Growth and characterization of tetravalent doped LiCoO$_2$ thin film cathodes

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Received 9 January 2009; accepted 24 June 2009

Titanium-doped LiCoO$_2$ thin films are grown by pulsed laser deposition technique on silicon substrates. Structure, AFM, FTIR and Raman are studied with respect to their deposition parameters, i.e., substrate temperature ($T_s$) and oxygen partial pressure ($pO_2$) in the deposition chamber. The films deposited in $pO_2 = 100$ mTorr showed good crystallinity on silicon substrates maintained at $T_s = 700^\circ$C. It is found that such a film crystallizes in the layered $\alpha$-NaFeO$_2$ structure. The influence of titanium doping on particle size and morphologies has been clearly studied. FTIR spectra displayed the characteristic IR dominant bands at 246 and 550 cm$^{-1}$ for titanium doped LiCoO$_2$ thin films. The Raman peaks observed for the films at 594 cm$^{-1}$ and 485 cm$^{-1}$ are ascribed to Raman active modes $A_{1g}$ and $E_g$, respectively. The electrochemical measurements were carried out on Li//LiTi$_{1-y}$Co$_{y}$O$_{2}$ cells. The Li//LiTi$_{1-y}$Co$_{y}$O$_{2}$ cell delivered a specific capacity of 225 mC/µm cm$^{2}$. The influence of titanium doping on the structural and electrochemical properties has been systematically studied.

Keywords: Ti doped LiCoO$_2$ PLD films, XRD, AFM, Raman and electrochemical

Due in large part to high-energy storage capacity, LiCoO$_2$ is the prototypical positive electrode material for lithium ion batteries. The increasing interest of LiCoO$_2$ thin films comes both from the technological application in all-solid-state microbatteries and the fundamental studies of lithium intercalation process into the oxide matrix. It’s layered $\alpha$-NaFeO$_2$-type structure (R3m space group) provides structural flexibility to introduce Li ion as mobile guest species. This oxide is considered to have high specific density, high voltage, long cycle life and good reversibility for lithium intercalation – deintercalation process. It is easy to prepare but its high cost and toxicity remain problems to be solved. Intensive investigations have been carried out on doped LiCo$_{1-x}$M$_x$O$_2$ oxides ($M = $ Mn, Cr, Al, Ti, B, Mg, etc.), which show interesting structural and electrochemical properties. Doping with non-transition metals such as titanium has gained increasing interest for the following reasons: (i) the low cost and low toxicity, (ii) the fact that titanium substitution for transition metal oxides leads to higher lithium intercalation voltages, (iii) the titanium doping stabilizes the layered structure and extends the cyclability and enhances the capability of the electrochemical cells.

The rock salt LiCoO$_2$ lattice consists of a close packed network of oxygen ions with lithium and cobalt ions on alternating (111) planes of the cubic rock salt sublattice. The Co and Li cations occupy the octahedral 8a and 8b sites, respectively, while oxygen anions are located on the 6c sites. The Co$_6$ octahedra are shared edges to form CoO$_2$ sheets and Li ions can move in two dimensional (2-D) directions between the CoO$_2$ slabs.

In spite of its importance, many physical properties of LiCoO$_2$ remain unknown or unpublished. We have shown in our research on the development of Lithiated Transition Metal Oxides (LTMOs) that LiCoO$_2$ and LiMn$_2$O$_4$ films deposited by Pulsed Laser Deposition (PLD) exhibit a high degree of preferred orientation or texturing. Preparation of titanium doped LiCoO$_2$ films may have advantages from a point of view of fundamental studies (because it is a binder free material with a well-defined interfacial area) and of the emerging field of microbatteries as well. Thin films of LiCoO$_2$ have been synthesized by a variety of techniques including sputtering, spray deposition, reaction of metals and pulsed laser deposition. In the fabrication of LiCoO$_2$ thin films formation of the 2-D structure is known to be crucial for obtaining a good mobility of the lithium ions. Various aspects of LiCoO$_2$ thin films prepared by RF...
sputtering\textsuperscript{7,8}, pulsed laser deposition\textsuperscript{8-12}, electrostatic spray\textsuperscript{13} and chemical vapour deposition\textsuperscript{14}, have been reported. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films\textsuperscript{15}. When PLD is carried out in the atmosphere of a chemically reactive gas (a process known as Reactive Pulsed Laser Deposition (RPLD)), the flux of the laser ablated material interacts with the gas molecules all along the transit from the target to the collector surface. The resulting deposited layer was found to have a chemical composition substantially the same as the base or starting material. Preliminary investigations on pulsed laser deposited LiCoO\textsubscript{2} thin films were carried out by Julien et al.\textsuperscript{9} Iriyama et al.\textsuperscript{10} prepared thin films of LiCoO\textsubscript{2} by PLD and studied the electrochemical performance. However, the investigations on the microstructural features of LiCoO\textsubscript{2} films that are essentially depend upon the deposition parameters give a scope for effective utilization of these thin films in the fabrication of microbatteries. In this paper, the structural and electrochemical properties of titanium doped LiCoO\textsubscript{2} films deposited on silicon substrates using the PLD technique from a sintered target have been presented.

