

INVESTIGATION OF LiCoO₂ THIN FILM BATTERY PROPERTIES WITH CHANGING Ar/O₂ GAS ATMOSPHERE

by

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Thin film batteries are considered the most promising next-generation batteries due to their superior safety and highly developed energy density. The deposition of LiCoO₂ thin films with 200 nm thickness was carried out by radio frequency magnetron sputtering. The LiCoO₂ thin films were deposited in Ar/O₂ gas mixture and coated samples which were deposited in 3% and 10% oxygen amounts, labeled as LCO-3 and LCO-10, respectively. Deposited LCO-3 and LCO-10 thin films possess phase purity and high crystallinity and have a uniform nanostructure with an average grain size of 30-60 nm with homogeneous dispersion. The cyclic voltammetry curves of LCO-3 and LCO-10 electrodes upon electrochemical cycling revealed phase transformations of both materials. The ionic conductivity of the LCO-10 thin films have been exhibited more convenient results than LCO-3 samples. The electrode manifests superior specific capacity of 48 μAh/cm² in the initial cycle. This study provides an information on how LiCoO₂ crystal structure and electrochemical properties are affected by changing deposition parameters such as the Ar/O₂ gas mixture.

Key words: *thin film batteries, radio frequency magnetron sputtering, LiCoO₂ cathode*

Introduction

Global energy demand over the past few centuries has been met by the combustion reaction of fossil fuels, which has led to global climate change due to the depletion of reserves and CO₂ emissions. A more sustainable method of energy production must be adopted so that technological development, as well as the growing population, can continue to meet the growing energy needs. Recently, electrochemical energy storage and conversion have been considered a more sustainable and environmentally friendly alternative to provide energy to meet the growing needs of mobile phones, portable electronic devices, robotic vacuum cleaners, and laptop computers. However, if it is desired to produce smaller-sized devices such as micro and nanoelectromechanical systems, batteries with smaller sizes and high-power density should be developed. In this case, thin-film batteries are the most promising candidates and alternatives for smaller-size devices. These batteries have various advantages including high energy density, excellent safety, increased cycle life, and a wide range of operating temperatures [1-8].

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Lithium cobalt oxide (LiCoO₂) was first invented in 1980 and the crystal structure of LiCoO₂ was reported in 1958. For a long time, it was stranded as the most commonly used positive electrode active material in commercial lithium-ion batteries. The LiCoO₂ has many unique advantages such as high compact density (4.2 g/cm³), excellent cycle life and capacity, and reliability, as well as including high lithium ions, compared to all other cathode materials. The LiCoO₂ shows a great high energy density of 740 Wh/kg (60 μAh/cm² for thin films) at 4.45 V and by increasing the upper cut-off voltage during the charge/discharge process [9-11]. Layered oxides like LiCoO₂ have interstitial spaces in the open framework where lithium ions bind preferred as lithium intercalation/de-intercalation sites. Lithium transition metal oxides (LiMO₂, M, Co, Fe, Ni, Mn, *etc.*) that have layered α-NaFeO₂ type rhombohedral crystal structure with a space group of R3m symmetry at higher temperature and distorted cubic structure with a space group Fd3m at lower temperature is one of the most studied materials in thin film batteries. This layered lattice structure of LiCoO₂, in which oxygen atoms are located in a cubic tight package frame and consisting of CoO₂ and lithium layers are formed along its *c*-axis to R-3m alternate space group with lattice parameters $a = 2.8138 \text{ \AA}$ and $c = 14.0516 \text{ \AA}$. This type of structure was defined as O₃- type LiCoO₂. O means that octahedrons have a central lithium-ions that is occupied by six oxygen atoms here and 3 in O₃ means ABCABC... package type of oxygen. The LiCoO₂ structure was stacked along the *c*-axis, so that Li-ions in the package allowed diffusion pathways both *a*- and *b*-axis [12-17].

