

LiCoO₂ thin-film cathodes grown by RF sputtering

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Abstract

LiCoO₂ thin-films have been grown by RF magnetron sputtering on silicon substrates covered with gold. As-grown films deposited at substrate temperature 500 °C were identified by XRD and RS as an HT hexagonal phase. The structure of the films prepared at substrate temperatures <300 °C were less well defined. Nevertheless, the films prepared at 200 °C have better electrochemical properties than the films prepared at higher temperatures. The determination of the composition of thin-films showed that the composition approaches to the stoichiometric one for discharge power of 60 W irrespective of substrate temperature. In other cases, a slight excess of Li was found. The films have promising properties to be used as cathodes in lithium-ion (Li-ion) batteries. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

LiMO₂ (M = Co, Ni, Mn) thin-film cathodes for Li secondary microbatteries have application in the microdevices as power sources [1–3]. These oxides are of most interest nowadays because they have high potentials versus a lithium anode (minimum of 3 V), are air stable in the fully lithiated state and show very good reversibility. LiCoO₂ has been studied more extensively owing to its favorable electrochemical properties and ease of manufacture [4,5]. Reactive sputtering is one of the most frequently used techniques since it enables the formation of homogeneous films with defined thickness. By varying the deposition conditions, it is possible to change the composition, crystallinity and morphology of the films.

In this work, LiCoO₂ thin-films were deposited by RF magnetron sputtering. X-ray diffraction (XRD) and Raman spectroscopy (RS) were used to investigate the microstructure of the films. The surface phase composition was investigated by reflection electron diffraction. The morphology was studied by electron microscopy and atomic force microscopy (AFM). The depth-profile of the films was measured by Auger electron spectroscopy (AES). Atomic absorption spectrometry (AAS) and EDAX analysis were used to

determine the chemical composition of sputtered films. Electrochemical studies were performed in order to investigate the use of the films as cathodes in lithium batteries.

2. Experimental

The films were prepared by radio frequency (RF) magnetron sputtering in the argon–oxygen atmosphere from 25 to 50 mm diameter targets without any post-deposition annealing. The targets for sputtering were prepared from LiCoO₂ commercial powder (Aldrich), pressed into pellets and sintered at 800 °C for 40 h.

The substrates were Si plates (1 cm² area) covered with SiO₂. Au layer served as a current collector. A 30 nm Ti layer was incorporated between the substrate and Au current collector in order to enhance the adhesion of Au onto the SiO₂ substrate.

Several substrate deposition temperatures (100, 200, 300, 400 and 500 °C) were used to observe the dependence of film properties on this deposition parameter. The film thickness was measured on the partially masked film with an Alphastep profilometer. The target-to-substrate distance was 20 and 40 mm for 25 and 50 mm target diameter, respectively. The RF discharge power applied for 25 mm target diameter was 15 W (the discharge power density per area is 3.05 W/cm²) and for 50 mm target diameter 20, 60 and 80 W

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(the discharge power density per area is 1.02, 3.06, 4.08 W/cm², respectively). According to the discharge power density is 15 W for 25 mm target diameter comparable with 60 W for 50 mm target diameter.

X-ray powder diffractometer DRON 3 using Cu K α radiation was used for characterization of LiCoO₂ films. Raman spectra of the LiCoO₂ films were measured at room temperature in the back scattering configuration using the Ramanscope 1000 Raman microscope (Renishaw). The excitation was performed with the Ar-ion laser (wavelength 514.5 nm). The polarization of the scattered light was not analyzed.

Physical electronics spectrometer SAM 660, equipped with cylindrical mirror analyzer operated at relative resolution of $\Delta E/E = 0.25\%$, was used for Auger analysis. Depth profiling was performed alternating the analysis to the removal of thin layers by 3 kV Argon ions bombardment. Ion beam was scanned over a surface area of 5 mm \times 5 mm. The sputtering rate, calculated on an National Physical Laboratory (NPL)—Community Bureau of Reference Ta₂O₅/Ta reference sample, was about 10 nm/min under these conditions.

For the surface phase composition, the measurements by reflection electron diffraction were carried out with the use of specialized electron diffraction equipment EMR-100, furnished with a filter of in-elastically-scattered electrons and registration system for measurement of intensity of amorphous patterns.

Electrodes were subjected to observation by scanning electron microscope Philips XL 30 CP (SE detector, accelerating voltage 10–30 kV). EDAX analysis was carried out.

Atomic absorption spectrometer, Varian spectra AA, using flame atomization system has been used for the determination of Li and Co content in the LiCoO₂ thin-films. Absorption spectral analysis measures the absorption of radiation in visible and ultraviolet regions by investigated sample. Characteristic absorption bands of Li and Co are at the 670.8 and 240.7 nm, respectively.

