly show the diffraction lines for Co_3O_4 and $LiCoO_2$. At high cobalt precursor flows, the Co_3O_4 peaks dominate the diffractogram, while they disappear completely for the lowest flow. This is most clear for the Co_3O_4 220 line at $31.3^\circ 2\theta$, which is not visible for a flow of 13.8 sccm. The disappearance of the Co_3O_4 511 and the Co_3O_4 400 lines also illustrates that no crystalline Co_3O_4 is formed at this precursor flow rate.

XRD results have shown that the best stoichiometry was obtained using a precursor flow of 13.8 sccm. To check the cobalt-to-lithium ratio of this sample, it was also analyzed by ICP-AES. The film has a composition of $Li:Co = 1.1:1$, a slight overstoichiometry in lithium.

To evaluate the effect of the oxygen flow (F_{O_2}), three different samples were prepared with $F_{O_2} = 50, 25$, and 1 sccm (series B). The deposition conditions are summarized in Table II. XRD (see Fig. 3) showed that the samples deposited under various F_{O_2} are different and that the $LiCoO_2$ 101 line was reduced for samples deposited at higher oxygen flows. A similar, but much weaker effect was observed for the 104 diffraction line.

The cyclic voltammetric results on series B are shown in Fig. 4. Three different transitions are generally observed for $LiCoO_2$ electrodes cycled between 3.3 and 4.3 V. In this range, lithium is removed from stoichiometric $LiCoO_2$, which has a slightly distorted hexagonal structure with the $R\bar{3}m$ space group. When extracting lithium from $LiCoO_2$ a second hexagonal phase is formed at a potential of ~ 3.9 V, and a two-phase coexistence region exists for Li_xCoO_2 with $0.75 < x < 0.93$. This gives rise to a large peak in the cyclic voltammogram. Two small peaks are observed at 4.1 and 4.2 V, between which a monoclinic phase exists due to reordering of lithium ions. At potentials of >4.2 V, the hexagonal structure is reappearing.¹⁷

It is clear that the three samples of series B behave, electrochemically, very similarly (Fig. 4). A visible trend shows that the samples deposited with a higher oxygen flow have a slightly smaller peak area. This clearly indicates a lower lithium (de-)intercalation capacity. However, these effects are only very marginal. Because the

Figure 3. (Color online) XRD patterns of series B deposited at different oxygen flows.

amount of electrochemically active $LiCoO_2$ is nearly the same for all samples, the difference observed in the XRD measurements (Fig. 3) indicate that the oxygen flow does not influence the crystallinity of the deposited material much, but only influences the crystallographic orientation.

Deposition temperature.— Various properties of LPCVD-processed $LiCoO_2$ layers are expected to be dependent on the deposition temperature, because many, if not all, processes in the deposition reactor (e.g., the decomposition reaction rates and precursor diffusion) are influenced by temperature. To investigate these effects, several samples were deposited with the susceptor temperatures varying from 300 to 600°C in steps of 50°C (series C in Table II). All other parameters were kept constant. The XRD results obtained with series C reveal large differences (Fig. 5).

Films deposited at 300 or 350°C contain only negligible amounts of crystalline materials. At deposition temperatures higher than 400°C, crystalline $LiCoO_2$ is indeed formed, as can be seen from the $LiCoO_2$ 101 and 104 lines at 37.3 and $45.3^\circ 2\theta$, respectively. Moreover, some Co_3O_4 is present in the films (for example, the 220 and 311 line at 31.3 and $36.9^\circ 2\theta$ in Fig. 5). This effect is strongest in the layer deposited at 450°C, where both the $LiCoO_2$ and Co_3O_4 crystal structures were observed most clearly. These results suggest that deposition at a higher temperature ($>450^\circ C$) yields a more crystalline film, but also that the lithium-to-cobalt ratio of the films changes with temperature. The low-temperature and high-

Figure 4. CV performed at $LiCoO_2$ series B, deposited with multiple oxygen flows.

Figure 5. (Color online) XRD patterns of LiCoO_2 thin films deposited at multiple temperatures (series C).

temperature phases of LiCoO_2 cannot be distinguished using these diffractograms because their diffraction patterns are highly coincident.¹⁸

Using SEM imaging (Fig. 6), it is confirmed that the sample deposited at 300 °C indeed shows an amorphous morphology, with an islandlike deposition structure. Deposition at higher temperatures gives rise to a more homogeneous and more crystalline film structure. SEM images were also used to determine the layer thickness, which was found to be ~ 90 nm for the film deposited at 500 °C.