Thin film batteries are mainly produced by physical vapor deposition methods, including magnetron sputtering, thermal and e-beam evaporation, atomic layer deposition, pulsed laser deposition, *etc.* The direct current and radio frequency (RF) magnetron sputtering is the most widely used technique to fabricate thin film LiCoO₂ cathode material. The deposition of LiCoO₂ films by RF magnetron sputtering is always in an oxygen gas atmosphere in order to achieve the perfect stoichiometric ratio between Co and O₂ atoms and an ideal layered structure. High rate crystal structure is one of the most important requirements for a successful Li-ion intercalation/de-intercalation process. In order to ensure a fine crystal structure, post-annealing process and substrate heating at high temperatures are required. The annealing process below 700 °C and the substrate heating process lower than 500 °C are important to obtain a well crystallized hexagonal LiCoO₂ thin films [18-23]. Recently various studies have been reported on some deposition parameters that influenced on the thin film quality, uniformity and electrochemical performance. These deposition parameters include deposition RF power, substrate heating temperature, the nature of the substrate, the working gas mixture (Ar, O₂, Ar/O₂), the vacuum chamber pressure, the ratio of Ar/O₂, the post-annealing conditions, *etc.* [24-26].

In this study, considering both the production of high purity products and the flexibility of use, the production of LiCoO₂ thin films was carried out using different O₂ gas atmospheres. The target material required to produce LiCoO₂ thin films is prepared using commercial LiCoO₂. The reason for using commercial powders here is to prevent the deposition and sintering conditions of the powders from being affected by-products and impurities. Thus, the uniformity of the thin films obtained is higher.

Experimental studies

Optimization of LiCoO₂ thin film production

A 2-inch (50.56 mm) diameter stainless steel mold was used to press the powders used for target material. The pressure exerted during compression was carried out at 200 bar. The pellets were separated from the mold without dispersion and the compression density

was highest at this pressure. The resulting pellets were subjected to partial sintering by changing the temperature and time as shown in fig. 1(a). The 24-hour sintering at 950 °C, where no reduction in diameter of the target material occurs and can be produced mechanically stable, was determined as the optimal condition. The deposition of LiCoO₂ thin films was carried out with the RF magnetron sputtering system. During the coating process, the applied power is gradually (2 W/per minute) increased until it reaches 125 W to prevent the target material from disintegrating and deteriorating. In this case, it was found that the most optimal conditions for the production of uniform and homogeneous LiCoO₂ thin films were these conditions. Therefore, silicon wafer and stainless steel with smooth surfaces were used as substrate materials. The LiCoO₂ coating process was performed in an Ar plasma environment at an ambient pressure of 10 mTorr and an Ar gas flow rate of 50 sccm for 120 minutes. A temperature of 250 °C was applied on the substrate material to form desired crystal structure. The deposition of the LiCoO₂ thin films in various orientations was determined according to O₂ amount in vacuum chamber. The experiments were carried out on thin-film coated samples which deposited in 3% and 10% O₂ amount, named as LCO-3 and LCO-10, respectively. The samples obtained as a result of the coating were annealed at 700 °C for two hours to increase their crystallinity. In order to determine the coating size of the LiCoO₂ thin films produced here, the surface profilometer device (KLA, TENCOR P15) was used. At this stage, a kind of masking process was performed by drawing from the middle surface of the non-coated Si wafer with a removable pen (when using acetone). Then, a coating process of 120 minutes was carried out on a working power of 125 W and LiCoO₂ thin film deposition was achieved on the entire surface (including in the area drawn with the removable pen). After the coating process is over, the coating samples are placed in an acetone solution and the drawn area was removed from the ink. The profilometer images taken from this gap can be clearly seen in fig. 1(b).