3. Results and discussion

Fig. 1 shows the XRD spectra of LiCoO₂ film sputtered at 100, 300 and 500 °C. The LiCoO₂ peaks are identified by indexes, whereas the peaks originating from Au film on the top of the substrate are indicated by asterisk. In spite of the fact that the most intensive peak arises from gold, this film can be identified as a high temperature (HT) hexagonal modification of LiCoO₂. The films sputtered at lower substrate temperatures (<300 °C) do not show so distinctly visible peaks, which suggests less well defined structure. Structure of other samples mentioned in this paper has the similar dependence on the temperature.

The results of XRD are supported by the Raman spectra. LiCoO₂ films deposited at the lowest medium and highest substrate temperatures (#K1 at 100 °C; #K3 at 300 °C; #K5

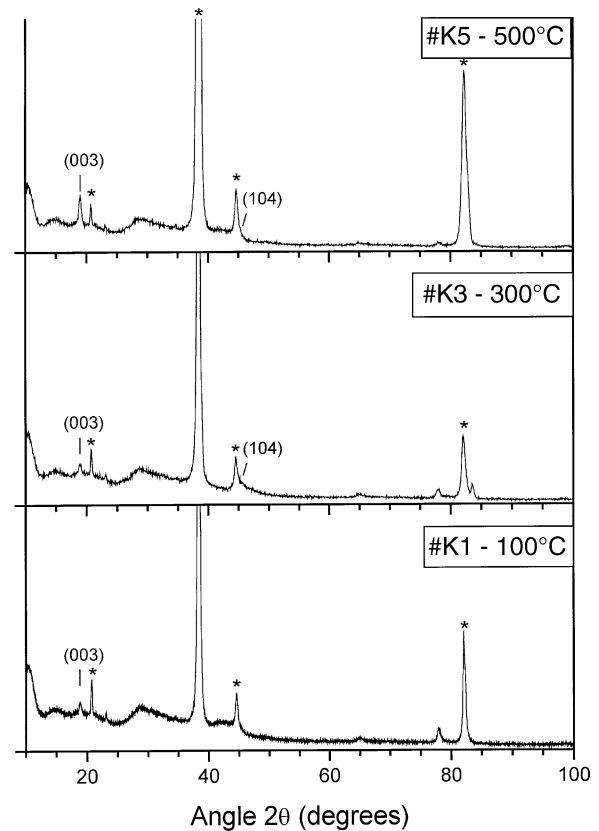


Fig. 1. X-ray diffractogram of a LiCoO₂ film grown at 100, 300, 500 °C. The diffraction peaks of the substrate are indicated by an asterisk (*).

at 500 °C) are compared in Fig. 2. Main results may be summarized as follows.

1. The bands at 486 and 592 cm⁻¹ dominating the curve #K5 can be identified with the phonon modes typical of the HT hexagonal modification of LiCoO₂, which have the E_g and A_{1g} symmetry, respectively [6]. The weak feature at 520 cm⁻¹ belongs to the silicon substrate (a

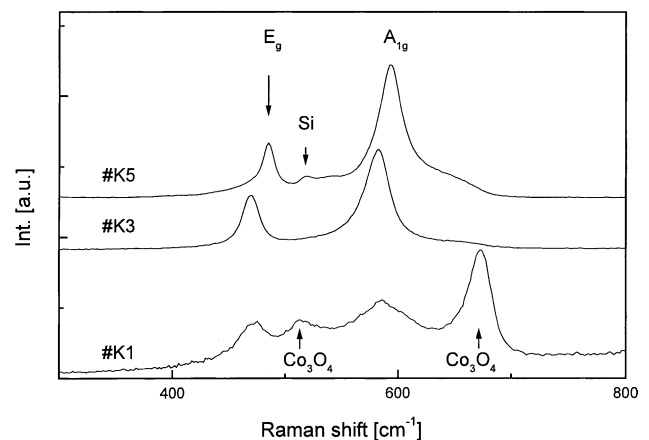


Fig. 2. The spectra of LiCoO₂ samples: #K1 prepared at 100 °C, #K3 deposited at 300 °C, #K5 prepared at 500 °C.

- part uncovered with gold). The spectrum of sample #K3 is very similar; there is no trace of the Si substrate and the peaks are shifted to lower frequency. This shift may be due to the lithium non-stoichiometry [6] and/or to the local heating.
- The spectrum for the #K1 sample is dominated by a band at 676 cm^{-1} , which obviously corresponds to the presence of Co_3O_4 the weak feature at about 515 cm^{-1} has probably the same origin [7]. The remaining bands are the same as in sample #K3.
 - Some inhomogeneities related both to the non-stoichiometry and the presence of cobalt oxide were observed on the samples when measurements were carried out at different spots of the surface. On some spots, there was also observed a peak at 1088 cm^{-1} characteristic for the presence of Li_2CoO_3 .

- When the excitation power was lowered below approximately $5 \times 10^3\text{ W cm}^{-2}$, a featureless broad band between 350 and 650 cm^{-1} was observed for the samples deposited at temperatures up to $300\text{ }^\circ\text{C}$ (e.g. #K1–#K3). An increase in the power obviously results in local annealing and recrystallization of the films to the HT phase.

