

Effect of XRD relative intensities of the Li (002) on surface, optical and electrochemical impedance spectroscopy analyses of the deposited LiCoO₂ thin film

H. Hakan Yudar¹ · Suat Pat¹ · Soner Özen¹ · Volkan Şenay² · Şadan Korkmaz¹ · Zerrin Pat³

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Abstract In this paper, the effect of RF power on LiCoO₂ thin films was investigated using X-ray diffractometer (XRD), atomic force microscopy, UV–Vis spectrophotometer, and potentiostat. The microstructural, surface, optical and electrochemical impedance measurements were performed to LiCoO₂ thin films, are used to for the fully solid-state battery cathode material. According to obtained results, the relative intensities of the Li (002) crystal phase in XRD patterns of deposited LiCoO₂ thin films were increased by increasing applied RF power, for the first time. The intensity of the LiCoO₂ (104) plane is nearly invariant. The relative intensities of the LiCoO₂ (113) plane were decreased by increasing RF power. The peak locations of the Li (002) and LiCoO₂ (104) were not changed. It was found that Li (002) relative intensities affect the all investigated parameters for the LiCoO₂ thin films. Especially, transmittance value increased about 20%. The band gap of the deposited film was changed 100–300 meV drastically. Deposited samples are shown high transparency in the visible region. Randles circuit was used for the equivalent circuit model. Nyquist plots, fitting parameters values and value of the circuit elements were estimated by ZSim software.

1 Introduction

LiMO₂ (M = Co, Ni or Mn) thin films as cathode materials is an important material for Li-ion battery and Li secondary micro batteries [1]. Especially, LiCoO₂ is an attractive cathode material for the secondary batteries [2]. Its theoretical capacity is 274 mAh/g. the LiCoO₂ material is an also p-type semiconductor. The band gap energy of the LiCoO₂ thin films is about 2.7 eV. This cathode material is used to quite common in industrial and research battery application due to excellent electrochemical properties, high capacity, high voltage and high electrode density. Li diffusion in the electrode is a very important because it estimates the power density and, it determines the capacity of the products. Li concentration in the crystal network of the film can affect the crystallographic, optical and surface properties [1–6, 8–14].

LiCoO₂ layers and thin films have been deposited by variously techniques such as RF magnetron sputtering [1], electrostatic spray pyrolysis [3], pulsed laser deposition [4], sol–gel [5] and etc. The deposition process can determine the film characteristic. Also, production parameters can play a critical role for the film quality and properties. In RF deposition, working parameters can change the crystallization and contents of the deposited layers. Thus, deposited film properties can change the battery potential and other electrochemical properties of a battery.

In this research article, LiCoO₂ layers were deposited by RF magnetron sputtering system at argon atmosphere. RF deposition power was select the variable parameter because this parameter can affect the film composition, properties, and characteristics. Deposited thin films were analyzed by using an X-ray diffractometer (XRD), atomic force microscopy (AFM), UV–Vis spectrophotometer, an interferometer, and potentiostat. Applied RF power changed the

✉ Suat Pat
suatpat@ogu.edu.tr

¹ Physics Department, Eskişehir Osmangazi University, Eskişehir, Turkey

² Education Faculty, Bayburt University, Bayburt, Turkey

³ Chemistry Department, Bilecik Seyh Edebali University, Bilecik, Turkey

relative intensity of the Li concentration among the LiCoO₂ crystal networks. It was found that Li (002) relative intensity was changed by the increasing RF power. So, surface, optical and electrochemical impedance spectroscopy analyses were done to determine the Li effect on the film properties. Some of the investigated properties were changed by drastically. The band gap energy was estimated in the range of 2.60–2.90 eV according to Li concentration in the film crystal structure. It found that band gap energy of the LiCoO₂ material shifted to lower values at low Li concentrations. It knows that the battery potential increases by the low Li concentration in the LiCoO₂ battery. Furthermore, Randles circuit determined as an equivalent circuits model. Obtained Nyquist plots, fitting parameters values and value of the circuit elements were estimated by ZSim software.