Figure 6. SEM images of samples from series C, deposited at 300, 400, 500, and 600 °C.

Figure 7. CV of LiCoO_2 layers series C (varying T_{dep}).

The samples of series C were also subjected to RBS and ICP-AES analyses in order to determine the amount of material deposited and the lithium/cobalt/oxygen ratio. From these analyses (Table III), it is clear that deposition at low temperatures yields films that deviate significantly from a lithium-cobalt ratio of 1:1. For temperatures below 400 °C, oxygen and lithium are found to be present in excess in the deposited films. A ratio of Li:Co:O of 1.3:1:2.7 is observed for the sample deposited at 350 °C, and even 3.3:1:7.1 at 300 °C. This result, combined with the absence of a crystalline phase in the XRD pattern (Fig. 5), indicates that the processes in the deposition reactor are not fully occurring at low temperatures and that the desired LiCoO_2 phase is not formed. Instead, various partially oxidized precursor residues might be present.

For the samples deposited at 400 and 450 °C, RBS/ICP-AES data show that oxygen is understoichiometric, while Co is somewhat overstoichiometric (Table III). This is consistent with the XRD results (Fig. 5), showing that a Co_3O_4 phase is formed. The Co_3O_4 phase has a lower oxygen-to-cobalt ratio compared to stoichiometric LiCoO_2 .

The data found with RBS and ICP, combined with the layer thickness found in the cross-sectional SEM images could be used to determine the density of the deposited film. The layer deposited at 500 °C has a density of ~ 3 g/cm³, which is slightly higher than the tap-density of a high-density powder.¹⁹

To examine the electrochemical performance of series C, five LiCoO_2 samples were prepared on a platinum current collector, at susceptor temperatures varying from 300 to 550 °C. It can be observed in Fig. 7 that the films deposited at low temperatures show hardly any electrochemical activity, while the samples deposited at higher temperatures have a more defined CV plot. The sample deposited at 550 °C shows a distinct behavior: after the first charge step, which reveals, as expected, a large peak at 3.95 V and two smaller peaks at 4.07 and 4.2 V, the discharge behavior is somewhat deviating because it shows a single broad peak that is shifted toward

Table III. ICP, RBS, and electrochemical results for the samples in series C, deposited at different temperatures.

Temperature (°C)	300	350	400	450	500	550	600
ICP Li:Co	1:0.3	1:0.8	1:1.6	1:1.7	1:1.2	1:1.2	1:1.0
RBS Co/cm ² ($\times 10^{15}$ atoms/cm ²)	41.8	129	179	190	167	172	172
RBS Co:O	1:7.1	1:2.7	1:1.8	1:1.9	1:1.9	1:1.8	1:1.8
Initial lithium (de)intercalation capacity (C/cm ² , 3.3 – 4.3 V)							
Charge	4.95×10^{-3}	9.08×10^{-3}	1.37×10^{-2}	1.29×10^{-2}	1.48×10^{-2}	2.02×10^{-2}	
Discharge	1.61×10^{-3}	1.84×10^{-3}	5.93×10^{-3}	9.94×10^{-3}	1.19×10^{-2}	1.58×10^{-2}	
Li ⁺ per Co (charge/discharge)	0.74/0.24	0.44/0.09	0.48/0.21	0.42/0.33	0.55/0.45	0.73/0.58

Figure 8. CV of series D (varying deposition times). The inset shows the charge and discharge capacities of these films.

more negative potentials. Also, duplicate samples show a similar behavior. To find the cause of this electrochemical degradation, more in-depth research is required.

The integral of a peak in a cyclic voltammogram divided by the scan rate equals the amount of charge (de-)intercalated. In this way, the discharge capacity of the first cycle was calculated from the CV plots shown in Fig. 7. Combining this with the number of Co atoms obtained with RBS, the reversibly extractable number of lithium ions per Co atom was calculated. For samples deposited at 500 and 550°C, the discharge capacity was found to be around ~ 0.55 Li per Co. This is the maximum amount of lithium that can be extracted and intercalated reversibly in LiCoO_2 .¹⁷ Because the sample deposited at 550°C shows a distinct discharge behavior, further experiments were limited to deposition at 500°C, where the best crystallinity and a good storage capacity were obtained.