Figs. 3 and 4 show AFM pictures of LiCoO_2 deposited on gold and silicon substrates at the lowest and highest deposition temperature 100 and $500\text{ }^\circ\text{C}$. A considerable effect of substrate properties on film crystallinity and morphology can be observed. The roughness of films on gold is considerable higher at both substrate temperatures. The grain size of films is at $500\text{ }^\circ\text{C}$ comparable for both substrates but at $100\text{ }^\circ\text{C}$ is on gold lower.

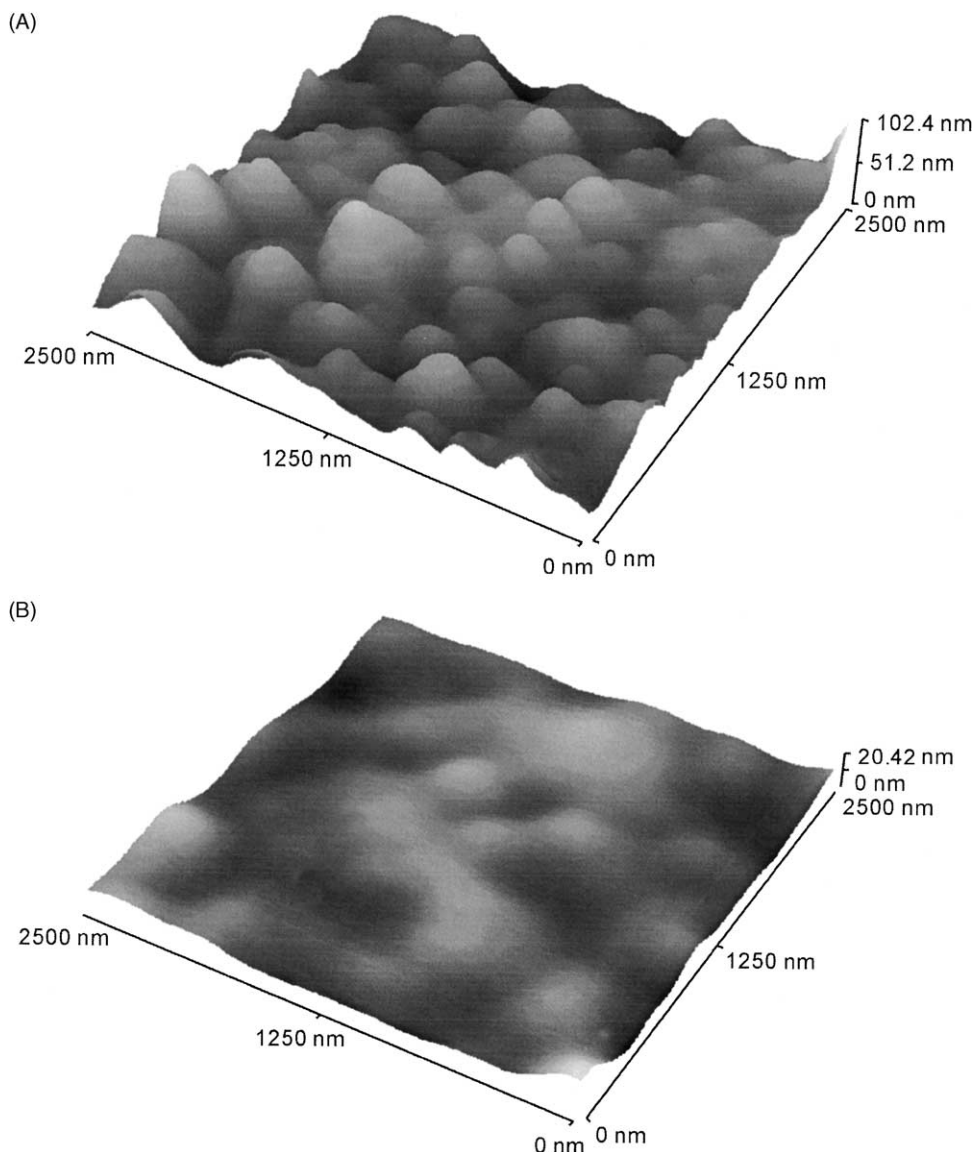


Fig. 3. AFM pictures of LiCoO_2 samples: (A) on gold, $100\text{ }^\circ\text{C}$; (B) on silicon, $100\text{ }^\circ\text{C}$; (C) on gold, $500\text{ }^\circ\text{C}$; (D) on silicon, $500\text{ }^\circ\text{C}$.