2 Experimental

LiCoO₂ thin film layers were produced by RF magnetron sputtering system. All thin films were deposited from the high purity 2-inch sputter gun at argon atmosphere. The thickness of the layer was 0.125 inch. Thin film deposition parameters are seen in Table 1. RF power was selected the variable parameter. Other working parameters were kept constant. The distance between the target and substrates was 50 mm. Microscope slides were used as substrate material. Before the deposition process, all substrates were cleaned with deionized distilled water by the ultrasonic bath.

3 Results and discussion

A PanAlytical Empyrean XRD device was used for the microstructural properties analyses. Obtained XRD spectra are seen in Fig. 1. As can be seen in Fig. 1, Li and LiCoO₂ crystal phases were detected. It found that the intensities of the phases depend on the power parameter in the deposition process. But, the intensities of the LiCoO₂ (104) are nearly invariant in all XRD patterns. Obtained peak and miller indices values for (104) and (113) are in good agreement with the literature [6, 7]. The Li peak for (002) was detected in XRD patterns. This

Table 1 Production parameters of samples

Parameters	S1	S2	S3	Unit
Pressure	7×10^{-2}	6×10^{-2}	7×10^{-2}	Torr
Power	125	100	75	Watt
Time	45	45	45	Minute
Gas	Argon	Argon	Argon	–

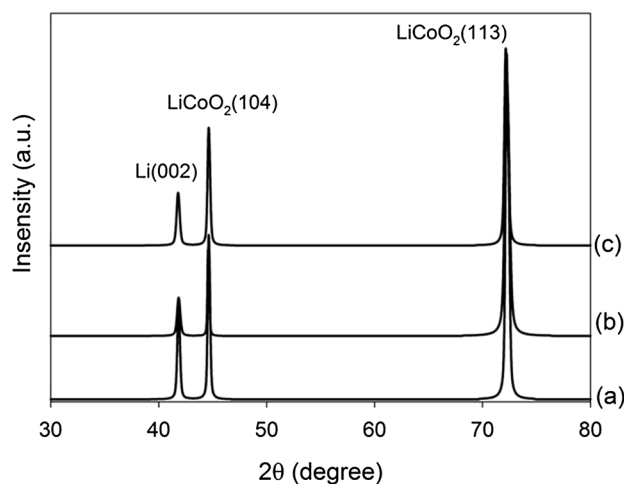


Fig. 1 XRD patterns for the a S1, b S2 and c S3 samples

peak also in good agreement with the related with Shuva et al. [8]. XRD peak positions didn't change. It was concluded that incorporation, strain, and cracks of the surface were similar to each other.

The XRD peak rate (PR) was calculated from the

$$PR = I/I_t \quad (1)$$

where I is the intensity of a determined peak, I_t is the total intensity value of the LiCoO₂ crystal peaks. Debye–Scherrer equation gives the maximum crystallite size for a coated layer. The crystallite size values were calculated using the Debye–Scherrer equation;

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2)$$

The dislocation density (δ) and microstrain (ϵ) were calculated from below formula;

$$\delta = \frac{1}{D^2} \quad (3)$$

and

$$\epsilon = \beta \cos \theta / 4 \quad (4)$$

where D is the mean crystalline size, λ is the wavelength of the used X-ray (0.15406 nm for Cu α), β is the full width of the half maximum of the selected peak and θ is the diffraction angle [9, 10]. The mean crystalline size of the peaks was calculated and given in Table 2. These values are smaller than the related references [11]. Peak analyses, peak rate, crystallite size, lattice strain and dislocation density values were determined. These values are listed in Table 2. According to the Table 2, Li (002) crystal phases has the biggest intensity for the deposited at applied power of 100 W. It was found that Li (002) and LiCoO₂ (104) peaks locations were invariant for XRD patterns. LiCoO₂ (113) peak location was shifted by applied RF power. It