Deposition time.— A series (series D) of samples was deposited at 500°C for 1, 2, 4, 6, and 8 h. The rest of the parameters were unaltered compared to the temperature-dependence experiments (series C) shown in Table II. Again the deposited samples were evaluated electrochemically. The CV plots (Fig. 8) show that the area under the oxidation and reduction peaks increases with deposition time. The potential at which the maximum current is observed in the CV plot also shifts with the deposition time, which is mainly due to the resistance of the liquid electrolyte. Using electrochemical impedance spectroscopy (not shown here), this resistance was found to be $\sim 70 \Omega$. For a peak current of 1.2 mA (for the layer with 8 h deposition time), an ohmic drop of 70Ω results in a shift of 84 mV from the equilibrium potential. This agrees well with the shift in Fig. 8. Also, a broadening of the oxidation and reduction peaks, which cannot be readily explained by ohmic losses, is observed for samples with a longer deposition time. This broadening can be attributed to the increased film thickness and longer diffusion pathways for lithium ions. Diffusion limitations will play a more important role for thicker solid electrodes.

The charge stored in the series C electrodes was calculated as previously and is shown in the inset of Fig. 8. This reveals that the charge increases linearly with deposition time, as expected. It can also be concluded that nucleation effects during thin-film deposition can be neglected at this scale because the linear fit of the data points passes the origin. The difference in charge and discharge capacity can be attributed to irreversible side reactions (e.g., oxidation of the liquid electrolyte,²⁰ the formation of the less electrochemically active spinel LiCo_2O_4 phase,²¹ or mechanical strain-induced degradation of the LiCoO_2 film).²²

Cycling stability.— To determine the stability of the optimized samples, a cycle-life experiment was performed. A sample was

Figure 9. (Color online) Cycling stability of LPCVD deposited LiCoO_2 films. Constant current charge and discharge cycle 10 (black), 20, 30, 40, and 50 (lightest shade of gray) are displayed for LiCoO_2 thin films with (A) and without (C) a protective layer of lithium phosphate, a SSE. The charge ($\blacktriangle, \blacklozenge$) and discharge ($\bullet, \blacksquare$) capacities for, respectively, the protected and unprotected LiCoO_2 films are shown in (B).

charged using a current density of $8.3 \mu\text{A cm}^{-2}$ until the cutoff potential of 4.1 V was reached. After a relaxation time of 1800 s, the sample was discharged to 3.0 V at the same current density, after which again a relaxation period of 1800 s followed. This procedure was repeated 50 times.

It was observed that a film of LiCoO_2 in liquid electrolyte degrades significantly during 50 cycles (Fig. 9B and C). This is mainly due to an increase in impedance, which can be concluded from the increase of the potential of the charging plateau, and the decrease of the potential of the discharge plateau. This indicates that a resistive interface is formed.

However, because the goal is to investigate the feasibility of CVD for an all-solid-state battery, a sample with an additional thin layer of SSE (lithium phosphate) was also tested under the same conditions (Fig. 9A and B). This sample showed a much more stable behavior and can be cycled without a major loss of capacity. Also, the plateau potentials remain unchanged, indicating that the loss of capacity for the original LiCoO_2 sample is due to the interaction of the liquid electrolyte with the thin-film electrode and does not influence the feasibility of CVD for all-solid-state batteries.

Conclusions

The influence of various LPCVD deposition parameters on the film properties of LiCoO_2 was investigated by material analyses and electrochemistry. It was found that using the chosen precursors, the lithium-to-cobalt ratio can be controlled well by varying the argon flow through the cobalt precursor bubbler. The oxygen flow had an impact on the crystal orientation of the deposited LiCoO_2 but did not significantly influence the electrochemical behavior of the films. It was shown that the most crystalline films are deposited at susceptor temperatures of 500°C or above. Because samples deposited at 550°C showed a distinct discharge behavior, experiments were limited to deposition at 500°C, where a good crystallinity and a high storage capacity are obtained. Reversible storage capacities around the theoretical value of 0.55 Li per LiCoO_2 formula unit were found.

Cycle-life experiments showed that, in liquid electrolyte setups, the significant degradation of capacity during cycling is mainly due to the interaction between the LiCoO_2 thin-film electrode and the liquid electrolyte. The addition of a thin layer of SSE enhanced the stability to a great extent, indicating that LPCVD-deposited LiCoO_2 thin films are suitable for application in all-solid-state thin-film microbatteries.

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