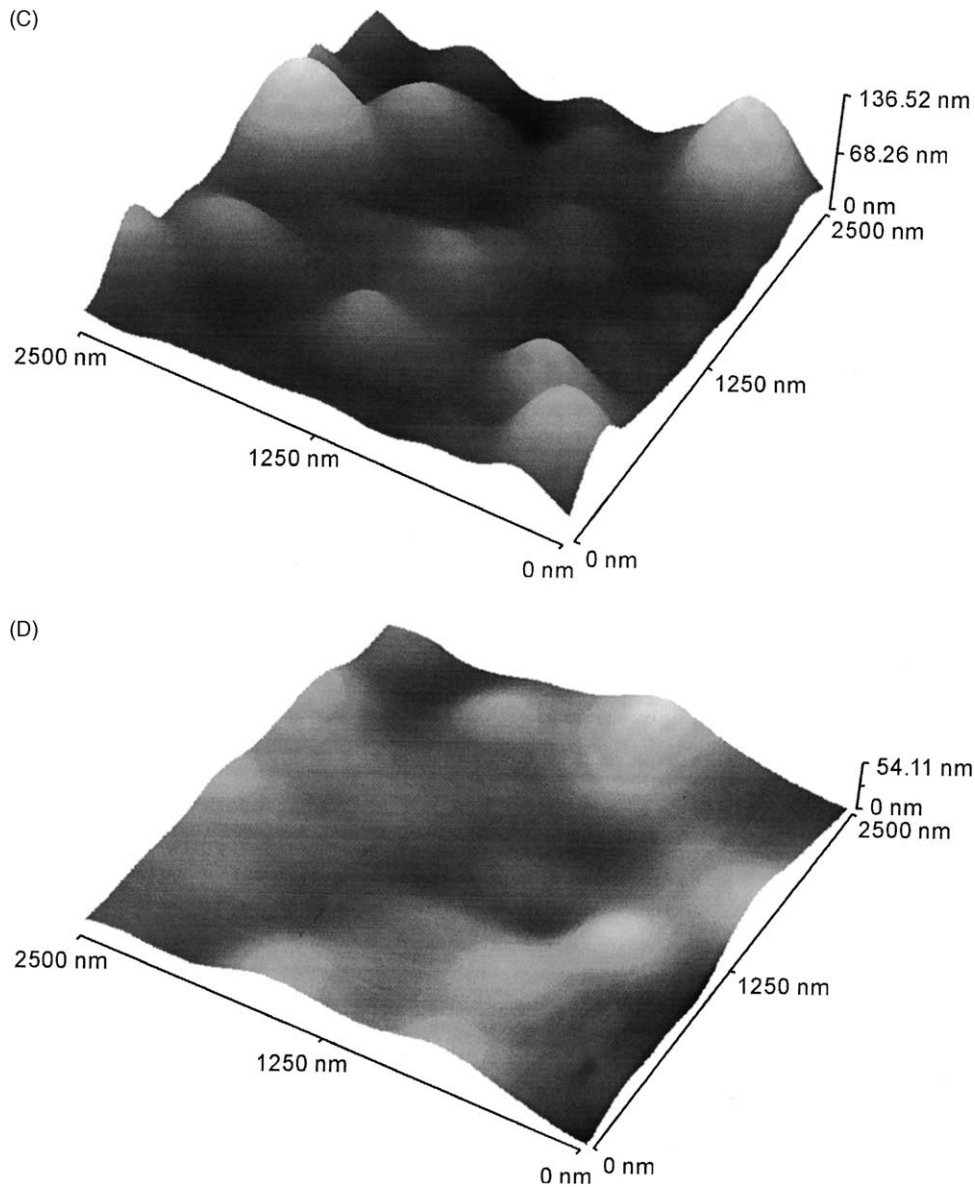


Fig. 3. (Continued).

For the study of the interfaces and the control of the cathode materials quality and composition, samples were analyzed by AES combined with Argon ions bombardment to obtain depth-profiles. The results for two samples, grown at two different substrate temperatures 200 and 400 °C, are reported in Figs. 4 and 5 respectively. On the outermost layer of the sample grown at 400 °C substrate temperature (#K7), the lithium KLL transition peak at 43 eV energy was well detectable, thus, enabling us to estimate the stoichiometry of the film as $\text{LiCo}_{0.8}\text{O}_{1.7}$. As the cobalt signal increased with the increasing depth, the Li peak became partially overlapped with the cobalt peak, which in oxidized form falls in the same energy range. The quantification of Li was hindered, but the O/Co atomic ratio remained close to the stoichiometric value. Enhanced diffusion and intermixing

of Ti and Au layers into cathode layer were observed, resulting in a broadening of the interface.