**Experimental Procedure**

Titanium doped LiCoO\textsubscript{2} thin films were grown by pulsed laser deposition technique on silicon substrates maintained at temperatures in the range 500-700°C in an oxygen partial pressure of 100 mTorr. The target was prepared by sintering a mixture of high purity LiCoO\textsubscript{2} and Ti powders (Cerac products) with excess of Li, i.e., Li/Co + Ti = 1.1 by adding Li\textsubscript{2}O. The mixture was crushed and pressed at 5 tons.cm\textsuperscript{-2} to make tablets 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800°C. The target was rotated at 10 rpm with an electric motor to avoid depletion of material at any given spot. The laser used in these experiments is the 248 nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was 1 × 3 mm and the energy 300 mJ. The power density at the target surface was 10 Jcm\textsuperscript{-2}. The target to substrate distance was maintained at 4 cm. The deposition temperature was maintained with a flow controller.

The structure of the films was characterized by X-ray diffraction (XRD) using a diffractometer (Philips model PW 1830) with nickel filtered CuK\textsubscript{α} radiation (\(\lambda = 1.5406 \) Å). The diffraction pattern were taken at room temperature in the range 5° < 2\( \theta < 60° \) using step scans. The step size and the scan rate were set at 0.1 and 0.2 °/min, respectively. The surface topography was investigated by atomic force microscopy (AFM) using a bench apparatus (Digital instruments, 3100 series).

FTIR absorption spectra were recorded at room temperature using a Brucker IFS 113v interferometer. The Raman spectra of the films were recorded between 200 and 1000 cm\textsuperscript{-1} at room temperature in a quasi-backscattering configuration at a spectral resolution of 2 cm\textsuperscript{-1}. The Raman-laser apparatus (Jobin-Yvon U1000) was equipped of holographic grating double-monochromator, an intermediate spatial filter and a computer-controlled photon-counting system. The emission from a laser (Spectra-Physics, 2020 argon-ion) with a wavelength of 514.5 nm was used. The frequency stability and the accuracy of the apparatus were checked recording the Raman spectrum of silicon. To avoid sample photo-decomposition or denaturation, RS spectra were recorded using a low power density of 100 W/cm\textsuperscript{2}.

The electrochemical measurements were carried out on Li//LiTi\textsubscript{2}Co\textsubscript{1-y}O\textsubscript{2} cells with lithium metal foil as anode and a LiTi\textsubscript{2}Co\textsubscript{1-y}O\textsubscript{2} film as cathode of 1.5 cm\textsuperscript{2} active area using Teflon home-made cell hardware. The silicon substrate was mounted on Ag wire with silver paint and covered by insulating epoxy leaving only the PLD film as active area. Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a Mac-Pile system in the potential range between 2.0 and 4.2 V. Quasi-open circuit voltage profiles were recorded using current pulses of 5 \(\mu\)Acm\textsuperscript{-2} supplied for 1 h followed by a relaxation period of 0.5 h. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps.

**Results and Discussion**

Pulsed laser deposited titanium doped LiCoO\textsubscript{2} thin films are pin hole free and well adherent to the substrate surface. The good film integrity is favour for electrochemical testing. The influence of substrate
temperature on the structure, surface morphology, was studied to understand the growth mechanism.

Structure

Figure 1 represents the X-ray diffraction pattern of pulsed laser deposited LiTi$_y$Co$_{1-y}$O$_2$ thin films grown at 700°C in an oxygen partial pressure of 100 mTorr. It is observed from the X-ray diffraction pattern that the entire finger prints visually (003), (101), (006), (102) and (104) are clearly identifiable thereby suggesting the formation of the α-NaFeO$_2$ structure. The pattern also indicate that the there is no existence of additive impurity peaks suggesting that the grown film is a solid solution of type LiTi$_y$Co$_{1-y}$O$_2$ in which the composition of 'y' may be ≤ 0.05. The evaluated hexagonal lattice parameters for the films are $a = 2.817$ Å and $c = 14.081$ Å which are slightly greater than pure LiCoO$_2$. The $c/a$ ratio, which is an indication of metal-metal layer distance or in other words hexagonal settings, is 4.99. The lattice parameter ‘a’ represents the intralayer metal-metal distance while ‘c’ is ascribed to inter slab distances. These values are in agreement with the reported values. Looking at the radius of Ti (0.605 Å), we can expect the partial replacement for low spin Co$^{3+}$ (0.545 Å) is the reason for increase of ‘a’ and ‘c’ values. This facilitates the easy insertion and extraction of lithium in LiTi$_y$Co$_{1-y}$O$_2$ films thereby increases the cyclability when used in battery fabrication. It can be noted that the ratio of the intensities of (003) and (104) ($I_{003}/I_{104}$) peaks is greater than unity, thereby suggesting no cation disorder which is also supplemented by the value of $c/a$, i.e., > 4.89.

