

Growth and Characterization of LiCoO₂ Thin Films for Microbatteries

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Abstract—LiCoO₂ thin films have been grown by pulsed laser deposition on stainless steel and SiO₂/Si substrates. The film deposited at 600°C in an oxygen partial pressure of 100mTorr shows an excellent crystallinity, stoichiometry and no impurity phase present. Microstructure and surface morphology of thin films were examined using a scanning electron microscope. The electrochemical properties of the thin films were studied with cyclic voltammetry and galvanostatic charge-discharge techniques in the potential range 3.0-4.2 V. The initial discharge capacity of the LiCoO₂ thin films deposited on the stainless steel and SiO₂/Si substrates reached 23 and 27 μAh/cm², respectively.

Index Terms—LiCoO₂, Pulsed laser deposition, Thin films, Electrochemical properties

I. INTRODUCTION

LiCoO₂ is a typical and most commonly used cathode material for rechargeable Li-ion batteries due to its high capacity (136 mAh/g) and good cycling stability. Due in large parts to this high energy storage capacity, LiCoO₂-based rechargeable batteries are now commonly used in high-end consumer electronics such as laptops and cell phones. There is also an increasing interest in fabrication thin film cathodes for application in all-solid-state microbatteries such as for on-chip applications [1]. Thin films also received much attention from studying the intrinsic electrochemical properties of lithiated transition metal oxides because no polymer binder and electronically conducting carbonaceous powders exist in thin film cathodes [2].

LiCoO₂ in its rhombohedral form is commonly used as intercalation compound in cathodes of Li-ion batteries. Depending on synthesis temperature LiCoO₂ comes in two crystallographic structures: LT-LiCoO₂O₄ has the lattice of the cubic spinel (space group Fd3m) while HT-LiCoO₂ has a hexagonal lattice (space group R3m) [3]. Crystalline LiCoO₂ adopts a layered structure of hexagonal symmetry when synthesized at temperatures above 400°C [4]. The

hexagonal lattice consists of layers of close-packed network of oxygen ions separated by alternating layer of lithium and cobalt ions. The edges of CoO₆ octahedra were shared to form CoO₂ sheets, and lithium ions can move in two-dimensional directions between the CoO₂ sheets.

Thin films of LiCoO₂ have been synthesized by a variety of techniques including RF sputtering deposition, low-pressure chemical-vapor deposition, oxidation of Co films in molten carbonate salts and pulsed laser deposition. In the fabrication of LiCoO₂ thin films, formation of the layered structure is known to be crucial for obtaining a good rechargeability of the batteries. Pulsed laser deposition (PLD) is a successful technique in the growth of materials containing volatile components with complex stoichiometry. For this reason, it is well suited to the films of lithiated transitional metal oxides, where lithium loss due to volatilization is a main concern in conventional evaporation methods. The electrochemical behavior of (003) highly textured LiCoO₂ thin films grown by PLD have been investigated by Striebel [5], Julien [6] and Iriyama et al. [7].

In this work, we report on the preparation, physical and electrochemical characterization of LiCoO₂ thin films grown on stainless steel and platinum coated SiO₂/Si substrates by PLD.

II. EXPERIMENTAL

A. Growth Conditions

LiCoO₂ thin films were grown by PLD on stainless steel and Pt coated SiO₂/Si substrates at 600°C. Since the concentration of lithium in the deposited films tends to be lower than that in its original target, to compensate the lithium loss, 15% extra Li₂O was doped into LiCoO₂ target. A schematic illustration of the PLD apparatus is shown in Fig. 1. Target and substrates were placed inside the vacuum chamber with a turbo-molecular pump yielding pressure less than 1×10^{-5} Torr. The target-substrate distance was kept at 35mm. During deposition, the target is rotated at 10 to 20 rpm to avoid depletion of material at any given spot. A Lambda Physik KrF excimer laser beam ($\lambda = 248\text{nm}$, pulse width = 25ns, laser energy = 150-160 mJ/pulse) was

incident on the target at an angle close to 45° at a repetition rate of 10 Hz. The focused spot size is 2×5 mm at the target resulting in a laser fluence of 2 J/cm^2 . Films deposition was carried out under 100mTorr oxygen partial pressure for 40 min.

