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Microstructural, surface and electrochemical properties of the nano layered $LiCoO_2$ thin film cathode for Li ion battery

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ABSTRACT

In this paper, $LiCoO_2$ thin films deposited onto the silver (Ag) coated glass (Ag/glass) substrate and then $LiCoO_2$/Ag/glass half-cells were test in full cell test procedure. X-ray diffractometer (XRD) analysis, surface imaging with a field emission scanning electron microscopy (FESEM), optical properties were used for the determination of the microstructural, surface and optical properties of the deposited thin films. The cyclic voltammetry (CV) and capacity measurement were done using a full cell test procedure in liquid ionic electrolyte. Pt or ITO coated glass were used as an opposite electrode in electrochemical test. According to the XRD measurements, some reflections corresponding to the $LiCoO_2$ and Ag layer (cathode current collector) were detected. All electrochemical tests were done in the 0.1 M $LiClO_4$ in propylene carbonate. The anodic oxidation and cathodic reduction were observed in CV experiments. Especially, oxidation and reduction peaks were clear in the experiment of the ITO coated electrode.

$LiCoO_2$ as an intercalation compounds are used to a novel electrochemical actuator and rechargeable thin film battery [1]. $LiCoO_2$ is a high specific capacity and high operating voltage cathode materials [2], it's potential and electrochemical performance of the cathode thin films is mainly related with Li concentration and microstructural properties of the layer [3–8]. In thin film, microstructural properties are changed by the production or preparation method. Because, the deposited thin films have a great defects and impurities, come from the precursor gas, chemicals or preparing methods. So, morphology, microstructure, composition are essential for the thin film material [8].

$LiCoO_2$ thin films have been deposited by RF magnetron sputtering [2] and pulsed laser deposition [7]. These manufacturing methods are conventional and commercial production methods with high precision production methods. At different applications such as medical, micro battery, sensors, wearable electronics, flexible battery and etc, $LiCoO_2$ cathode materials have been deposition on the different substrate materials such as onto Pt or Pt/Ti/quartz glass [8], $SrTiO_3$ (001) [9], stainless steel [10], SiO_2/Si (SOS) [11] substrates. Cathode current collectors generally deposited on the electron beam or evaporation methods. In this paper, silver cathode collector was deposited by thermionic vacuum arc. For the planar battery application, the crystal structure of the cathode current collector layer can change the microstructural properties of the cathode thin film layers.

In this paper, a $LiCoO_2$ thin film was deposited on the Ag coated glass substrate. For the determination of the microstructure, surface, optical and electrochemical properties, X-ray diffractometer, field emission scanning electron microscopy, UV–Vis spectrophotometer and potentiostat/galvanostat devices were used. Battery test were done by half-cell test in liquid electrolyte. Prepared half-cell with $LiCoO_2$ thin film were test in 0.1 M $LiClO_4$ in propylene carbonate. As an opposite electrode, Pt metal or ITO coated glass were used.

The $LiCoO_2$ thin films were deposited on silver coated glass substrate. The Ag deposition was realized by thermionic vacuum arc (TVA) method. TVA is a rapid plasma assisted thin film deposition technology. It works in high vacuum conditions. TVA method has two electrodes. These are anode, contains evaporation material and cathode is an electron gun including tungsten filament. Firstly, thermionic electrons emitted from the tungsten filament and then were focused the electrons onto evaporation material by a Wehnelt

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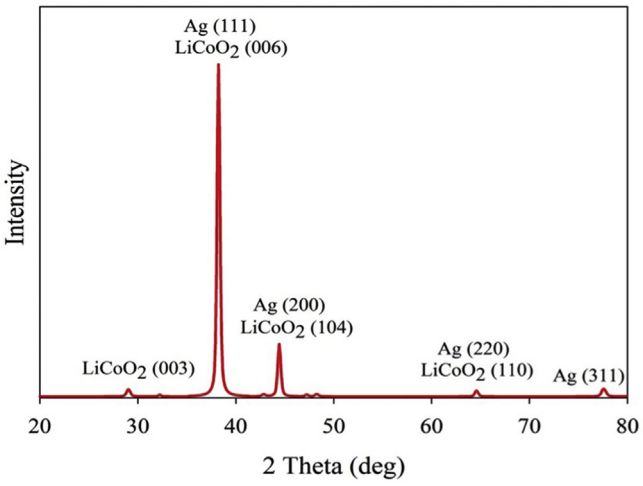

Fig. 1. XRD pattern of the $LiCoO_2$ thin film on Ag coated glass.