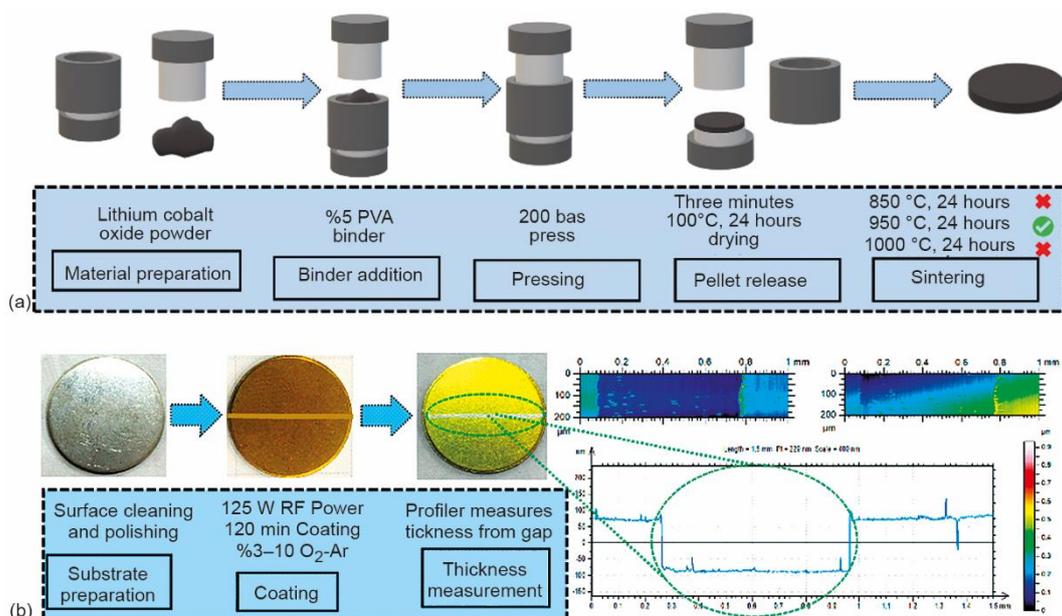


Figure 1. (a) Production process of LiCoO₂ target material and (b) production and thickness measurement process of LiCoO₂ thin films

Structural characterization of LiCoO₂ thin films

The morphology, composition and characteristic (coating thickness, roughness, and uniformity of coating) of the sample surface of LiCoO₂ thin films were determined by images obtained by field emission scanning electron microscope (FESEM-Quanta 450 FEG) and atomic force microscope (AFM). For AFM analyses, NTEGRA PRIMA-NT-MDT brand and model device were used. Measurements were carried out in semi-contact mode and arranged as 1.83 μm on the *x*- and *y*-axis for LCO-3 and LCO-10 samples. Elemental analyses of these samples and determination of the regions occupied by the elements were carried out by electron dispersion spectroscopy (EDS). The Raman spectrometer (Kaiser Raman RXN1) instrument was used to determine the amorphous and crystalline characteristics of LiCoO₂ thin films. The X-ray diffractometer (XRD-Rigaku D/MAX 2200) was used to describe the atomic and molecular structure of LiCoO₂ thin films. In order to switch to 3-D designs in thin film batteries, the coating thickness of the materials produced as thin films must be optimized.

Electrochemical characterization of LiCoO₂ thin films

Circular stainless steel, which is used as an electrode substrate material for electrochemical tests, has a diameter of 1.55 cm. The same coating procedure was applied to this material and electrodes were obtained after deposition. Coin type CR2032 half cells included LiCoO₂ thin films coated with stainless steel as the cathode and metallic lithium plate as the anode. The 1 M LiPF₆ (Sigma Aldrich, $\geq 99.99\%$) dissolved in propylene carbonate (PC-Sigma Aldrich, 99%) and ethylene carbonate (EC-Sigma Aldrich, 99%) (1:1 by volume) is used as a liquid electrolyte. Thin film battery cells are assembled in an argon-filled glove box (MBraun MB10 Compact). A monolayer polyethylene (Celgard) was also used as the separator. The cyclic voltammetry (CV) tests were performed to LCO-3 and LCO-10 electrodes. The potential window for the CV tests were 2.5 and 4.2 V and the scan rate was 0.1 mV/s. Galvanostatic charge/discharge of the samples was also tested between 2.5 and 4.2 V Li⁺/Li at 0.1C rate. The frequency ranging from 0.01 Hz to 10 kHz with an amplitude of 5 mV is provided for the electrochemical impedance spectrometry (EIS) analysis. All electrochemical characterization tests were carried out by potentiostat/ galvanostat (Gamry Instruments Reference 3000).

