LiCoO$_2$ and SnO$_2$ Thin Film Electrodes for Lithium-Ion Battery Applications

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Abstract

There is an increasing need for small dimension, ultra-lightweight, portable power supplies due to the miniaturization of consumer electronic devices. Rechargeable thin film lithium-ion batteries have the potential to fulfill the growing demands for micro-energy storage devices. However, rechargeable battery technology and fabrication processes have not kept pace with the advances made in device technology. Economical fabrication methods lending excellent microstructural and compositional control in the thin film battery electrodes have yet to be fully developed. In this study, spin coating has been used to demonstrate the flexibility of the approach to produce both anode (SnO$_2$) and cathode (LiCoO$_2$) thin films. Results on the microstructure, crystal structure, and electrochemical properties of the thin film electrodes are described and discussed.

Keywords
LiCoO$_2$; SnO$_2$; spin coating; microstructure; thin film battery; economical

1. Introduction

Thin film batteries have become desirable energy storage devices for the diverse group of consumer portable devices and space related government applications. Sputtering, chemical vapor deposition (CVD), and evaporation have often been used to fabricate the various components of thin film batteries. Kanehori et al. [1] used all three to develop a prototype thin film battery in the early 1980’s. In the 1990’s, sputtering and evaporation were used to produce commercially feasible thin film lithium batteries of type Li metal/solid electrolyte(TiS$_2$ or LiMn$_2$O$_4$) [2]. Thin film lithium and lithium-ion batteries incorporating thin film LiCoO$_2$ cathodes were also produced by sputtering and evaporation [3-7]. Although the performance of the thin film batteries recently fabricated by physical vapor deposition (PVD) methods has been satisfactory, economical and versatile processing techniques are desirable to reduce the cost and improve microstructural and compositional control of the thin film electrodes.

Spin coating is a viable technique that is easy and relatively economical due to the reduced real estate and instrumentation. It can be used to produce a wide variety of electrochemically active cathode thin films. V$_2$O$_5$ thin films fabricated by spin coating on Ni/Si substrates were found to reversibly cycle greater than 3 equivalents of Li$^+$ per unit of V$_2$O$_5$. The spin coating approach was also used to prepare thin films of LiMn$_2$O$_4$ for use as a cathode material in thin film batteries. Other lithium containing transition metal oxide compounds such as LiMn$_n$Ni$_{1-x}$O$_2$, LiMn$_{2-x}$Co$_x$O$_4$, and LiNi$_{1-x}$Co$_x$O$_2$ were also synthesized by a spin coating method, but were not evaluated electrochemically. Similarly, Kushida et al. used sol-gel science and spin coating to produce LiCoO$_2$ thin films on Si substrates, but they did not investigate the electrochemical properties of the films. Electrical resistivity and cyclic
voltammetry analyses of spin coated LiCoO$_2$ thin films on glass and aluminum foil substrates were conducted by Ehrlich et al.$^{12}$ A variety of precursor formulations designed to enhance wetting during spin coating were used to produce LiCoO$_2$ films on Pt/Ti coated Si substrates. The sol-gel produced films showed larger grain size and better electrochemical properties with increasing final anneal temperature.$^{13}$ A sol-gel spin coating process incorporating a crack preventing component, poly(vinylpyrrolidone), in the precursor solution was used to produce LiCoO$_2$ thin films on Au and quartz substrates which showed good electrochemical properties.$^{14}$

Spin coating has not been widely used to produce anode thin films for lithium-ion batteries. However, low-pressure chemical vapor deposition has been used to produce thin films of SnO$_2$ which cycled well out to $\sim$120 cycles.$^{15,16}$ The electrochemical properties of sputter deposited SnO$_2$ anode thin films were investigated by Nam et al.$^{17}$ Electron beam evaporation has also been used to fabricate thin film SnO$_2$ and Si doped SnO$_2$ anodes.$^{18}$

Following these initial studies on SnO$_2$ and LiCoO$_2$, spin coating has been used in this study to synthesize cathode and anode films. LiCoO$_2$ thin films on both stainless steel and gold coated alumina substrates were synthesized. Thin films of SnO$_2$ on stainless steel were also synthesized. The properties of the electroactive thin film materials were examined using x-ray diffraction, scanning electron microscopy, and electrochemical cycling. The advantages of using a gold coated alumina substrate rather than a stainless steel substrate for the cathode current collector are discussed. The morphological change of the SnO$_2$ thin film due to electrochemical cycling is also discussed. Although the fabrication techniques described in this paper have not been optimized, the results show the potential of using spin coating methods to synthesize high quality anode and cathode films for thin film lithium-ion batteries.

