Optimization of a potential manufacturing process for thin-film $LiCoO_2$ cathodes

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Abstract

A radio frequency (RF) magnetron sputter deposition process designed for low-cost, high-rate fabrication of $LiCoO_2$ (LCO) thin films was developed and used to fabricate approximately phase pure cathodes with the $R\bar{3}m$ crystal structure, strong (104) preferred orientation and high discharge capacities. Starting from a typical set of processing conditions for LCO films, the values of key deposition and post-deposition parameters were systematically changed to increase the deposition rate, simplify the sputter deposition process and minimize process gas use without compromising the structural properties and electrochemical performance. Cathodes were deposited onto Waspaloy (58Ni-19Cr-14Co-Mo-Ti-Al-Fe [wt%]) foil current collectors to provide enhanced thermal stability during post-deposition annealing. The best properties were attained using a process pressure of 0.5 Pa, an RF power density of 5.5 W cm^{-2}, and a post-deposition anneal in air at 600 ˚C for 2 hours. A sintered sputter target, oxygen gas flow and substrate heating were not required. This set of conditions resulted in a high deposition rate of ~700-790 nm h^{-1}, allowing the formation of a relatively thick (~2.8-3.2 μm) film in 4 hours. Furthermore, high maximum specific and areal discharge capacities of 132 mAh g^{-1} / 62 μAh cm^{-2}μm^{-1} and 172 μAh cm^{-2} were attained during galvanostatic cycling at a rate of 0.1 C with an organic liquid electrolyte, which are among the highest values reported. Cycling rate tests showed that the thin-film LCO cathodes could deliver capacity up to a cycling rate of at least 2 C without causing any significant cell damage.

Keywords: thin-film cathode, lithium cobalt oxide, radio frequency magnetron sputtering, manufacturing process, Waspaloy.

1. Introduction

There is a growing demand for compact electronic devices that can be worn or implanted in the body, connect with a network of other devices, and harvest their own energy [1]. These devices require power sources that store more energy in less space, maintain full charge capacity for longer and operate more safely than conventional lithium-ion batteries [1–6]. Thin-film solid-state lithium batteries ≤10 μm in thickness with low volume fractions of inactive materials and high-quality, low impedance interfaces could satisfy these requirements. Interest in these batteries has grown significantly since the development of thin-film Li | lithium phosphorus oxynitride (LiPON) | $LiCoO_2$ (LCO) cells at Oak Ridge National Laboratory in the 1990s [7]. While these cells have demonstrated some outstanding properties – such as the ability to undergo over 40,000 charge-discharge cycles before failure – commercial manufacturing is still on a small scale [8,9]. Several challenges related to electrochemical performance and manufacturability must be addressed before thin-film cells can make a substantial impact on the rechargeable battery market.

Many studies have attempted to improve the performance of the Li | LiPON | LCO cell by optimizing the processing of each layer. Particular attention has been given to the LCO cathode, usually fabricated by radio frequency (RF) magnetron sputtering, since its electrochemical performance is particularly sensitive to its structure, which in turn is dependent on the deposition conditions. As-deposited LCO films are often amorphous or nanocrystalline, but the electrochemical properties are much improved by post-deposition annealing, which typically results in a polycrystalline structure consisting of rhombohedral ($R\bar{3}$m) crystallites with lithium, cobalt and oxygen atoms arranged into separate layers perpendicular to the c-axis [7,10]. This crystal structure is commonly referred to as ‘HT-

LCO' (high temperature LCO) [2].

Thin films deposited from the vapour phase often show a preferred crystallographic orientation [11]. Since lithium ion motion occurs within the (003) planes in LCO, it is desirable for these planes to intersect the cathode surface, minimizing the impedance of the cathode-electrolyte interface [10,12]. Previous reports have shown that this condition is most readily satisfied by the parallel alignment of (104) and (101) planes with the film surface [2,10,13–17]. Numerous investigations have studied the effects of altering the main RF sputter deposition and post-deposition processing conditions (RF power density, process pressure, process gas composition, substrate material, substrate temperature during deposition and post-deposition annealing temperature) on the properties of LCO thin films [2,7,17–34]. Most studies report similar processing conditions: an RF power density of ~2-5 W cm^{-2}, a deposition pressure of at least 1 Pa, a mixed argon-oxygen process gas, an unheated metal-coated ceramic substrate, and post-deposition annealing in air or an oxygen/argon-oxygen atmosphere at 600-700 ˚C for 1-2 hours. Relatively few studies have explored conditions that deviate significantly from these ranges [19,21,24,29,33–36]. Thus, it may be possible to achieve favourable structural and electrochemical properties across a markedly wider variety of processing conditions.