Result and discussion

The surface morphologies of LCO-3 and LCO-10 samples were obtained from AFM and FE-SEM analyses and these can be seen in fig. 2. The root mean square (Sq) value is known as the standard deviation of the surface height profile from the average height. It is known that the Sq value in ideal thin films is lower than 10 nm. When the relevant results are examined, it is understood that Sq value of LCO-3 and LCO-10 samples are 2.304 and 6.086, respectively. It has also been proven by the results that the roughness is less at low oxygen ratios. All thin film samples exhibit homogeneous grain size distribution and morphology however particle sizes were differentiated from 20-30 nm (LCO-3) to 40-60 nm (LCO-10) for both samples. It is observed that porosity and particle size increase with increasing oxygen ratio up to a point. The FE-SEM images were found to be consistent with the AFM images obtained from the thin film materials. When the EDS results were examined, the O₂ and Co atoms ratio was calculated as 1.67 (O:Co) for LCO-3. Although a deviation from the stoichiometry is observed for LCO-3, LCO-10 shows results close to the desired stoichiometry with a ratio of O₂ and Co approximately 2.06 (O: Co). These results indicate that the LCO-3 sample

has a similar molecule formula with Co₃O₄ and the LCO-10 sample is so close to LiCoO₂ crystal structure [27-29].