In the sample grown at a substrate temperature of 200 °C (#K9), Li was not detectable, neither on the surface nor in the depth and the atomic ratio O/Co in the bulk of the film was equal to 1.5. At variance with the previous sample, this one exhibited sharp and well-defined interfaces between layers. With an exception for carbon, no impurities were found in these films. Carbon concentration decreases rapidly from the surface into deeper layer and disappears in approximately 20 nm depth. The measurement of residual gas composition in the chamber of turbomolecular pump does not show any presence of carbon and it allows us to propose the following explanation: CO_2 molecules, which are present in the ambient air, are absorbed on the film surface, react

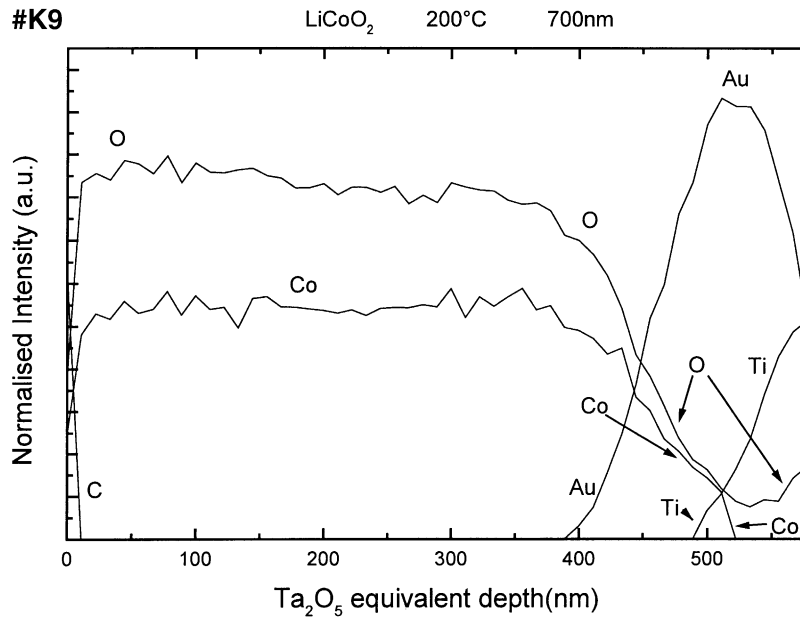


Fig. 4. Auger depth-profile of sample #K9 deposited at 200 °C.

with Li₂O and form Li₂CO₃. Such a chemical reaction suggests the presence of free unbound Li₂O on the film surface. This Li₂CO₃ layer can affect the transport properties of the multilayer battery.

To confirm the Li₂CO₃ presence on the film surface the phase composition of LiCoO₂ films was investigated by reflection electron diffraction. There is no magnetic lens in the space between the sample and the photo-plate, which allows more accurate measurements compared with the device using microscope. The sample-to-film distance was 600 mm and the electron acceleration voltage was 75 kV.

In general, the accuracy of this method is not too high, however, it is high enough to determine exactly all phases present in the surface layer of our samples. It should be noted that this technique allows getting information from thin surface layer (≤ 10 nm). It was found that surface phase composition was different from deeper film layers, which were determined by XRD previously. For all deposition temperature (100, 200, 300, 400 and 500 °C) we received the picture with the same radii of diffraction rings (a typical picture is in Fig. 6). The comparison of calculated interlayer spacing d with tabular values of Li₂CO₃ is in Table 1. The

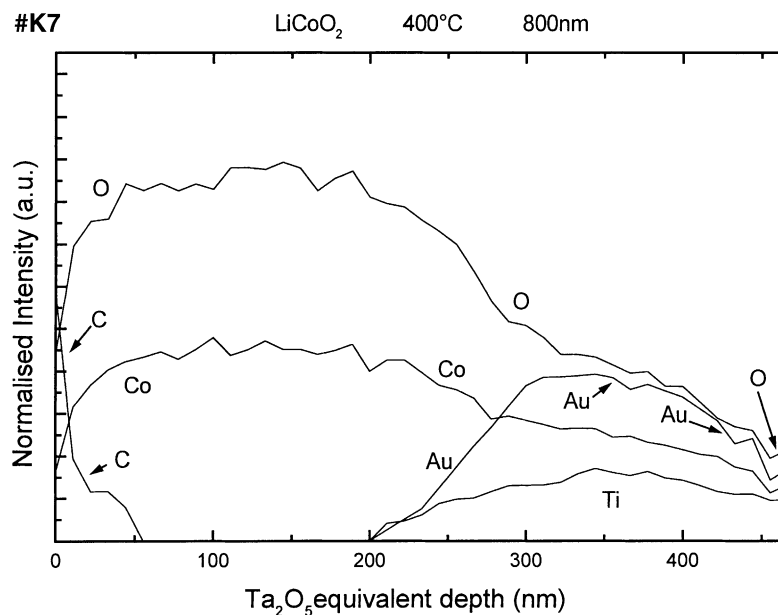


Fig. 5. Auger depth-profile of sample #K7 deposited at 400 °C.