To be commercially viable, the LCO film fabrication process must be as productive and efficient as possible. High deposition rates, minimal use of process gases and low-temperature, short-duration annealing treatments are therefore desirable. The high temperature annealing treatments used in most studies place severe demands on the substrate material, which must act as the cathode current collector during battery operation but resist excessive oxidation and elemental interdiffusion during heat treatment, providing an additional incentive to reduce the annealing temperature. While many studies have used thin films of gold or platinum deposited on a ceramic [2,7,20,24,25,33,37,38], Filippin *et al.* [18] have recently proposed the use of an oxidation resistant Ni-Al-Cr alloy, which may provide greater stability during annealing and cycling. Usually, the deposition rate achieved by RF sputtering is directly proportional to the power density applied to the target [39]. Furthermore, a high power density may lead to favourable film properties, since several reports have shown that increasing the power density increases the crystallinity of as-deposited LCO films and reduces the formation of the electrochemically inactive cubic ($Fd\bar{3}m$) Co_3O_4 phase [17,28,29]. The deposition rate is also sensitive to the process gas pressure; an increase in the pressure reduces the mean free path of sputtered atoms so that a smaller proportion reach the substrate, while a decrease in pressure reduces the frequency of collisions between the gas ions and the target, thereby lowering the sputtering rate [40]. An optimum balance between these two effects is therefore required to maximize the deposition rate.

The pressures most frequently reported for LCO deposition are rather high compared to those used to deposit other materials. For example, indium tin oxide films, which are widely used as transparent electrodes in touch screens and solar cells, are typically sputter deposited at pressures between 0.3 Pa and 0.6 Pa [41]. Lowering the pressure for LCO deposition may increase the deposition rate and reduce gas consumption, but previous studies have shown that it could also increase the volume fraction of Co_3O_4 and concentration of lithium in excess of its stoichiometric value [2,18,21,33,34]. Nevertheless, the improvements brought about by increasing the power density may offset any deleterious effects from reducing the process pressure. This presents the possibility of fabricating thin-film LCO cathodes using conditions suited to large-scale manufacturing without significantly impairing electrochemical performance, which is the focus of this report.

2. Experimental details

2.1. Sputtering target and substrate preparation

Film deposition was performed by RF magnetron sputtering using 3” diameter LCO powder targets. The targets were produced by first drying commercial $LiCoO_2$ powder (Sigma Aldrich, 99.8%) at 80 °C inside a chamber furnace (Carbolite CSF 1200) and then lightly pressing the powder into a copper disc containing a 2 mm deep circular depression of 3” diameter with a glass microscope slide. A fresh target was prepared for each deposition.

The two substrate materials used for structural and chemical characterization experiments were 200-600 μm thick <100> oriented polished silicon wafers (various suppliers) and ~250 μm thick Waspaloy (58Ni-19Cr-14Co-Mo-Ti-Al-Fe [wt%]) foil (HAYNES® 282® alloy, Goodfellow Cambridge Ltd). The Waspaloy substrate was chosen on the basis of its high temperature stability in gas turbine engines, according to the manufacturer [42], and the success of Fillipin *et al.* [18] in using a nickel-based alloy as a current collector for thin-film LCO cathodes. These materials were cut into 10*10 mm square substrates. Additionally, circular Waspaloy substrates of 15 mm diameter were produced by laser cutting (Scitech Precision Ltd, Rutherford Appleton Laboratory, UK) to allow electrochemical testing of LCO films in coin cells. For the first experiment (50 charge-discharge cycles at a rate of 0.1 C), the native oxide layer on the Waspaloy surface was left in-situ; however, for the subsequent rate test experiment the oxide layer was removed by grinding on a series of silicon carbide papers, finishing on a 4000 grit paper. All substrates were cleaned by successive sonication in acetone, ethanol and isopropanol.

2.2. Thin film deposition and post-deposition annealing

LCO films were deposited in a magnetron sputtering system (Ion Tech Ltd) with a circular magnetron source and a target-to-substrate distance of ~6.5 cm (target-to-substrate distances reported previously for the RF magnetron sputter deposition of LCO range from ~4 cm [2] to a maximum of ~13 cm [19,33], but they are mostly between 5 and 10 cm). The base pressure immediately prior to sputtering was less than 10^{-4} Pa. Pure argon process gas (BOC Pureshield 99.998 %) was used in all depositions rather than the argon-oxygen mixtures typically used in the literature, since several reports indicate that the $Ar:O_2$ ratio has only a weak effect on film structure [2,17,23]. Targets were sputtered (with the substrates shielded) for at least 30 minutes prior to deposition to remove any surface contamination. No substrate heating was used in any of the experiments. The other key deposition conditions (process pressure, RF power density and deposition duration) were varied systematically.