2. Experimental

2.1 Cathode Synthesis

Spin coating was used in this study as depicted in Figure 1. Thin films of LiCoO$_2$ were synthesized on stainless steel and gold coated alumina substrates using the procedure shown in Figure 2. The 304 stainless steel substrates (Goodfellow) were punched and flattened 1 cm$^2$ disks 0.125 mm thick. The Superstrate S41-41 alumina substrates (Coorstek) were 1 mm thick as received and were cut into 0.8 cm x 0.8 cm squares. The alumina substrate was coated with gold using thermal evaporation on two sides and at least two edges. Electrical continuity from the face to the obverse was checked using a Fluke multimeter. Stoichiometric amounts of lithium acetate dihydrate (99.999%, Aldrich) and cobalt acetate tetrahydrate (98%, Aldrich) were dissolved in anhydrous methanol (99.8%, Aldrich) to make a 1 mM solution. 1 mL of precursor solution was pipetted onto the substrate per deposition. Typical spin coating parameters were a spin speed of 3000 rpm and a spin time of 30 s. Immediately following the spin coating procedure, the sample was transferred to a 100°C hotplate for 1 minute to remove any remaining methanol followed by a 1 minute 525°C anneal in
air on a homemade, resistive heating pyrolysis station with embedded thermocouple. The procedure was repeated until the desired amount of electrode material was achieved. In this study, an empirical approach was employed to determine the approximate number of spin coating depositions necessary to achieve ultimate reversible capacities in the 50-100 μAh/cm² range. A final air anneal was performed at 800°C in a tube furnace for 10 minutes to achieve the polycrystalline high T LiCoO₂ phase. A semi-rapid thermal annealing procedure was adopted for the final anneal in which a quartz sled was preheated to 800°C, then pulled to the end of the open tube where the sample was placed in the center of the sled, and finally the sled was pushed back into the hot zone of the tube furnace for the 10 minute anneal in standing air. A typical number of deposition steps to fabricate a thin film cathode was 30.

2.2 Anode Synthesis

Thin films of SnO₂ were synthesized on stainless steel substrates as shown in Figure 3. The stainless steel disks were prepared in the same fashion mentioned above in the Cathode Synthesis section. A dilute solution of colloidal tin (IV) oxide in water was prepared from the as-received ammonia stabilized colloidal suspension (Alfa). The as-received solution was a 15% dispersion of SnO₂ in water and it was further diluted using the volumetric ratio, as-received colloidal SnO₂ : distilled H₂O = 2:5. 1 mL of precursor solution was pipetted onto the substrate per deposition. Typical spin coating parameters were a spin speed of 3000 rpm and a spin time of 30 s. Immediately following the spin coating procedure, the sample was transferred to a 150°C hotplate for 2 minutes to remove any remaining water and then placed directly onto a preheated 400°C resistively heated, thermocouple embedded heating station in air for 5 minutes to remove any residual ammonia. The procedure was repeated until achieving the desired amount of electrode material. An empirical method was used to determine the number of spin coat depositions necessary to achieve ~ 40-100 μAh/cm² of reversible capacity. A typical number of depositions to fabricate a thin film anode was 3.

2.3 Characterization of Electrodes

2.3.1 Phase Analysis

X-ray diffraction (XRD) was used to perform phase analyses on the substrates and as-prepared thin film electrodes. The instrument used in this study incorporated a state-of-the-art detector (XRD, Philips PW3040PRO, θ/θ powder diffractometer with X-calorator detector and Cu radiation source). Two-theta scans were typically taken from 10° to 90° with a step size of 0.05°.

2.3.2 Microstructural Analysis

The microstructure of the films was examined using a scanning electron microscope (FEG-SEM, Philips XL30) and a contact mode atomic force microscope (AFM, Veeco).