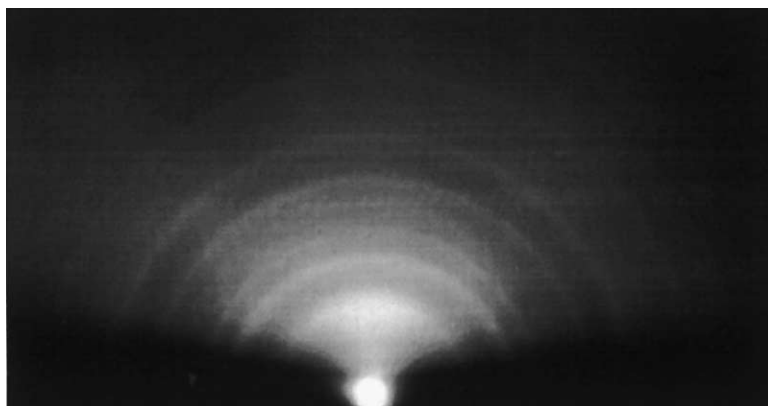


Fig. 6. Reflection electron diffraction patterns of LiCoO₂ film, deposited at 100 °C.

presence of Li₂CO₃ is, therefore, confirmed on the surface of films prepared at all used temperatures.

Atomic Absorption Spectrometer was used to determine the Li and Co content in the LiCoO₂ thin-films. Li/Co atomic ratio and the dependence on deposition conditions of sputtered films were examined in detail. It was found that neither the substrate temperature nor material of substrate has significant effect on the Li/Co ratio in prepared films (see Fig. 7). The main parameter influencing the Li/Co ratio is the RF discharge power. Nevertheless, there is no simple relationship between them. The composition nearest to the stoichiometric one (Li/Co = 1) was observed for a power of 60 W.

Complete stoichiometry of LiCoO₂ films was calculated from Li and Co content determined by AAS analysis and from Co and O determined by EDAX analysis. Both analysis were made for films sputtered at a discharge power of 60 and 20 W. The results are summarized in Table 2. In samples thicker than 800 nm the oxygen content is nearly stoichiometric. In samples thinner than 800 nm, the high oxygen content originates not only from LiCoO₂ layer but also from the SiO₂ substrate underneath, which is proved by silicon identification in thin samples.

Electrochemical properties of LiCoO₂ thin-films deposited on Au covered Si/SiO₂ substrates at different substrate

temperatures were studied using cyclic voltammetry in the potential range 2.1–4.5 V at a scan rate of 1 mV/s and by charge/discharge measurements (constant current cycling) with the constant current of 1 or 5 × 10⁻⁵ A, cut-off voltage of 4.5 and 2.1 V for charge and discharge period, respectively. Cut-off time was 125 h. All measurements were carried out in three-electrode cells containing 1 M lithium perchlorate in dry propylene carbonate as an electrolyte and lithium rods as both reference and counter electrode. The water content in the electrolyte was never higher than 20 ppm.

The voltammograms of cathodes sputtered at 200, 400, and 500 °C from 25 mm diameter target (at discharge power 15 W) were measured in five cycles. From comparison of the current densities and cycleability in the respective curves (see Figs. 8–10) follows that the electrochemical properties of the LiCoO₂ film prepared at 200 °C are better than those of the films prepared at higher temperatures.

Two peaks appear on the ascending parts of voltammograms recorded on samples prepared at higher temperatures. They are not developed on the voltammogram measured on the film prepared at 200 °C. We suppose that this difference is related to the different crystalline degree of the two films.

Charge/discharge curves were recorded for Li/LiCoO₂ cells using LiCoO₂ thin-films grown at various temperatures.

Table 1
Comparison of calculated interlayer spacing *d* with tabular values of Li₂CO₃

<i>R</i> (experimental, mm)	<i>d</i> (calculated, nm)	<i>d</i> (tabular Li ₂ CO ₃ , nm)	<i>hkl</i>	Deviation (%)
6.2	4.16	4.164	–1 1 0	0.7
6.8	3.79	3.797	2 0 0	0.08
8.9	2.90	2.918	–2 0 2	0.66
8.9	2.90	2.812	0 0 2	3.09
9.9	2.61	2.627	–1 1 2	0.80
10.5	2.46	2.431	–3 1 1	1.08
11.3	2.28	2.276	0 2 1	0.32
12.6	2.05	2.081	–2 2 0	1.60
13.8	1.87	1.867	3 1 1	0.14
16.4	1.57	1.565	–5 1 1	0.52
20.2	1.28	1.287	5 1 1	0.76