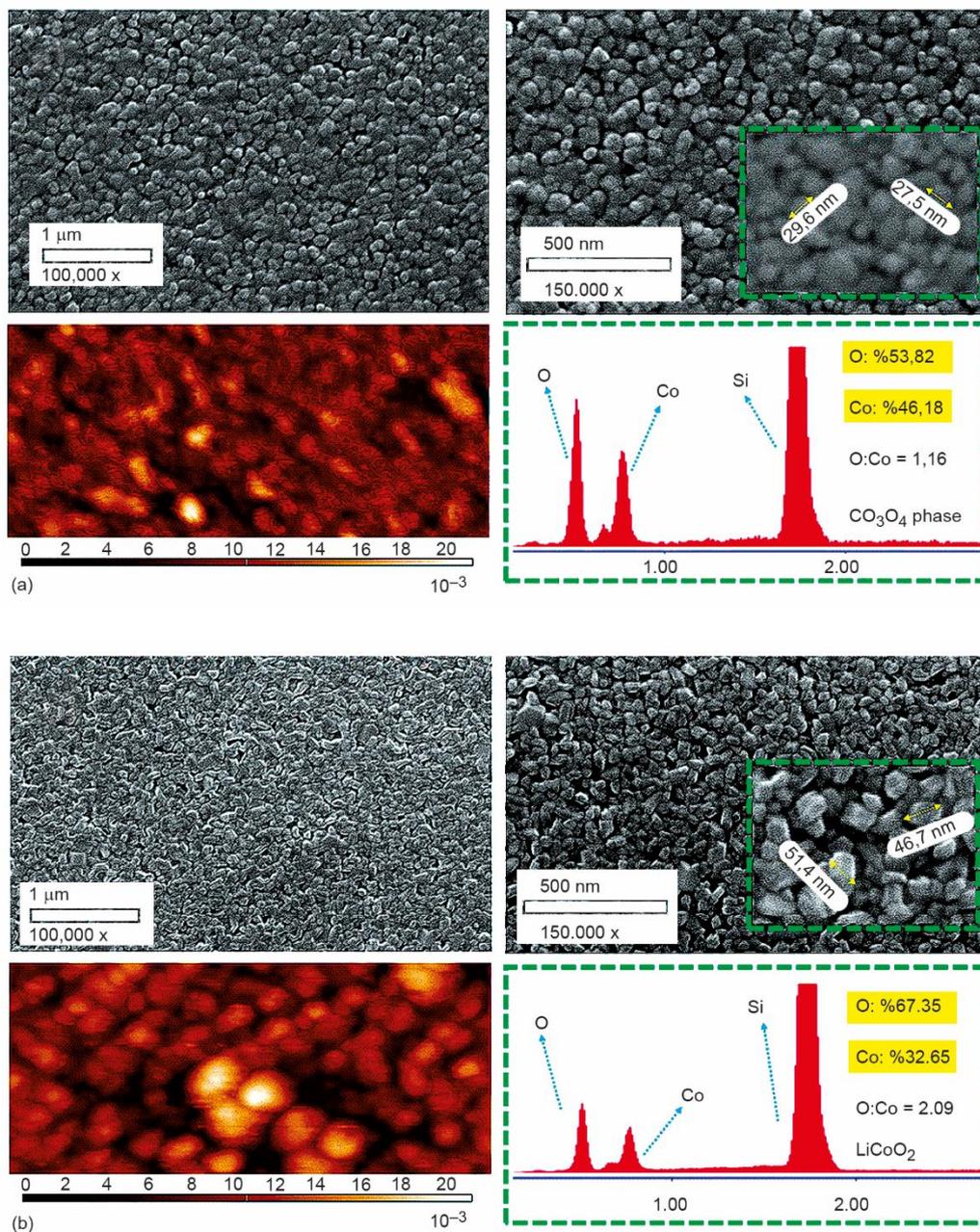


Figure 2. (a) The Fe-SEM, AFM and EDS analyses for LCO-3 thin films and (b) the Fe-SEM, AFM and EDS analyses for LCO-10 thin films

The XRD patterns and Raman spectra of LCO-3 and LCO-10 thin films were given in fig. 3. Both of these samples were subjected to 250 °C substrate heating during the coating process and coated materials were annealed at 750 °C for six hours. Non-heat-treated samples had a dense clustering and were not shown any data from XRD analysis, whereas sharper and clearer XRD patterns were obtained from the annealed and substrate-heated samples. As shown in fig. 3, orientation was obtained at (003), (220), (311), (222), (400), (009), and (110) directions, respectively, for the peaks obtained at $2\theta = 19^\circ, 36^\circ, 37^\circ, 38^\circ, 45^\circ, 59^\circ,$ and 65° for LCO-3 and LCO-10 thin films. Films with a thickness of 0.2 μm to 0.5 μm , which are deposited by the RF magnetron sputtering method with a low O₂ atmosphere (LCO-3) and crystallized by annealing in the air environment at 750 °C, exhibit a highly preferred orientation in line with the planes of (003) that grains parallel to the substrate. In contrast, by using the high rate of Ar/O₂ gas mixture (LCO-10), accumulation is obtained in the preferred (101) or (104) planes after deposition of thin film and subsequent heat treatment and reduces preferred orientation in (003) direction. The LiCoO₂ thin films deposited in (003) direction is known not to perform well Li-ion diffusion. When XRD patterns are examined, Co₃O₄ impurity phases are seen in the structure that deposited in the low Ar/O₂ gas mixture. For this reason, it was aimed to reduce this phase by giving higher ratio of O₂ gas during deposition [30-32].