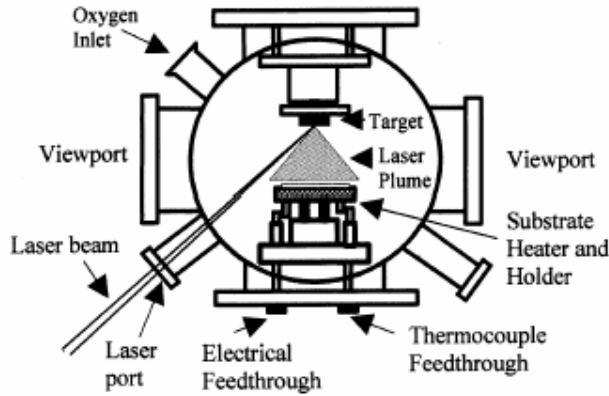


Fig. 1. Schematic diagram of the pulsed laser deposition system.

B. X-ray Diffraction and SEM Analysis

Structure and crystallinity of the deposited thin films were measured using a Shimadzu XRD-6000 X-ray diffractometer with Cu $K\alpha$ radiation. The data were collected in the 2θ range of $10\text{-}70^\circ$ at a scan rate of $2^\circ/\text{min}$. Surface morphology of the thin films was characterized using a JEOL JSM-5600LV scanning electron microscope. The fractured cross-sections of the thin films deposited on SiO_2/Si substrates were also characterized by an SEM to estimate the thickness and growth rate.

C. Electrochemical Measurements

Electrochemical measurements were carried out on Li/LiCoO_2 cells with a lithium metal foil as anode and a polycrystalline film as cathode of 0.785cm^2 active area using a Solartron 1287 two terminal cell test system with both the reference and counter electrodes connected to the anode and working electrode to the cathode. Li metal foil was used as both the anode and the reference voltage electrode. The electrolyte solution was 1 M LiFP_6 in a 1:1 (by volume) ethylene carbonate (EC)-diethylene carbonate (DEC) solution. Cyclic voltammetry was carried out between 3.5 and 4.4 versus Li/Li^+ at a slow sweep rate of 0.1 mV s^{-1} . Galvanostatic charge-discharge cycling test was carried out in the potential range between 3.0 and 4.2 V using constant current density $15 \mu\text{A/cm}^2$.

III. RESULTS AND DISCUSSION

Pulsed laser deposited LiCoO_2 films are pin-hole free as revealed from the optical microscopy and well adherent to the substrate surface. Crystallinity and surface morphology are greatly influenced by deposition parameters including substrate temperature, target-substrate distance, oxygen

partial pressure and laser energy. The optimized deposition parameters in the present investigation are 600°C substrate temperature, 35mm target-substrate distance, 100mTorr oxygen partial pressure and 150-160 mJ laser energy.

A. X-ray Diffraction

Fig. 2 shows the XRD spectra of the target, the stainless steel substrate without deposition and the thin film deposited on the stainless steel substrate (SS). The expected LiCoO_2 powder diffraction positions are shown at the bottom. The spectrum (a) reveals a polycrystalline structure of the LiCoO_2 target. For LiCoO_2 thin film, the LiCoO_2 (003) peak at $2\theta = 18.78^\circ$ is the strongest peak in Fig. 2 (c). In addition, the LiCoO_2 (006) and (009) peaks respectively at 38.28° and 59.15° , though very weak, can be observed. Other reflections are associated with the SS. The reflection peaks such as LiCoO_2 (101), (012) and (104), which are obvious in target spectrum (a), cannot be observed in Fig. 2 (c). Absence of the reflections other than (00l) peaks indicates that the film has a preferred c-axis (003) orientation to the substrate surface which is often observed in PLD processing [8], [9].