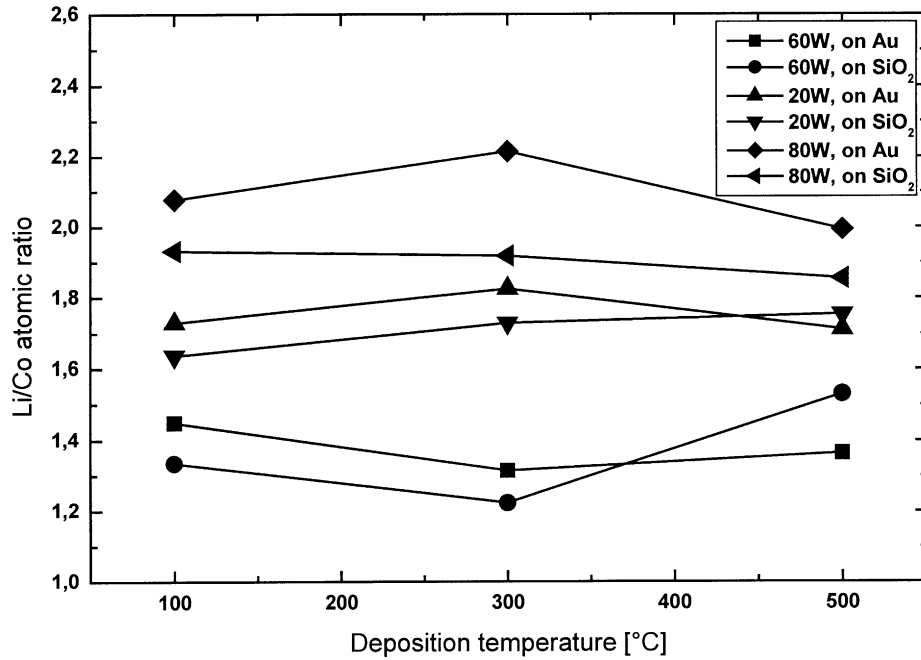


Fig. 7. Dependence of Li/Co atomic ratio on deposition parameters.

Table 2
The composition of sputtered films obtained from AAS and BDAX analysis

Li (μg)	Co (μg)	O (at.%)	Co (at.%)	Si (at.%)	O _{calc} (μg)	Stoichiometry	T _s (°C)	d (nm)	P (W)
9.0	65.7	72.3	27.7	0	46.1	Li _{1.2} CoO _{2.6}	100	870	60
15.5	100.3	67.8	32.2	0	57.3	Li _{1.3} CoO _{2.1}	100	817	60
13.1	81.4	64.2	30.0	0	47.1	Li _{1.4} CoO _{2.1}	500	900	60
11.8	64.9	77.9	15.6	2.8	87.7	Li _{1.5} CoO _{5.0}	300	460	60
9.3	57.9	79.8	13.9	5.0	89.6	Li _{1.4} CoO _{5.7}	500	400	60
2.3	10.7	58.4	4.2	12.1	35.2	Li _{1.8} CoO _{14.0}	300	90	20
2.3	10.7	47.7	4.4	11.0	31.7	Li _{1.8} CoO _{11.0}	300	90	20

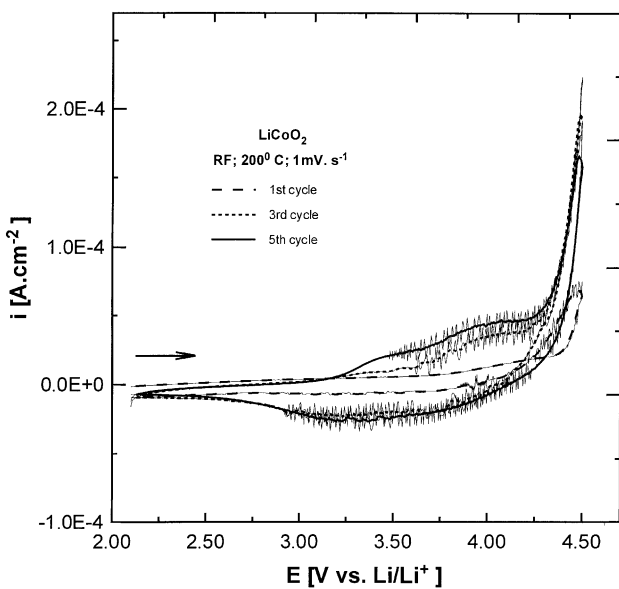


Fig. 8. Cyclic voltammograms of LiCoO₂ prepared at 200 °C from 25 mm target (15 W).

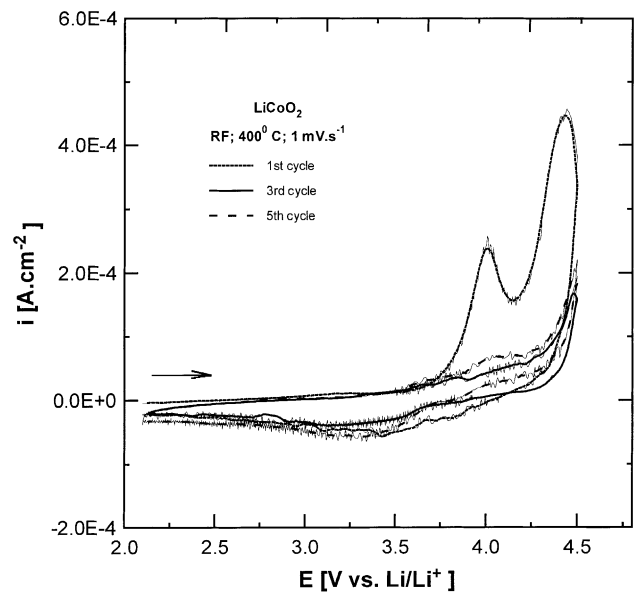


Fig. 9. Cyclic voltammograms of LiCoO₂ prepared at 400 °C from 25 mm target (15 W).