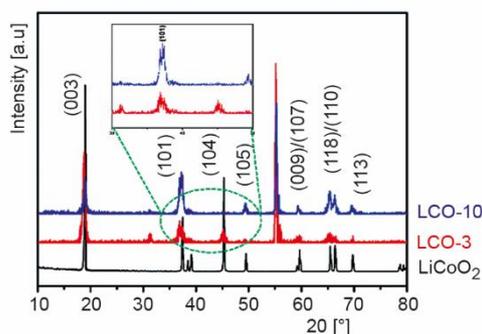


Figure 3. The XRD patterns for LiCoO₂ powder, LCO-3 thin film, and LCO-10 thin films

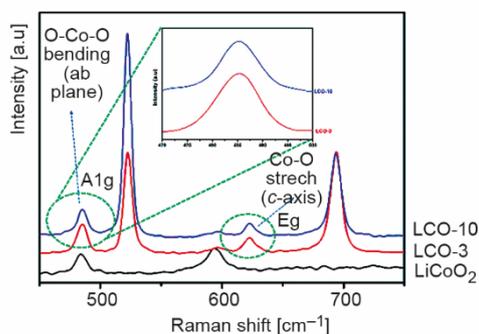


Figure 4. Raman spectra for LiCoO₂ powder, LCO-3 thin film, and LCO-10 thin films

Because the R3m and Fd3m XRD patterns are overlapping each other, divided peaks of (018)/(110) and (006)/(012) directions are the only evidence of the existence of the hexagonal LiCoO₂ phase. Therefore, X-ray diffraction peaks should be supported by Raman spectroscopy results to better distinguish between hexagonal and cubic phases. It has been proven that the thin film composition and commercial powder containing the same components are structurally discriminated from each other in fig. 4 [33]. The weak peak starting at 475 1/cm and ending at 500 1/cm is known as the Eg mode, which is obtained by stretching the Co-O bond made by the O atom on the *c*-axis in the thin films and LiCoO₂ powder. The vibration mode obtained by bending the O-C-O bond made by the O atom in the *ab*-plane in the LiCoO₂ crystal structure is known as the A1g mode. These modes prove the rhombohedral structure in R3m space group in LiCoO₂ thin films. It is also possible to detect the secondary product Co₃O₄, which can appear from Raman peaks of LCO-3 thin films as impurity phase, however, the impurity phase decreased in LCO-10 thin films [34].

Figures 5(a) and 5(c) show the cyclic voltammograms in the first ten for Li/LiCoO₂ half cells obtained from thin films with various Ar/O₂ gas mixture. The scanning rate has been

set to 0.01 mV/s and tests were carried out a voltage window of 3.0 V and 4.2 V. The LCO-3 and LCO-10 samples have 1.88 cm² electrode area and both samples have approximated thickness of 200 nm. It seems that the first CV curve shows excellent stability and reversibility for both samples. There is no major difference in the CV profile of LCO-10 in subsequent cycles. The anodic and cathodic peaks have been identified between 3.4-3.6 V and 3.8-4 V which refers to the phase transformation into the layered structure of the LiCoO₂. It is attributed to the placement of lithium ions between the hexagonal electrode layers during discharge to form monoclinic phase [35]. The anodic peak is known as the voltage range of lithium ions separated from the electrode layers during charging and transferred to electrolyte. Increasing the oxygen content allowed most of the deposited thin films to be converted into the desired LiCoO₂ phase. Thus, irregularities in the crystalline structure were prevented and the formation of impurities in the structure was avoided [36].