Surface morphology

The surface morphology of laser ablated titanium doped LiCoO$_2$ thin films have been recorded by Atomic Force Microscopy (AFM) in a simple contact mode of operation. Figure 2 represents the surface morphology of titanium doped LiCoO$_2$ thin films deposited on silicon substrate held at different substrate temperatures. The atomic force microscopy data demonstrated that the pulsed laser deposited titanium doped LiCoO$_2$ thin films are homogeneous and uniform with regard to the surface topography and thickness over an area of 1 cm$^2$. The root mean square surface roughness is found to be less than 10 nm. With a short target-substrate distance, the films produced exhibit a dense layer with grain size of the films significantly small when the films deposited at
lower substrate temperatures (<500°C). Whereas the titanium doped LiCoO$_2$ thin films formed at higher substrate temperatures >500°C composed of roughly ablated spherical clusters with average particle size of >100 nm. The crystallite size increased with increasing substrate temperature. The grain size of the films formed at 700° is 200 nm.

FTIR studies

The LiCoO$_2$ possesses the R3m space group, D$^3_{3d}$ spectroscopic symmetry. According to the results of the theoretical factor-group analysis, two modes are active in the Raman spectrum ($A_{1g}$ & $E_g$) and four modes are active in the infrared spectrum ($2A_{2u}$ & $2E_u$) of the LiCoO$_2$ crystal$^{17}$. Figure 3 shows the FTIR spectra of titanium doped LiCoO$_2$ thin films deposited on silicon maintained at temperature in the range 500-700°C in an oxygen partial pressure pO$_2$ = 100 mTorr. These spectra displayed the characteristic IR dominant bands at 246 and 550 cm$^{-1}$ for titanium doped LiCoO$_2$ thin films. The former is attributed to the asymmetric stretching mode of the octahedral LiO$_6$ units, while the latter is due to the asymmetric stretching vibration of CoO$_6$ groups. The FTIR features represented are in good agreement with elemental analysis. For films deposited in the range 500-700°C, the low wave number IR-band displayed the fingerprint for the Li-O vibration.

Raman studies

The Experimental Raman Spectra of titanium doped LiCoO$_2$ thin films grown at various substrate temperatures recorded in the wave number range 200-800 cm$^{-1}$ is shown in Fig. 4. The titanium doped LiCoO$_2$ has a layered structure and can be assigned to the space group R3m and the atoms (Co, Li and O) are located in the Wyckoff sites 3a, 3b and 6c respectively. The Raman peaks observed for the films at 594 cm$^{-1}$ and 485 cm$^{-1}$ are ascribed to Raman active modes $A_{1g}$ and $E_g$ respectively. Since the Raman modes are entirely due to oxygen atoms, hence the symmetric motions involve Co-O stretching and O-Co-O bending vibrations. These Raman modes are observed to be slightly broader than that of pure LiCoO$_2$ films due to polyhedra distortion in pristine LiCoO$_2$, indicating the incorporation of Ti into Co sites. It is clearly seen from the Raman spectra that the grown films have no impurity peaks.

Information for the structural quality of the titanium doped LiCoO$_2$ thin films can be given considering the Raman data using the shape and the frequency of two peaks located in the low- and high-frequency region of the spectra. When the PLD films are grown from target, the oscillator strength of the $A_{1g}$ stretching mode of RS spectra rose with a narrow full-width at half maximum (FWHM). This phenomenon is due to the well-defined R3m–type structure of the films and the regular distortion of CoO$_6$ octahedra. As the stretching mode is sensitive to the film morphology, low FWHM values provide
The incremental capacity curve (-d charge capacity in the same potential window.)

slight lower averaged potential allows for deeper metal like transition of the LiCoO

2.6 and 4.2 V. The voltage plateau at 3.65 V in the charge curve of LiCoO

2. The open circuit voltage (OCV). The initial open-circuit profile should prove a close approximation to the potential range 2.6-4.2 V; as such, the voltage measurements were carried out at a rate of C/100 in

The PLD film as active area. Electrochemical properties

Titanium doped LiCoO films were prepared by pulsed laser deposition. The films were found to be uniform with regard to the surface topography and well adherent to the substrate surface. Structural properties of the films have been investigated as a function of deposition conditions. The films deposited in P_{02} = 100 mTorr showed good crystallinity on silicon substrates maintained at T_s = 700°C. It was found that such a film crystals in the layered α-NaFeO2 structure. The influence of titanium doping on particle size and morphologies has been clearly evidenced. FTIR spectra displayed the characteristic IR dominant bands at 246 and 550 cm⁻¹ for titanium doped LiCoO₂ thin films. The Raman peaks observed for the films at 594 cm⁻¹ and 485 cm⁻¹ are ascribed to Raman active modes A_{1g} and E_g respectively. The electrochemical measurements were carried out on Li/LiTi_{x}Co_{1-y}O₂ cells. The Li/LiTi_{x}Co_{1-y}O₂ cell delivered a specific capacity of 225 mC/µm cm². Overall, these results indicate that the pulsed laser deposition method can be used to grow films with promise for application in lithium microbatteries.

References