Table 2 Calculated parameters of XRD samples

Sample	Peaks	Peak rate	Crystallite size (nm)	Lattice strain	Dislocation density (cm^{-2})	Microstrain
S1	41.8	0.09	30	3.40E-03	1.13E+11	0.07
	44.6	0.23	34	2.80E-03	8.43E+10	0.06
	72.2	0.68	27	2.30E-03	1.40E+11	0.09
S2	41.8	0.17	26	3.90E-03	1.48E+11	0.08
	44.6	0.27	44	2.20E-03	5.26E+10	0.05
	72.3	0.56	20	3.00E-03	2.39E+11	0.11
S3	41.8	0.12	26	3.90E-03	1.48E+11	0.08
	44.6	0.33	32	3.00E-03	9.90E+10	0.07
	72.1	0.55	25	2.40E-03	1.54E+11	0.09

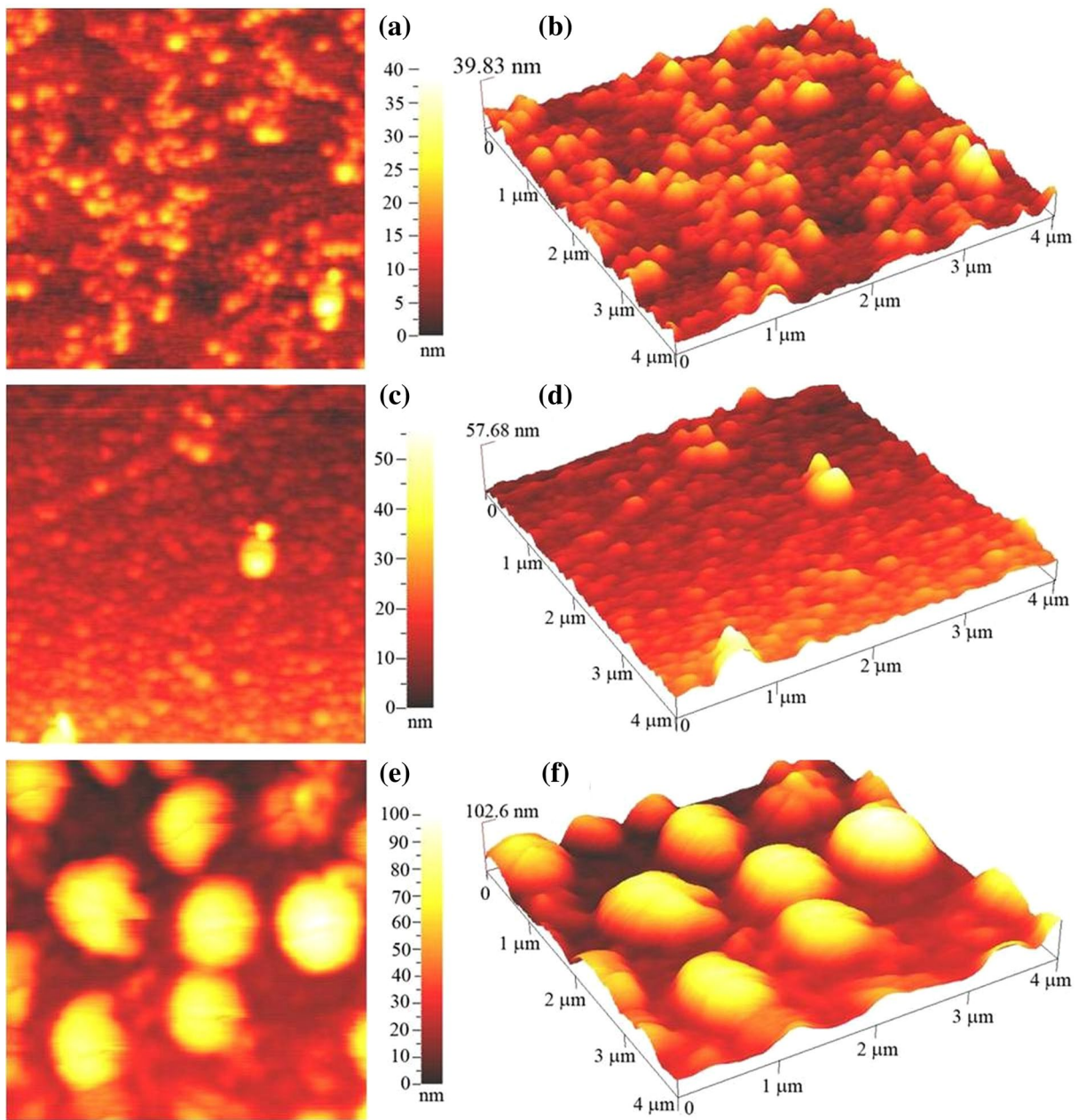


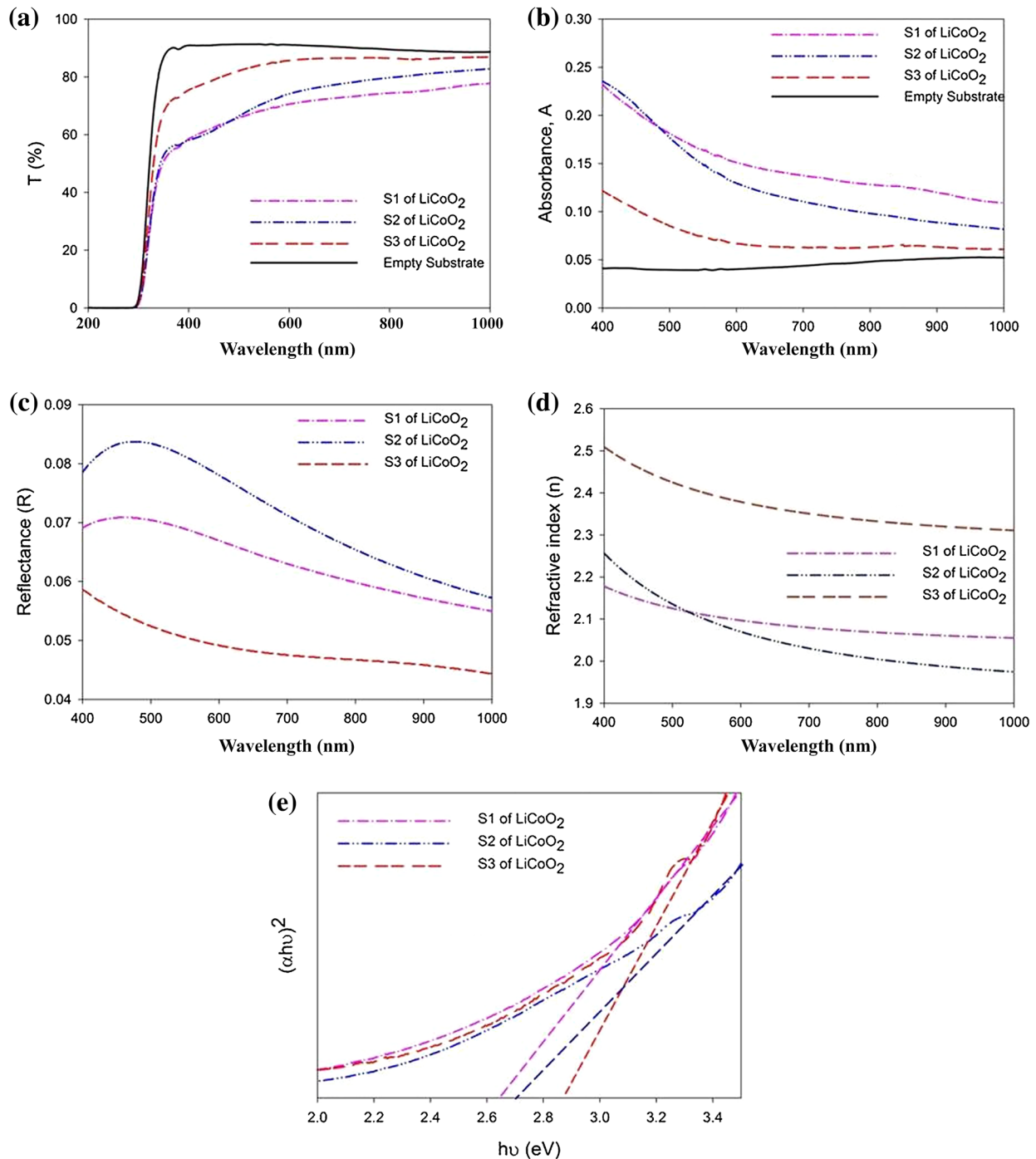
Fig. 2 AFM images of LiCoO_2 surface **a** 2D and **b** 3D for S1, **c** 2D and **d** 3D for S2, **e** 2D and **f** 3D for S3 sample