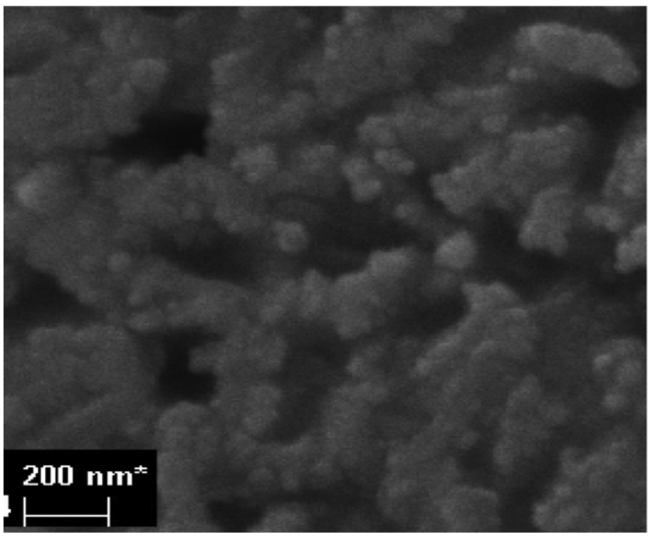

Fig. 2. FESEM images of the $LiCoO_2$ thin film on Ag coated glass.

cylinder. Materials start the evaporation, firstly. After that, material plasma generates in the inter-electrodic region [12–14]. The parameters of the TVA deposition are pressure (1×10^{-4} torr), applied voltage (800 V), filament current (18 A), bombarding current (0.7 A), and deposition period (180 s). One another plasma assistant deposition technology is a RF magnetron sputtering [3,15,16]. It was used for the production of the $LiCoO_2$ thin films deposited on the Ag coated glass sample. The $LiCoO_2$ thin film was deposited from 2-inch sputtering target. The distance of the sample holder from the target was approximately 50 mm. The working pressure for the RF sputtering was adjusted to 6×10^{-2} torr. RF power supply of 13.56 MHz was used. RF power of 70 W was used during the deposition for 2700 s.

PANalytical Emprean X-ray diffraction (XRD) tool was used for the thin film analysis. Pixel 3D detector was mounted to the diffractometer and Bragg-Brentano geometry was used for the analysis. XRD analysis was realized with CuKα radiation ($\lambda = 1.54$ A) in the range of 20–80°. Fig. 1 shows the in-plane XRD pattern of the $LiCoO_2$/Ag/glass half-cell deposited at Ar of 100% gas pressures. The layers show Bragg peaks corresponding to the reflections of the half-cell. Obtained XRD pattern of the $LiCoO_2$ thin film on Ag coated glass is seen in Fig. 1. The defined miller indices for $LiCoO_2$ thin film are (003), (006), (104) and (110). Zhang and Grant show the XRD spectra of the power and textured $LiCoO_2$ [1]. They are very different from the each other. The obtained XRD spectrum is similar with the XRD patterns in the textured $LiCoO_2$. JCPDS card number is 44–145. Compared the paper published by Zhu et al., XRD reflection of the $LiCoO_2$ planes found as to be a stronger [8]. Zhu et al. shows that deposition temperatures affect the intensities of the reflection planes. Our XRD pattern results are good harmony with the paper published by Zhu et al.