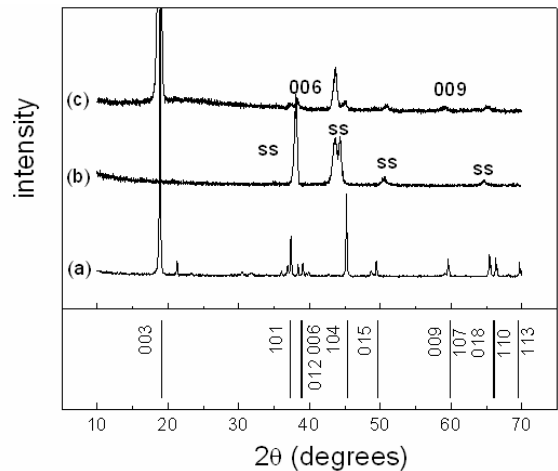


Fig. 2. XRD $\theta/2\theta$ spectra for LiCoO_2 thin film on SS substrate. (a) LiCoO_2 target. (b) Stainless steel substrate. (c) LiCoO_2 thin film grown on SS substrate.

Fig. 3 shows the XRD patterns of the thin films deposited on the SiO_2/Si substrate and on the Pt coated the SiO_2/Si substrate. The expected LiCoO_2 powder diffraction positions are also shown at the bottom. Only LiCoO_2 (003) peak at $2\theta = 18.78^\circ$ can be clearly observed in spectrum (c) when deposited on Pt coated SiO_2/Si substrate. The expected LiCoO_2 (006) peak is, if present, obscured by the Pt peaks. While we can see clearly LiCoO_2 (003), (006), (009) and (104) peaks from spectrum (b) when deposited directly on SiO_2/Si substrate. The strong intensity of LiCoO_2 (003) peak in spectrum (c) indicates that the thin film is still preferred c-axis orientation when deposited on Pt coated SiO_2/Si substrate. Assume LiCoO_2 (104) also exists in spectrum (c) but obscured by Pt peak, the emergence of (104) reflection indicates smaller degree of the c-axis orientation of thin film deposited on Pt coated SiO_2/Si substrate.

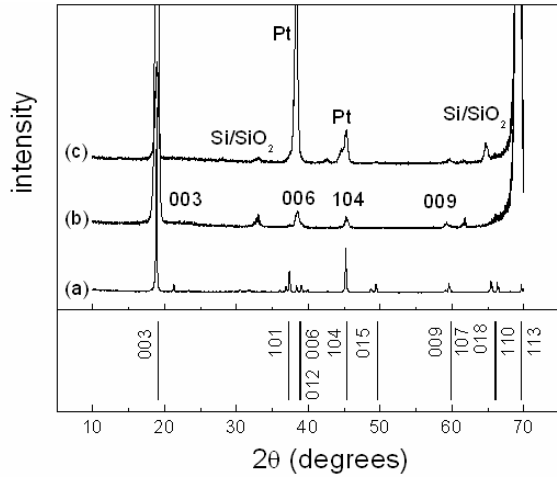


Fig. 3. XRD $\theta/2\theta$ spectra for LiCoO_2 thin film on Si/SiO_2 substrate. (a) LiCoO_2 target. (b) LiCoO_2 thin film grown on Si/SiO_2 substrate. (c) LiCoO_2 thin film grown on Pt coated Si/SiO_2 substrate.

B. SEM Measurements

Fig. 4 shows SEM micrographs of the LiCoO_2 thin films grown on the SS and Pt coated SiO_2/Si substrates at the same deposition conditions. When deposited on the SS substrate, Fig. 5a shows the relatively smooth surface with a few splashed particles and the film exhibits a dense layer with small grains. Figs. 4b and 4d show the cross-sectional view of the LiCoO_2 thin films on the SiO_2/Si and SS substrate deposited at the same time. The film thickness of the LiCoO_2 thin film deposited on the SS substrate estimated from Fig. 4b is about 370 nm corresponding to the deposition rate of about 9 nm/min. When deposited on the Pt coated SiO_2/Si substrate as shown in Fig. 4c, discrete particle clusters were formed on the top of the layer increasing the surface roughness while underneath the LiCoO_2 thin film still exhibits very dense morphology and significantly small grain size. The surface roughness of the thin film is believed to be associated with the coating of the Pt layer since if deposited directly on the SiO_2/Si substrate, a very smooth surface can be obtained. Fig. 5d shows the cross-sectional view of LiCoO_2 thin film on the Pt coated SiO_2/Si substrate. The film thickness is about 450 nm similar to the thickness of the thin film deposited on SS substrate. The deposition rate of LiCoO_2 thin film deposited on the Pt coated SiO_2/Si substrate is about 11 nm/min.