Table 3 Results of surface characterization of the coated samples

Samples	RMS (nm)	Ssk	Skr
S1	4.8	0.96	1.02
S2	2.0	1.77	8.44
S3	21.4	0.57	−0.50

was found that maximum peak rate of the Li (002) peak was in the 100 W deposition processes.

An ambios Q-scope AFM device was used for the determining the surface images, average roughness, skewness (Ssk) and kurtosis (Skr) value of the surface height distribution of the coated samples. These images and measured values are seen in Fig. 2 and Table 3.

**Fig. 3** Transmittance (a), absorbance (b), reflectance (c), refractive index (d) and bandgap spectra (e) of the coated layers

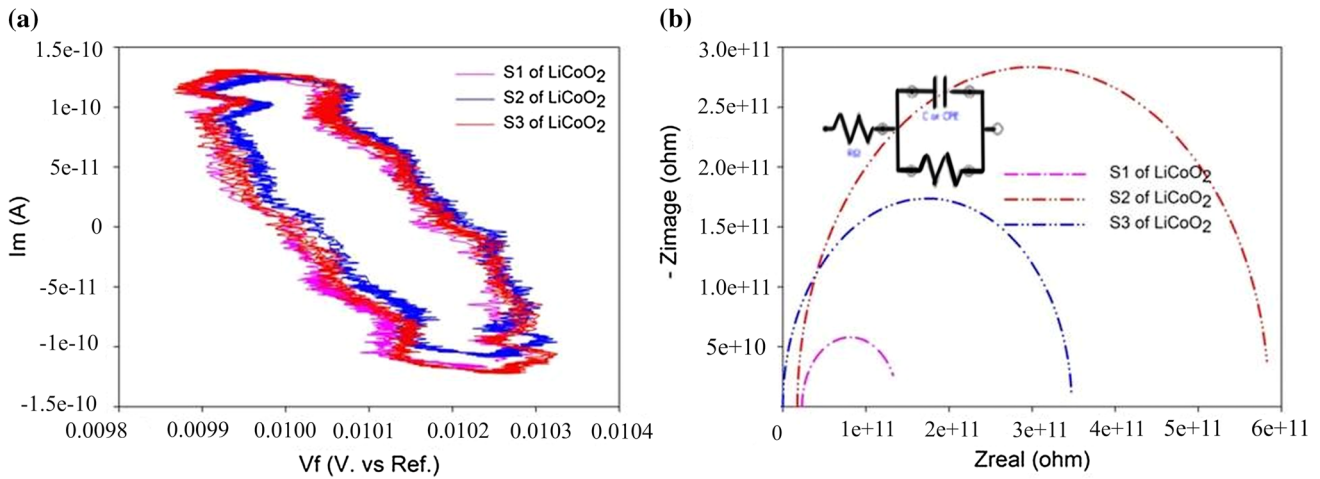


Fig. 4 **a** Current–voltage (I–V) and **b** Nyquist plot of the coated layer

Table 4 Nyquist plots fitting parameter for the randles circuit

Sample	Symbol	Value	Unit
S1	R	1.75E+08	Ω
	C	1.89E-12	F
	R	5.68E+11	Ω
S2	R	2.31E+10	Ω
	C	3.28E-11	F
	R	1.16E+11	Ω
S3	R	1.92E+04	Ω
	C	1.32E-12	F
	R	3.48E+11	Ω