The surface image of the $LiCoO_2$ thin film was obtained by field emission scanning electron microscopy (FESEM). A Zeiss supra 40 V P was used for the surface imaging. The surface of the $LiCoO_2$ thin film on Ag coated glass is illustrated in Fig. 2. FESEM image of the surface was obtained at 50.000× magnification. The long surface channels are not only seen in Fig. 2, but very small granules are detected in the surface images. This means that the surface area of the coated $LiCoO_2$ is bigger than a flat surface, So, Li^+ ions in charge/discharge test can move easily in the channels and holes. Another property of the electrode is transmittance value. The transmittance spectrum of the $LiCoO_2$ layers deposited onto Ag coated glass was measured by Unico UV–Vis spectrophotometer. The transmittance reflectance and absorbance spectrum is

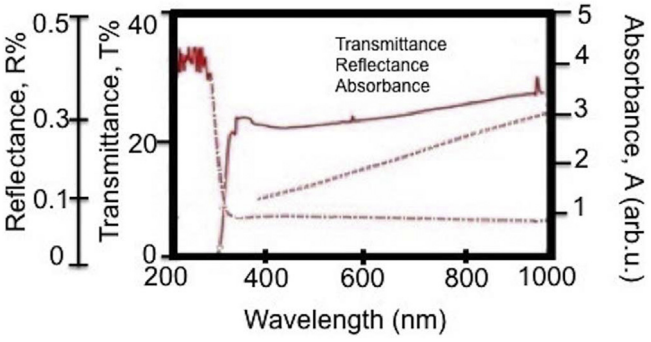

Fig. 3. Optical (a) transparency, (b) absorbance, and (c) reflectance spectra of the $LiCoO_2$/Ag/glass half-cell.

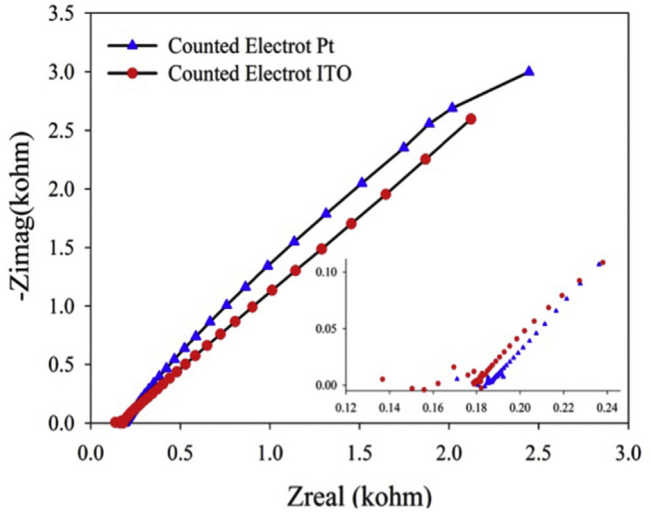

Fig. 4. Nyquist spectra of the full cell test with Pt or ITO coated glass as a counter electrode.

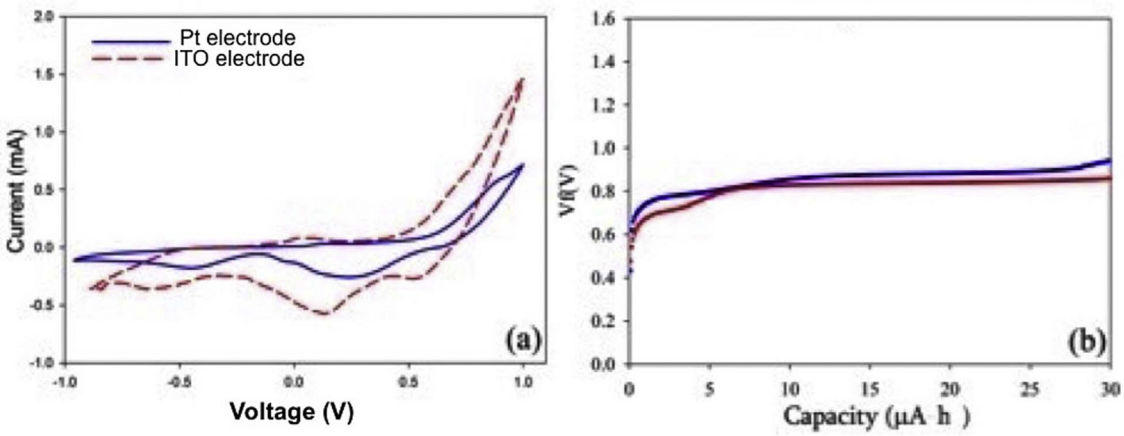

Fig. 5. (a) CV and, (b) Capacity (μAh)-Voltage (V_f) graphs obtained by full cell tests.

seen in Fig. 3. Because of the Ag metal layers, the transmittance value was obtained too low. So, $LiCoO_2$/Ag/glass half-cell structure has low transparency.