C. Electrochemical Studies

Fig. 5 shows cyclic voltammograms of the thin films deposited on the SS and Pt coated SiO_2/Si substrates. In Fig. 5a, the large anodic and cathodic peaks at 4.00 V and 3.80 V correspond to a first-order phase transition between two different hexagonal phases in the range of $0 < x < 1/4$ in $\text{Li}_{1-x}\text{CoO}_2$ [10]. In Fig. 5b, the large anodic and cathodic peaks are at 3.98 V and 3.85 V, respectively. The smaller peak potential separation of Fig. 5b can be explained by smaller grain size of the LiCoO_2 thin film on the SiO_2/Si

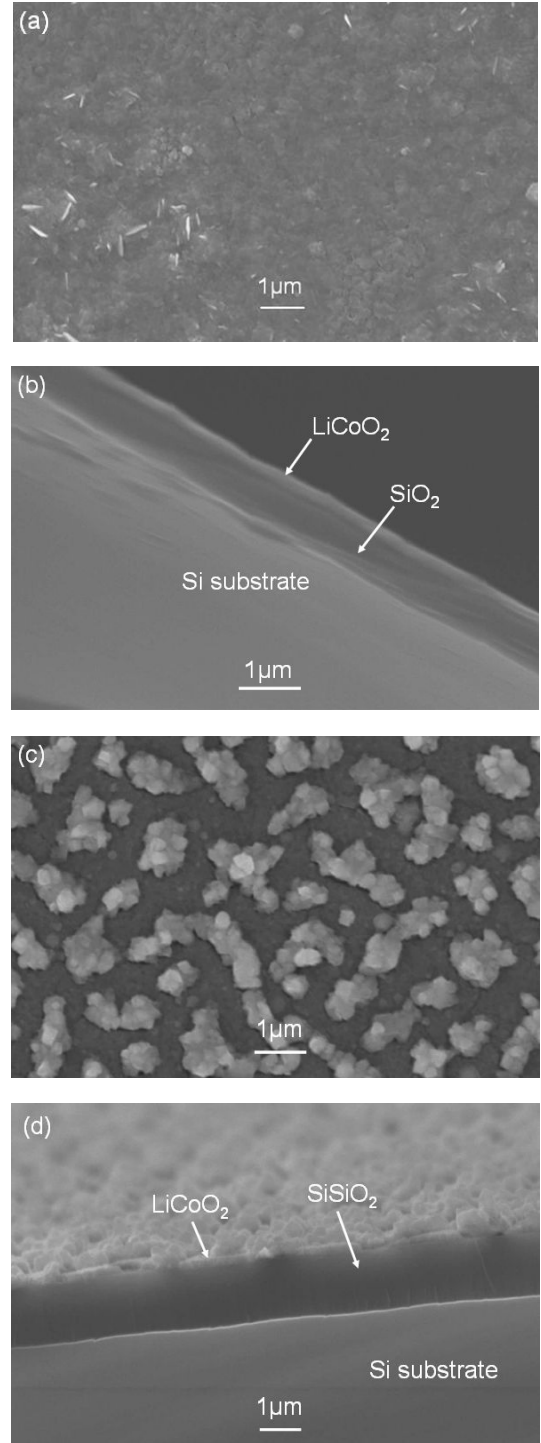


Fig. 4. SEM image of LiCoO_2 thin film prepared by PLD (a) surface image of thin film deposited on SS substrate. (b) Cross-section image of thin film deposited on Si/SiO_2 substrate. (c) Surface image of thin film deposited on Pt coated Si/SiO_2 substrate. (d) Cross-section image of thin film deposited on Pt coated Si/SiO_2 substrate.

substrate. When the potential is higher than 4.0 V, the lithium-ion extraction/insertion proceeds in the host of a single phase. Order-disorder phase transitions from the hexagonal to a monoclinic phase and from the monoclinic to another hexagonal phase at composition near $\text{Li}_{0.5}\text{CoO}_2$ take

place at 4.06 and 4.16 V, respectively, which can be barely seen in Figs. 5a and 5b.