Table 3
Specific capacities measured on LiCoO₂ thin-films

Sample	Temperature (°C)	Thickness (μm)	Current (mA)	Specific capacity (mAh/g)			
				1st cycle	3rd cycle	5th cycle	10th cycle
#K2	200	65	0.50	160	140	140	140
#K6	400	>2.00	0.50	60	60	50	
#K5	500	1.80	0.50	110	140	250	400
#K14	600	0.500	0.50	190	180	180	
#K17	400	0.290	0.50	160	120		

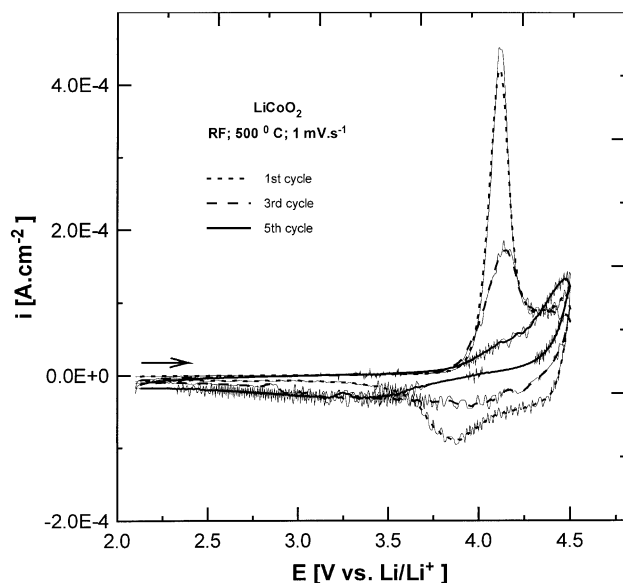


Fig. 10. Cyclic voltammograms of LiCoO₂ prepared at 500 °C from 25 mm target (15 W).

Specific capacities are listed in Table 3. Surprisingly, good properties were exhibited by a cathode prepared at 200 °C that, despite to the low crystallinity reached the specific capacity of 140 mAh/g even in the 10th cycle. The missing values in higher cycles are related to a peeled-off film. No relation between specific capacity and sputtering temperature is evident. Even the values of two electrodes sputtered at 400 °C differ. That can be explained by the inhomogeneity of film thickness resulting from the small 25 mm diameter target. The greater 50 mm diameter target improves the homogeneity of film thickness. Further measurements with films sputtered from 50 mm diameter target, are in program.

4. Conclusion

In this work, LiCoO₂ thin-films were deposited by RF magnetron sputtering. The films grown at 500 °C were identified by XRD as a (HT) hexagonal phase. The results from XRD were supported by the Raman spectra. Two

maxima at 486 and 592 cm⁻¹ frequencies appearing on the Raman spectra corresponded with the phonon modes typical of the (HT) hexagonal phase. The structure of the films prepared at lower substrate temperatures (<300 °C) were less defined.

Depth-profile analysis of films revealed enhanced diffusion of Ti/Au layers on the top of the substrates into cathode layer at the substrate temperature 400 °C compared with the layer prepared at 200 °C. Carbon concentration decreases rapidly from surface into deeper layer and disappears in a depth of 20 nm. The presence of Li₂CO₃ phase on the surface of the films deposited at all substrate temperature was confirmed by the reflection electron diffraction. Since no carbon was found by analysis of the residual gas composition in the chamber of turbomolecular pump, we assume that Li₂CO₃ arises from CO₂ absorbed on the film surface from the ambient air and Li₂O. Consequently, such a chemical reaction suggests the presence of free unbound Li₂O on the film surface.

Neither substrate temperature nor substrate material has a significant effect on Li/Co atomic ratio of LiCoO₂ thin-films. The main parameter influencing the film composition is a RF discharge power. The composition nearest to the stoichiometric one was observed for the power of 60 W.

The complete stoichiometry determination revealed that the oxygen content of LiCoO₂ films is stoichiometric. An excess of oxygen in samples thinner than 800 nm originates from the SiO₂ substrate, which was proved by silicon identification in thin samples.

A comparison of the current densities and cycleability in the respective curves reveals that the electrochemical properties of the LiCoO₂ film prepared at 200 °C are better than those of the films prepared at higher temperatures.

The films are interesting potential materials to be used as cathodes in lithium-ion (Li-ion) batteries. The RF magnetron sputtering was proved as a suitable method for preparation of LiCoO₂ thin-film cathode.

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