2.3.3 Electrochemical Analysis
The electrochemical properties of the thin film electrodes were examined using a conventional 3 electrode type cell as shown in Figure 4. The samples were all dried in a vacuum oven for at least 12 hours at 105°C and placed inside an argon filled glove box (Vacuum Atmospheres, Hawthorn, CA, < 10 ppm O₂ and H₂O) for fabrication of half-cells. The half-cells were fabricated in the glove box using lithium foil and a glass fiber separator (Whatman GF/D) together with the electrode films and 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (2:1) electrolyte (Merck). The 3 electrode cells were placed in desiccant jars with electrical feedthroughs, removed from the glove box, and allowed to equilibrate for 12 hours prior to galvanostatic cycling (Arbin Instruments). All charge/discharge experiments had the cycling voltages limited between 20 mV-1.2V and 3.1V-4.2V for the anodes and cathodes, respectively. The LiCoO₂ on stainless steel experiment was performed at a current density of 100 μA·cm⁻² (corresponding to ~ C/1.7 rate) while the LiCoO₂ on gold coated alumina experiment used a current density of 31.25 μA·cm⁻² (corresponding to ~ C/2.5 rate). The SnO₂ on stainless steel experiment was carried out at a current density of 40 μA·cm⁻² (corresponding to ~ 1C rate). All of the tests included a 60 s rest between each charge or discharge half cycle.

3. Results and Discussion

3.1 LiCoO₂ Thin Films on Stainless Steel

The XRD of the stainless steel substrate and 30 spin (30S) sample are shown together in Figures 5a and 5c, respectively. The XRD pattern for 30S shows R̅3m phase LiCoO₂ with peaks matching JCPDS Pattern (82-0340)¹⁹. After confirming the presence of LiCoO₂, SEM was used to determine the morphology of the as-prepared films as shown in Figure 6. Slight porosity is seen in the as-prepared film along with hexagonally faceted grains 500 nm or less in diameter. Following the investigation of the microstructure of the as-prepared film, the sample was dried well and prepared for half-cell cycling. The capacity versus cycle number for the 1st ten cycles of the galvanostatic test are shown in Fig. 7 along with the corresponding coulombic efficiency. One can see that in the first charge, the capacity is ~ 325 μAh. However, the discharge capacity in the 1st cycle drops to ~ 110 μAh, corresponding to a coulombic efficiency of only 36%. In subsequent cycles, the coulombic efficiency gradually increases to ~ 85% by the 10th cycle. The poor coulombic efficiency in the first few cycles indicated that although lithium ions could be de-intercalated from the LiCoO₂, a much lower amount of lithium was able to be intercalated back into the host structure. We suspect that there could be an adverse reaction between the film and the substrate, or the film itself could be highly defective.

Post-cycling SEM results of the same sample are shown in Figure 8. Figure 8a shows that the post-cycled film exhibits two distinct regions, a light region and a dark region. The light region seems to be more narrow and interconnected than the larger dark regions. Close-up views of the light and dark regions are seen in Figures 8b and 8c, respectively. The light region appears to be very similar in nature to the pre-cycled morphology shown in Figure 6b, while the dark region appears to have substantially larger grains.
containing many micro-cracks. There are several possible explanations for the differences in microstructure. One possible explanation is that one of the regions has become electrically insulated from the current collector due to interfacial film formation. For example, if the light region became electrically insulated during the 800°C annealing step, the material directly above may not cycle at all and appear exactly as it did prior to electrochemical cycling. Furthermore, if one assumes that the dark region is still in good electrical contact with the current collector, it would experience a much higher current density due to the decrease in active area. The excessive current density could lead to significant intragranular stresses, micro-cracking, and grain growth as seen in Figure 8c. Micro-cracking and other deleterious cycling related effects were also seen by Wang et al.\textsuperscript{20,21} After forming the aforementioned hypothesis, the researchers decided to intentionally form an “interfacial” phase by only depositing 10 layers of LiCoO\textsubscript{2} precursor followed by a longer 1 h anneal in air. The researchers hoped that XRD could detect some impurity phase formation. The XRD pattern of the long annealed sample is shown in Figure 5b. Upon careful indexing of the resultant peaks using the JCPDS database, the following phases were identified: Li\textsubscript{2}CO\textsubscript{3}, Li\textsubscript{2}CrO\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, CoFe\textsubscript{2}O\textsubscript{4}, CoCr\textsubscript{2}O\textsubscript{4}, LiCoO\textsubscript{2}, and stainless steel. Therefore, it is reasonable to suspect that similar impurity phases were also present in the 30S sample, leading to the poor performance of the cathode.