The planar battery structure was used as to be a half-cell including cathode material and current collector. This type battery is more preferred battery production methods for the thin film battery [17–20]. By using $LiCoO_2$/Ag/glass half-cell, a full cell tests were done by electrochemical in liquid electrolyte. Electrochemical test was promoted using 0.1 M $LiClO_4$ in propylene carbonate. As a counter electrode, Pt and ITO glass was used, respectively. An open full cell test set up was prepared for the electrochemical impedance spectroscopy (EIS) measurement. Direct-contact four-point setup was used for all measurements. The opposite electrodes were Pt or ITO coated glass, respectively. The EIS spectra were recorded from 1 MHz to 10 mHz. Scanned rate was 10 mV/s. The Nyquist graph of the full cell tests are seen in Fig. 4. The cyclic voltammetry (CV) measurements at scan rate of 10 mV/s and capacity (μAh)-voltage graphs are illustrated in Fig. 5a and Fig. 5b, respectively. Obtained capacity values obtained for the full cells are show good harmony with related literature [17–20]. It found that the full-cell with ITO coated glass gives the sharper peak according to the Pt electrode for CV measurements, As can be seen in from Fig. 5a, at different counter electrode (Pt or ITO coated glass) similar results were observed for the CV analysis. In Fig. 5b, prepared full cell were completed using had cell and counter electrode in liquid ionic solutions with three electrode configuration. According to obtained results in Fig. 5b, a different property was detected in the capacity graphs using by Pt or ITO coated glass prepared different counter electrode. In ITO electrode, negative current is bigger than the full-cell with Pt electrode. In Pt electrode using, obtained potential of the prepared full cell is slightly higher than the cell prepared by ITO electrode. On the contrary of the result, the cell with ITO electrode is more stable in the plateau region.

A half-cell was prepared by nano layered $LiCoO_2$ thin film. The $LiCoO_2$ thin films were deposited onto Ag coated glass substrate. The microstructural, surface, optical and electrochemical properties of the nano layered $LiCoO_2$ thin film cathode for Li ion battery were investigated in full cell test procedure. Deposited layers onto Ag/glass substrate have great cracks and voids. The cracks and voids can generate a lot of free space and surface. This surface structure could increase the electrochemical performance. Besides of this, Li^+ ions can intercalation/decalation of the cathode layer free according to compact and low roughness surface.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.vacuum.2018.03.043.