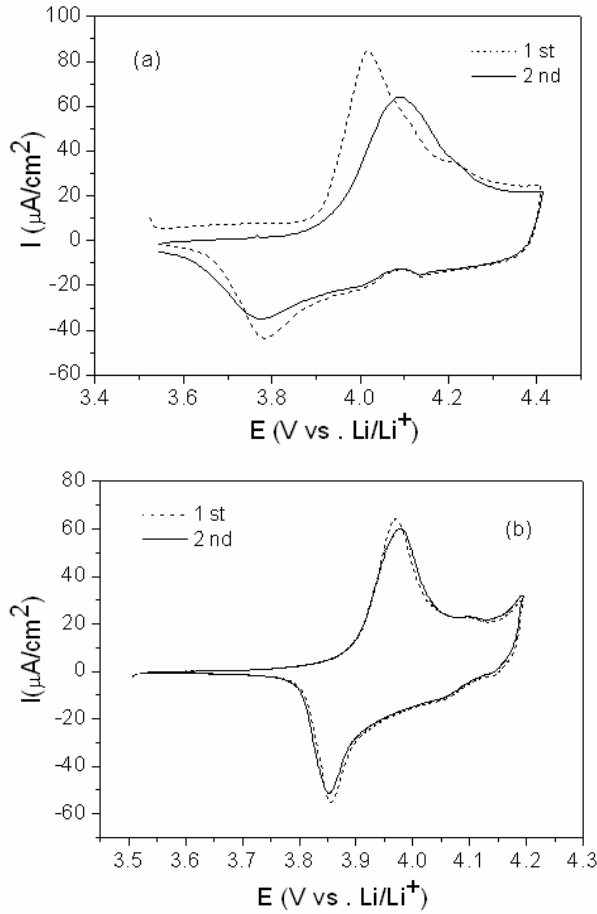


Fig. 5. Cyclic voltammograms of LiCoO₂ thin films deposited on SS substrates and Pt coated Si/SiO₂ substrates. (a) SS substrate. (b) Pt coated Si/SiO₂ substrate

The first 10 cycles charge-discharge spectra of Li//LiCoO₂ cell on the SS substrate are shown in Fig. 6a. The cell was cycled between 3.0 and 4.2 V at constant current density of 15 μA/cm². The dashed lines in Fig. 6a indicate the first charge and discharge curves. The well known two-phase voltage plateau [11] at around 3.9 V is clearly seen. The shape of the charge and discharge curves is similar and 76% of the extracted Li can be reintercalated during discharge. However, the two-phase plateau of discharge curves is getting less evident with number of cycling. Fig. 6b shows the corresponding charge-discharge capacity vs. cycle number. The square and triangle respectively denote the charge and discharge cycles. The first charge and discharge capacity are respectively 30.32 and 23.20 μAh/cm², or 87.35 and 62.70 μAh/cm² μm according to the estimated thickness 370nm from SEM. The initial discharge capacity of 23.20 μAh/cm² decreases to 20.98 μAh/cm² after 10 cycles corresponding to a capacity loss of 0.95% per cycle.

The first 10 cycles charge-discharge curves of Li//LiCoO₂ cell on the Pt coated SiO₂/Si substrate are shown in Fig. 7a. The cell was cycled between 3.0 and 4.2 V at constant