3.2 \textit{LiCoO\textsubscript{2} Thin Films on Gold Coated Alumina}

After observing the poor performance of the thin film cathode on stainless steel, it was desirable to change substrate materials. A good choice, one adopted in previous work by Neudecker et al\textsuperscript{22}, seemed to be gold coated alumina. XRD of the gold coated alumina substrate and 30A sample are shown together in Figures 9a and 9b, respectively. Other than substrate peaks, the only peaks indexed were the (003), (104), and (002) rhombohedral LiCoO\textsubscript{2} peaks. The microstructure of the uncycled LiCoO\textsubscript{2} film is seen in Figure 10. The film appears to be dense and composed of modestly faceted, high aspect ratio grains with diameters less than 1 μm. The surface topology of the uncycled film is shown in the AFM images of Figures 11a and 11b. One can see that the film is not very smooth, probably due to the nature of the alumina substrate. The capacity versus cycle number for thirty cycles of the galvanostatic test are shown in Fig. 12a along with the corresponding coulombic efficiency, Fig. 12b. One can see that in the first charge, the capacity is ~ 58 μAh. The discharge capacity in the 1\textsuperscript{st} cycle drops to ~ 50 μAh, corresponding to a good 1\textsuperscript{st} cycle coulombic efficiency of 86%, much better than the 36% seen for the stainless steel substrate sample. By the 5\textsuperscript{th} cycle, the coulombic efficiency had increased to ~ 97%, the steady value observed for each subsequent cycle up to 30 cycles. Fig. 13a shows the post-cycled plan view SEM of the LiCoO\textsubscript{2} film. The morphology of the film appears to be unchanged from that shown in the pre-cycling SEM shown previously in Fig. 10. The cross-sectional view of the post-cycled LiCoO\textsubscript{2} film on gold coated alumina is shown in Fig. 13b. The cross-sectional image shows that although the film has a rough surface, it is still a continuous film with no obvious cracking in the film’s bulk. The film thickness is estimated to be ~1 μm from Fig. 13b. After being satisfied with the improvements made by
utilizing a different substrate for the LiCoO₂ cathode, the focus shifted towards examination of the electrochemical properties of spin coated SnO₂ thin films.

3.3 SnO₂ Thin Films on Stainless Steel

Fig. 14a and 14b show the XRD patterns of an uncoated stainless steel substrate and SnO₂ coated stainless steel, respectively. From the XRD pattern, three broad, low intensity peaks were identified corresponding to SnO₂. The broad peaks indicate the nanocrystalline nature of the SnO₂ thin film. The small grain size is a result of the precursor colloidal solution (~15 nm SnO₂ particles), low heat treatment temperature, and short annealing time. The SEM image of the uncycled SnO₂ thin film is shown in Fig. 15. From the SEM image, one can see that the SnO₂ thin film is continuous, with only a few small cracks or voids. The actual grain size of the SnO₂ thin film can be estimated at ~ 20-50 nm as shown in the height AFM image of Fig. 16. The results of the half-cell galvanostatic cycling experiment performed on the SnO₂ thin film are shown in Fig. 17. The capacity versus cycle data and corresponding coulombic efficiencies are shown in Figs. 17a and 17b, respectively. Although the first cycle irreversible loss is quite high (~70%), the remaining cycles have a steady capacity up to the 20th cycle. About 50% of the initial capacity is expected to be lost in the case of materials like SnO₂ due to the large consumption of Li in the irreversible formation of Li₂O. In an attempt to explain the extra capacity loss, post-cycle SEM on the SnO₂ thin film was performed after the 20th cycle. The SEM result is shown in Fig. 18. It appears that regions of the film have peeled, while other regions (for example, the area above the scale marker on the right side of the image) have remained well-adhered to the substrate. The large scale morphological change in the SnO₂ film caused by the well-known volume expansion/contraction phenomenon experienced by Sn based anode materials is the most likely source of the unusually high irreversible loss observed.

4. Conclusion

In this paper, spin coating has been shown to be a viable, economical processing method for the production of both cathode and anode thin films for lithium-ion batteries. The importance of substrate selection on the electrochemical properties of spin coated LiCoO₂ thin films has been emphasized. The choice of a stainless steel substrate led to poor cycling performance accompanied by the formation of intragranular micro-cracks during cycling. A careful XRD study identified several impurity phases which could be responsible for the poor cycling performance in the case of the stainless steel substrate. Conversely, gold coated alumina proved to be a good choice for the substrate. The LiCoO₂ thin film on Au-alumina had low 1st cycle irreversible loss and cycled well for the 30 cycle experiment. Spin coated SnO₂ thin films on stainless steel substrates showed higher than normal irreversible capacity in the 1st cycle. However, the good capacity retention of the SnO₂ thin films up to the 20th cycle indicates their potential for use as anodes in thin film lithium-ion batteries. Spin coating has been shown to be an effective fabrication method for synthesizing good quality
cathodes and anodes for thin film lithium-ion batteries. Spin coating can be used as a processing technique in the future to produce doped lithiated transition metal oxides, samples for in-situ AFM electrode investigations, and studies on the substrate/active material interface.