References

[1] H. Zhang, P.S. Grant, An electrochemical microactuator based on highly textured LiCoO 2, Sensor. Actuator. B Chem. 176 (2013) 52–57.
[2] S.W. Jeon, J.K. Lim, S.H. Lim, S.M. Lee, As-deposited LiCoO 2 thin film cathodes prepared by rf magnetron sputtering, Electrochim. Acta 51 (2) (2005) 268–273.
[3] H.H. Yudar, S. Pat, S. Özen, V. Şenay, Ş. Korkmaz, Z. Pat, Effect of XRD relative intensities of the Li (002) on surface, optical and electrochemical impedance spectroscopy analyses of the deposited LiCoO2 thin film, J. Mater. Sci. Mater. Electron. 28 (13) (2017) 9289–9294.
[4] M.C. Rao, Optical absorption studies of LiCoO2 thin films grown by pulsed laser depositions, Int. J. Pure Apll. Phys. 6 (2010) 365–370.
[5] H.L. Liu, T.Y. Ou-Yang, H.H. Tsai, P.A. Lin, H.T. Jeng, G.J. Shu, F.C. Chou, Electronic structure and lattice dynamics of LixCoO2 single crystals, N. J. Phys. 17 (10) (2015) 103004.
[6] D. Ensling, A. Thissen, S. Laubach, P.C. Schmidt, W. Jaegermann, Electronic structure of LiCoO 2 thin films: a combined photoemission spectroscopy and density functional theory study, Phys. Rev. B 82 (19) (2010) 195431.
[7] Combinatorial Synthesis of Epitaxial LiCoO2 Thin Films on SrTiO3(001) via On-Substrate Sintering of Li2CO3 and CoO by Pulsed Laser Deposition
[8] X. Zhu, Z. Guo, G. Du, P. Zhang, H. Liu, LiCoO 2 cathode thin film fabricated by RF sputtering for lithium ion microbatteries, Surf. Coating. Technol. 204 (11) (2010) 1710–1714.
[9] S. Maruyama, O. Kubokawa, K. Nanbu, K. Fujimoto, Y. Matsumoto, Combinatorial synthesis of epitaxial LiCoO2 thin films on SrTiO3(001) via on-substrate sintering of Li2CO3 and CoO by pulsed laser deposition, ACS Comb. Sci. 18 (6) (2016) 343–348.
[10] M. Antaya, J.R. Dahn, J.S. Preston, E. Rossen, J.N. Reimers, Preparation and characterization of LiCoO2 thin films by laser ablation deposition, J. Electrochem. Soc. 140 (3) (1993) 575–578.
[11] H. Xia, S.Y. Meng, L. Lu, G. Ceder, Electrochemical behavior and Li diffusion study of $LiCoO_2$ thin film electrodes prepared by PLD, Adv. Mater. Micro Nano Syst. 1 (2007).
[12] S. Pat, M.Z. Balbağ, Ş. Korkmaz, Mechanical properties of deposited carbon thin films on sapphire substrates using atomic force microscopy (AFM), Ceram. Int. 40 (7) (2014) 10159–10162.
[13] T. Akan, N. Ekem, S. Pat, U.G. Issever, M.Z. Balbag, M.I. Cenik, R. Vladoiu, G. Musa, Boron thin film deposition by using Thermionic Vacuum Arc (TVA) technology, Mater. Lett. 61 (1) (2007) 23–26.
[14] S. Özen, V. Şenay, S. Pat, Ş. Korkmaz, The influence of voltage applied between the electrodes on optical and morphological properties of the InGaN thin films grown by thermionic vacuum arc, Scanning 38 (1) (2016) 14–20.
[15] S. Pat, M. Kokkokoglu, Characterization of deposited AlN thin films at various

nitrogen concentrations by RF reactive sputtering, J. Optoelectron. Adv. Mater. Rapid Commun. 4 (6) (2010) 855–858.
[16] Ş. Volkan, S. Özen, S. Pat, Ş. Korkmaz, Optical and surface properties of LiFePO4 thin films prepared by RF magnetron sputtering, Eur. Phys. J. Atom. Mol. Opt. Phys. 69 (3) (2015) 76.
[17] A.A. Talin, D. Ruzmetov, A. Kolmakov, K. McKelvey, N. Ware, F. El Gabaly, B. Dunn, H.S. White, Fabrication, testing, and simulation of all-solid-state three-dimensional Li-ion batteries, ACS Appl. Mater. Interfaces 8 (47) (2016) 32385–32391.
[18] J.F. Oudenhoven, L. Baggetto, P.H. Notten, All-Solid-State lithium-ion micro-batteries: a review of various three-dimensional concepts, Adv. Energy. Mater. 1 (1) (2011) 10–33.
[19] H. Xia, H.L. Wang, W. Xiao, M.O. Lai, L. Lu, Thin film Li electrolytes for all-solid-state micro-batteries, Int. J. Surf. Sci. Eng. 3 (1–2) (2009) 23–43.
[20] N.J. Dudney, Solid-state thin-film rechargeable batteries, Mater. Sci. Eng., B 116 (3) (2005) 245–249.