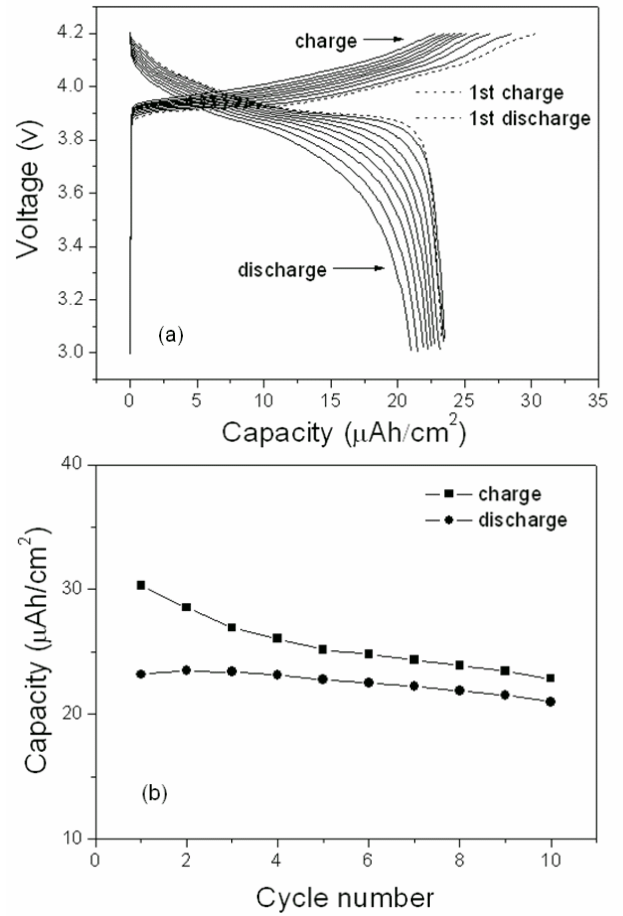


Fig. 6. (a) Charge-discharge profiles of thin film deposited on SS substrate. (b) Charge-discharge capacities vs. cycle number of thin film deposited on SS substrate.

current density of 15 μA/cm². The dashed lines in Fig. 7a indicate the first charge and discharge curves. The well known two-phase voltage plateau at around 3.9 V is also clearly obtained. The shape of the charge and discharge curves is similar and 74% of the extracted Li can be reintercalated during discharge. The two-phase plateau of discharge curves is still evident even after 10 cycles, which is different with the characteristics of charge-discharge curves of LiCoO₂ thin film grown on the SS substrate. Fig. 7b shows the corresponding charge-discharge capacity vs. cycle number. The square and triangles respectively denote the charge and discharge cycles. The first charge and discharge capacity are 36.53 and 27.17 μAh/cm², or 81.17 and 60.37 μAh/cm² μm with estimated thickness 450nm from SEM. The initial discharge capacity of 27.17 μAh/cm² decreases to 23.07 μAh/cm² after 10 cycles corresponding to a capacity loss of 1.5% per cycle.

The incremental capacity curve ($\Delta Q/\Delta V$) versus cell voltage of Li//LiCoO₂ thin film cell derived from the first charge-discharge curve in Figs. 6 and 7 is shown in Fig. 8. Fig. 8a shows the incremental capacity curve of Li//LiCoO₂ cell on SS substrate. The major peak at 3.9 V corresponds to a first-order phase transition between two different

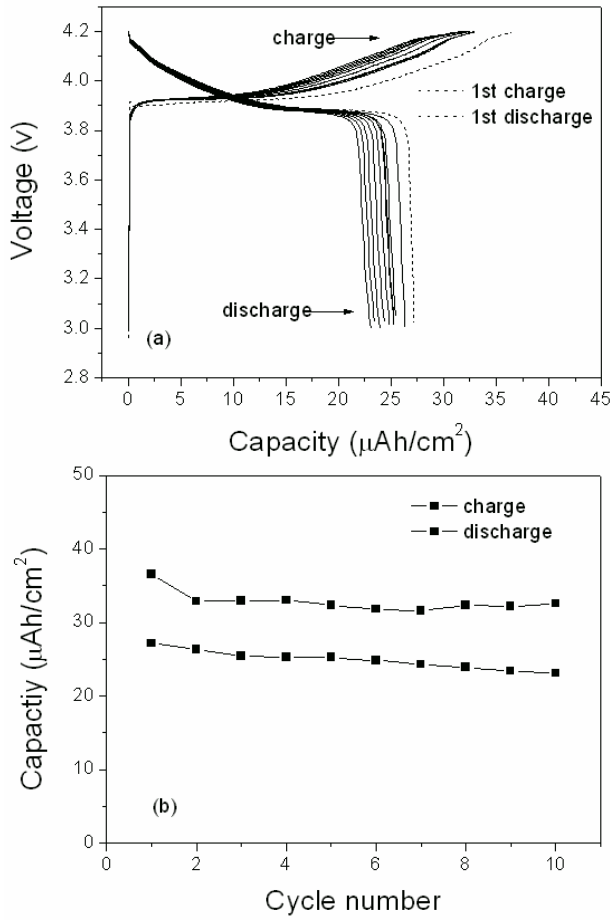


Fig. 7. (a) Charge-discharge profiles of thin film deposited on Pt coated Si/SiO₂ substrate. (b) Charge-discharge capacities vs. cycle number of thin film deposited on Pt coated Si/SiO₂ substrate.