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References

[19] JCPDS Pattern 82-0340, International Centre for Diffraction Data, Newtown Square, PA, USA.

**Figure Captions**

1. Schematic depicting the spin coating process.

2. Flowchart showing the synthesis of thin film LiCoO$_2$ cathodes on rigid substrates.

3. Flowchart outlining the synthesis of thin film SnO$_2$ anodes on rigid substrates.

4. “Hockey-puck” cell used for electrochemical characterization.

5. XRD of (a) stainless steel substrates (unannealed), (b) stainless steel/LiCoO$_2$ thin film (10S/final anneal), and (c) stainless steel/LiCoO$_2$ thin film (30S/final anneal).

6. SEM image of as-prepared LiCoO$_2$ thin film on stainless steel (30S/final anneal) at (a) 11266x and (b) area outlined by black rectangle in (a) at 45063x.

7. Half-cell battery cycling test of LiCoO$_2$ thin film on stainless steel (30S/final anneal). (a) Capacity versus cycle number and (b) coulombic efficiency versus cycle number.

8. SEM image of galvanostatically cycled (10 cycles) LiCoO$_2$ thin film on stainless steel (30S/final anneal) at (a) 800x; (b) area I outlined by black rectangle in (a) at 25600x; and (c) area II outlined by black rectangle in (a) at 25600x.

9. XRD of (a) gold/alumina substrate (unannealed) and (b) LiCoO$_2$ thin film on gold/alumina (30A/final anneal).

10. SEM image of as-prepared LiCoO$_2$ thin film on gold/alumina (30A/final anneal) at 24569x.

11. Contact AFM images of as-prepared LiCoO$_2$ thin film on gold/alumina (30A/final anneal), 5 μm x 5 μm scan area, (a) top view and (b) surface plot.

12. Half-cell battery cycling test of LiCoO$_2$ thin film on gold/alumina (30A/final anneal). (a) Capacity versus cycle number and (b) coulombic efficiency versus cycle number.
13. SEM image of galvanostatically cycled (30 cycles) LiCoO$_2$ thin film on gold/alumina (30Å/final anneal) at (a) 19388x; and (b) cross-section, 16012x.

14. XRD of (a) stainless steel substrate (unannealed) and (b) SnO$_2$ thin film on stainless steel (3S/final anneal).

15. SEM image of as-prepared SnO$_2$ thin film on stainless steel (3S/final anneal) at 76242x.

16. Contact AFM image of as-prepared SnO$_2$ thin film on stainless steel (3S/final anneal), 375 nm x 375 nm scan area, top view.

17. Half-cell battery cycling test of SnO$_2$ thin film on stainless steel (3S/final anneal). (a) Capacity versus cycle number and (b) coulombic efficiency versus cycle number.

18. SEM image of galvanostatically cycled (20 cycles) SnO$_2$ thin film on stainless steel (3S/final anneal) at 76049x.
**SPIN COATING**

- Substrate
- Vacuum chuck
- Deposited Precursor
Figure 2

Stainless Steel Substrate
Stoichiometric amounts of lithium acetate and cobalt acetate in anhydrous methanol.

Deposit prepared solution onto 1 cm² s.s. substrate disk.
Pre-heat at 100° C on hotplate in air for 2 minutes to remove methanol.
Heat at 525° C in air for 1 minute.
Heat cathode in air at 800° C for 10 minutes and dry in vacuum oven at 105°C for 12 hours.

Au-Al₂O₃ substrate
Stoichiometric amounts of lithium acetate and cobalt acetate in anhydrous methanol.

Deposit prepared solution onto 0.64 cm² Au-Al₂O₃ substrate.
Pre-heat at 100° C on hotplate in air for 2 minutes to remove methanol.
Heat at 525° C in air for 1 minute.
Heat cathode in air at 800° C for 10 minutes and dry in vacuum oven at 105°C for 12 hours.

Desired amount of electrode.
Figure 3

Stainless Steel Substrate

Prepare solution of diluted colloidal suspension of tin (IV) oxide in water.

Spin Coat

Deposit prepared solution onto 1 cm² s.s. substrate disk.

Pre-heat at 150°C on hotplate in air for 2 minutes to remove residual water.

Heat at 400°C in air for 5 minutes to remove any residual ammonia.

Dry anode in vacuum oven at 105°C for 12 hours.

Desired amount of electrode.