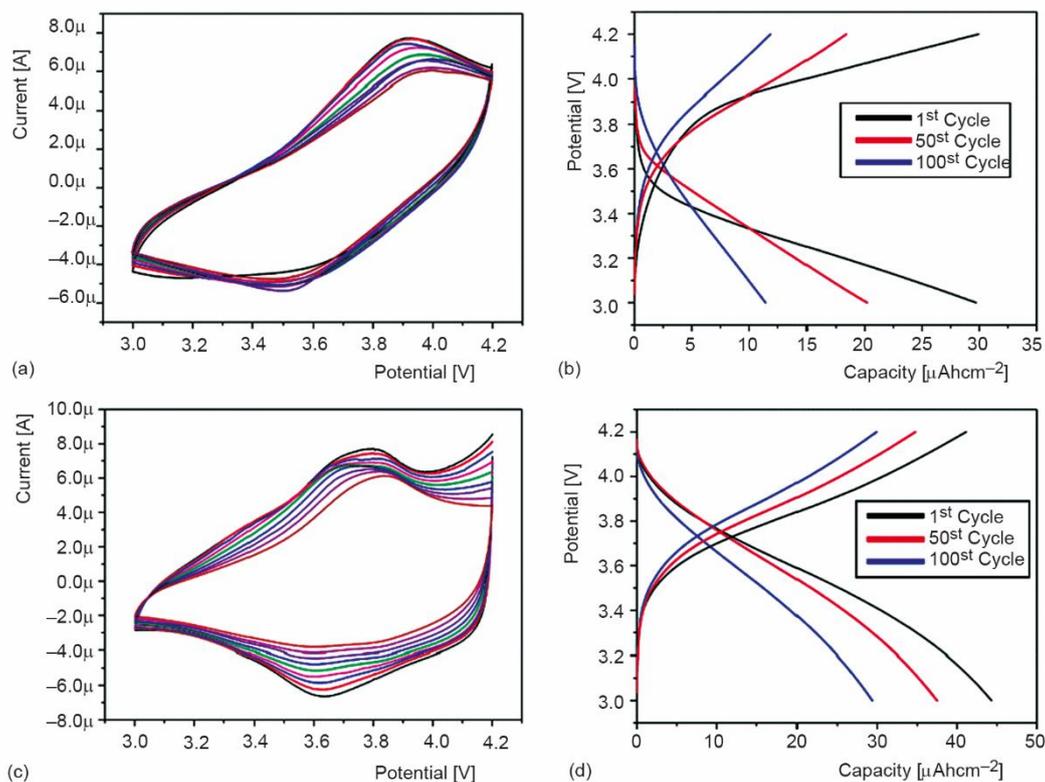


Figure 5. (a) The CV measurement of LCO-3, (b) galvanostatic charge/discharge tests of LCO-3, (c) CV measurement of LCO-10, and (d) galvanostatic charge/discharge tests of LCO-10

Galvanostatic charge/discharge tests of thin-film electrodes (LCO-3 and LCO-10) were performed at a constant current density of 6 μA ($C/2$) and between 3.0 V and 4.2 V. The results are presented in the 1st, 50th, and 100th charge-discharge curves in figs. 5(b) and 5(d). The initial discharge capacity of thin film cathodes produced in an environment containing a higher O₂ ratio is 48 $\mu\text{Ah/cm}^2$. The LCO-10 thin films have improved the diffusion pathways

in which Li-ions can be intercalated and have had a positive effect on cycle performance. At the end of the 100th cycle, it was determined that discharge capacities of 13 $\mu\text{Ah}/\text{cm}^2$ and 29 $\mu\text{Ah}/\text{cm}^2$ were obtained for LCO-3 and LCO-10 thin films, respectively. The reduction peaks were slightly altered toward lower potential for the anodes deposited at a lower O₂ ratio, referring to the presence of the Co₃O₄ impurity phase. Since the Li-ion cannot be entered into the Co₃O₄ of the spinel phase, it may be associated with a decrease in electrochemical performance. As a result of the intercalation reactions that occur during the charge/discharge processes, the structure of the material is disrupted by the input and output of Li-ions between the electrode layers and the battery capacity has decreased considerably [37].