hexagonal phases, which is similar to that observed in the cyclic voltammogram data. The difference between the corresponding peak positions during deintercalation and intercalation of Li is about 20 mV indicating that the polarization in the cell is small. Two minor peaks are also seen at above 4 V, which are associated with order/disorder transitions at composition near Li_{0.5}CoO₂. Fig. 8b shows the incremental capacity curve of Li//LiCoO₂ cell on Pt coated SiO₂/Si substrate. The characteristic of Fig. 8b is very similar to that in Fig. 8a. The major peak is also at 3.9 V and the difference between the major peak positions during deintercalation and intercalation of Li is about 30 mV.

IV. CONCLUSION

LiCoO₂ thin films have been grown by pulsed laser deposition on the stainless steel and Pt coated SiO₂/Si substrates. The thin films grown on both substrates show good crystallinity and (003) out-of plan texture. The electrochemical properties of the thin films grown on both substrates are similar. The first-order phase transition between two different hexagonal phases at about 3.9 V has been confirmed by the cyclic voltammogram, constant current charge-discharge and incremental capacity curves.

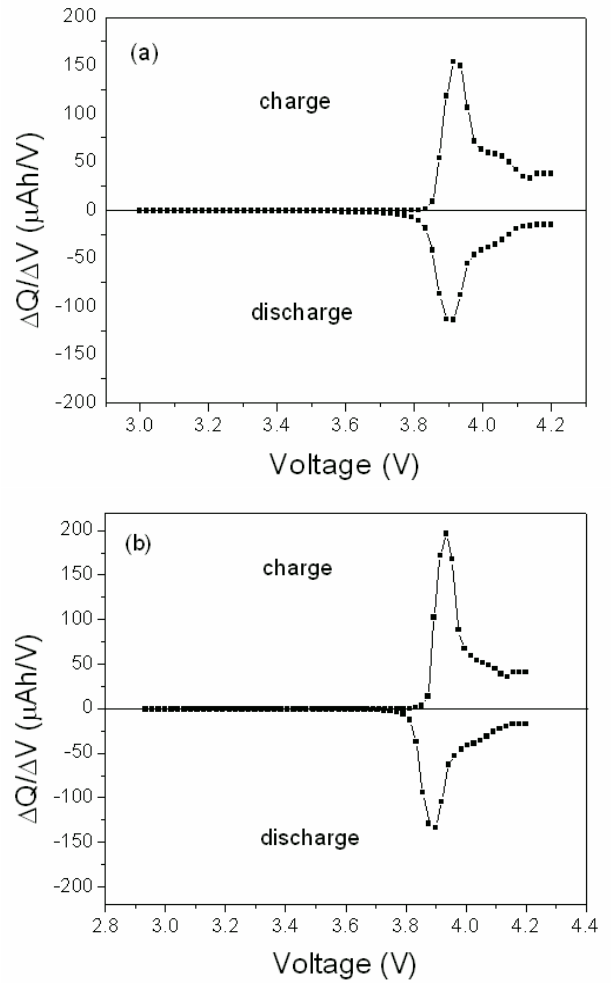


Fig. 8. (a) Incremental capacity ($\Delta Q/\Delta V$) versus cell voltage for the first charge-discharge cycle of Li//LiCoO₂ cell with LiCoO₂ thin film deposited on SS substrate. (b) shows the incremental capacity ($\Delta Q/\Delta V$) of Li//LiCoO₂ cell with LiCoO₂ thin film deposited on Pt coated Si/SiO₂ substrate.

For constant current cycling between 3.0 and 4.2 V at constant charge current of 15 $\mu\text{A}/\text{cm}^2$, the LiCoO₂ thin film deposited on the stainless steel substrate had a initial capacity of 23.20 $\mu\text{Ah}/\text{cm}^2$ with decreasing 0.95% per cycle, and the LiCoO₂ thin film deposited on the Pt coated SiO₂/Si substrate had a initial capacity of 27.17 $\mu\text{Ah}/\text{cm}^2$ with decreasing 1.5% per cycle. Overall, the results indicate that the pulsed laser deposition method can be used to grow the LiCoO₂ thin films for the application in the lithium microbatteries.

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