As can be seen in Fig. 2, the surface properties, average roughness, Ssk and Skr of the LiCoO₂ layers are completely different. LiCoO₂ later at deposited at 75 W has a more rough surface, measured as 21.4 nm. The rough surface is important for secondary thin film battery. The more and faster ionic transportation realizes at high surface roughness values of deposited layers [12–14]. Ssk and Skr are the values related with homogeny particle distribution over the surfaces.

The films were deposited on the glass substrates to determine optical properties of the layers. An Unico UV–Vis double beam spectrophotometer and Filmetrics F20 interferometer were used for the measurement of the transmittance, absorbance, reflectance, refractive index and thickness of the deposited layers. Measured spectra are seen in Fig. 3. The spectra were recorded in the range of 400–100 nm. Transparency of the layer was decreased by increasing RF power, dramatically. Transmittance (T) graph via wavelength is seen in Fig. 3a. The deposited film thickness increases with the applied RF power [10,

15]. Absorbance (A) and reflectance (R) graphs via wavelength are plotted in Fig. 3b. Absorbance and reflectance values for lower applied power are distinct from another sample. Although surface roughness is biggest for the LiCoO₂ deposited at 125 W, the graphs are already similar to another deposited sample at 100 W for transparency, absorbance, reflectance and band gap values. These are illustrated in Fig. 3c, d. As know as, battery potential and band gap of the LiCoO₂ depends on the Li concentrations. The band gap energy of the LiCoO₂ thin films strongly depends on the Li concentration in the Li_xCoO₂ crystal formation [2, 16–19]. Band gap values are shifted to higher energy levels once increasing Li concentration, x value. x value is smaller than the 1. Battery voltage vs Li⁺/Li is increased by decreasing x values [18]. The band gap energy of the deposited LiCoO₂ thin films was calculated by the equations [10, 20, 21];

$$ahv = B(hv - E_g)^n \tag{5}$$

where α is absorption coefficient, B is a constant, E_g is the band gap of the deposited thin film, n is the exponent. Founded band gap from the graphs are shown in Fig. 3e. As can be seen in Fig. 3e, the band gap values are in 2.65–2.90 eV. Li concentration and preferred crystal formations effects the band gap. Biggest bang gap values was obtained at applied power of 75 W. These values are very good agreement with theoretical and experimental results [6–10].

Electrochemical impedance spectroscopy (EIS) and current–voltage measurements are employed to investigate the electrochemical properties of LiCoO₂ layers. A Gamry reference 3000 device was used for the measurements. Obtained results are illustrated in Fig. 4a, b. AC impedance spectroscopy was performed in the range of 1 MHz–1 Hz.

The scanning rate is 5 mV/s RMS. ZSimp software was used for the equivalent circuit modeling and fitting parameter determinations. Nyquist plot fitting parameter for the Randles equivalent circuit were summarized in Table 4.

4 Conclusions

In this paper, LiCoO₂ thin films layers with high transparency for rechargeable solid state transparent batteries were deposited by RF magnetron sputtering at argon atmosphere. Deposition time is only 45 min. The microstructure, optical, surface, and electrochemical properties were investigated. The effect of the Li (002) plane in XRD pattern on surface structure, roughness, grain sizes, lattice strain, dislocation density, microstrain, transparency, absorbance, reflectance, refractive index, band gap, Nyquist plot and Randles equivalent circuit fitting parameters were determined. It is shown that Li (002) concentration is key parameters for the investigated properties. It was found that the transparency of the film is related with the Li (002) crystal phases in the deposited layers. Li (002) concentration was changed by the only RF applied power. All peak locations were detected at the same two-theta values. As a result, it is concluded that the findings of the present study well demonstrated the fully transparent cathode materials were produced. Also, Li contents change the surface color of the layer according to transmittance and reflection results.

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