Figure 6 shows EIS tests for thin-film cathodes and LiCoO₂ powder at pre-charge and post-charge conditions. Each Nyquist curves consisted of a semicircle in the higher frequency region, which is corresponded to the charge transfer resistance, followed by a nearly 45° straight line in the low frequency region that appointed as diffusion parameter. When the pre-cycle tests were examined, it was determined that the charge transfer resistance and diffusion rates of the LCO-3 samples were quite large compared to other samples. The increase in the oxygen content during deposition leads to enhanced proportion of LiCoO₂ phases in the composition. At the same time, it was determined that the interactions between the electrode interface and the electrolyte were weak in the LCO-3 samples. Therefore, when the pre-cycle Nyquist curves were examined, it was found that the charge transfer resistance decreased and the diffusion values increased according to the post-cycle values. The charge transfer resistances were determined as 990 Ohm, 1985 Ohm, and 2700 Ohm respectively in the LiCoO₂ powder, LCO-3, and LCO-10 samples for the pre-cycle cycle [38].

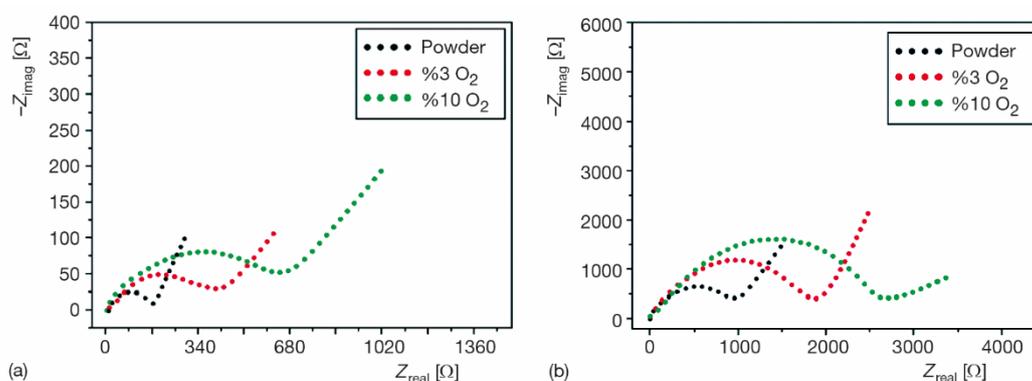


Figure 6. The EIS tests for LiCoO₂ powder, LCO-3 and LCO-10 samples in (a) pre-charge and (b) post-charge conditions

Conclusion

The LiCoO₂ target materials were produced in several conditions and the 2-inch targets that were prepared in 24-hour sintering at 950 °C were selected as the most proper ones. Thin film deposition process is carried out using this target material. Combining substrate heating process, a permanent working pressure for all processes and annealing of thin films at 650 °C, LiCoO₂ thin films with a wide range thickness of 200 nm have been deposited using the RF magnetron sputtering method. The O₂ gas composition of 3% and 10% in the vacuum chamber as a variable factor was emphasized in this study. The FE-SEM imag-

es, AFM images, and XRD results show that the LiCoO₂ films grown by the RF magnetron sputtering method has a smooth surface, uniform particle size distribution and a crystalline structure after annealing. The Raman results revealed that the LCO-3 and LCO-10 thin-films consist of both Co-O and O-Co-O units and impurity Co₂O₃ phase in LCO-3 sample. The LCO-10 thin film batteries show an increased Li-ion intercalation property between 3.0 V and 4.2 V. The phase transformation of the LCO-3 and LCO-10 electrodes upon electrochemical cycle has been obviously identified by CV measurement. The EIS result of the thin-film battery at a different cycle reveals that the charge transfer resistance is a key parameter to understand electrochemical activity. The LCO-10 thin-film batteries also exhibit a high initial discharge capacity of 48 μAh/cm², and the charge–discharge curve of each cycle is almost identical up to 100th cycle.

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Nomenclature

AFM	– atomic force microscope	LCO	– lithium cobalt oxide
CV	– cyclic voltammetry	RF	– radio frequency
EDS	– electron dispersion spectroscopy	Sq	– root mean square
EIS	– electrochemical impedance spectroscopy	XRD	– X-ray diffraction
FE-SEM	– field emission scanning electron microscope		

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