The LCO films were characterized in as-deposited and annealed conditions. Annealing treatments were performed in air within a chamber furnace (Carbolite CSF 1200); the samples were placed on a bed of LCO powder within a covered alumina crucible to suppress the loss of volatile lithium by increasing the concentration of lithium in the vapour phase. The other key annealing conditions (temperature, duration and heating/cooling rate) were varied systematically along with the deposition conditions.

2.3. *Structural and chemical characterization*

The crystallographic properties of the LCO films and powder were characterized by X-ray diffraction (XRD) using copper K-alpha radiation and a θ-2θ geometry (Malvern Panalytical Empyrean). Diffraction patterns were viewed in CrystalDiffract software (CrystalMaker Software Ltd) and indexed by comparing to reference powder patterns [43–46] from the Inorganic Crystal Structure Database and patterns collected from the bare substrates. Scanning electron microscopy (SEM) was performed with a field emission microscope (Zeiss Merlin) operating at an accelerating voltage of 5-10 kV and a probe current of 1 nA. Secondary electron micrographs were used to characterize the surface and cross-sectional morphologies of the films and to make film thickness measurements at several locations. An energy-dispersive X-ray (EDX) detector (Oxford Instruments XMax 150mm^2) attached to this instrument was used to determine the O/Co atomic ratio of optimized LCO films deposited on silicon substrates by performing elemental mapping on the surface of each sample. A map resolution of 1024*1024 pixels was used with a pixel dwell time of 10 μs. AZtec® software (Oxford Instruments Nanotechnology Tools Limited) was used to analyse the X-ray spectra measured in "TruMap" scans and calculate elemental concentrations. These film samples were then dissolved in aqua regia and diluted with 2 % nitric acid to produce analyte solutions for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (PerkinElmer Optima 8000), which was used to determine the Li/Co atomic ratios. A plasma focused ion beam (PFIB) instrument (Thermo Scientific Helios G4 PFIB CXe DualBeam) with SEM column was used to mill trenches into cycled and uncycled LCO films on Waspaloy substrates and image the trench surfaces. An EDX detector (Oxford Instruments Ultim Max 170) attached to this instrument was used to measure the elemental composition across the Waspaloy-LCO interfaces on glancing trench surfaces.

2.4. Electrochemical characterization

Optimized LCO films deposited on Waspaloy were tested electrochemically in 2032 type coin cells with a lithium metal anode and liquid electrolyte (lithium hexafluorophosphate solution 746711, Merck) containing 1 M $LiPF_6$ in a 1:1 volume ratio of ethylene carbonate and dimethyl carbonate. The liquid electrolyte was absorbed by a glass fibre separator inserted between the lithium metal anode and LCO cathode. Prior to testing, the maximum attainable charge capacities were calculated using the LCO film masses determined by weighing the substrates before and after deposition and the theoretical specific capacity of $LiCoO_2$ on extracting 0.5 moles of lithium (136.9 mAh g^{-1}). After assembly, each cell was left to rest for at least 24 hours before testing to allow the open circuit voltage (OCV) to stabilize. The cycling experiments were performed using a MACCOR Series 4600A Automated Battery Test System. A galvanostatic cycling experiment consisting of 50 charge-discharge cycles between 3.0 and 4.3 V was performed at a rate of 0.1 C (charge or discharge time = 1/C-rate = 10 hours). A rate test experiment was performed on a separate set of cells and consisted of consecutive segments of galvanostatic cycling between 3.0 and 4.2 V at different C-rates (ten cycles at 0.1 C, five cycles at 0.5 C, five cycles at 1 C, five cycles at 2 C, five cycles at 5 C and a final five cycles at 0.1 C). In all cases, the currents for each C-rate were determined from the calculated maximum attainable cathode capacity values. A similar “LCO-free” coin cell was constructed with a bare Waspaloy disc on the positive side, and cyclic voltammetry (CV) was performed using a Biologic MPG-2 battery cycler to analyse the electrochemical activity of the Waspaloy. A nominal scan rate of 0.033 mV/s was used to perform five voltage scans between 3.0 V and 4.3 V vs the lithium counter electrode. All cells were held at 30 ˚C during testing.

3. Results and discussion

3.1. *Optimization of fabrication conditions for ease of processing, deposition rate and structural properties*

A set of LCO films was fabricated using the conditions in Table 1. The process pressure was less than half the levels reported in most previous studies and the power density was at the upper end of the range of values typically used (Section 1). Each of the as-deposited films was subjected to a different post-deposition annealing temperature to determine the optimum value for this set of deposition conditions.

Table 1 Initial set of deposition and post-deposition annealing conditions used in the optimization of the deposition rate and structural properties of LCO films.

Parameter	**Value**
Substrate	Waspaloy foil
Process pressure	0.5 Pa
RF power density	4.4 W cm^{-2}
Deposition duration	2.5 hours
Annealing temperatures	300 ˚C, 400 ˚C, 500 ˚C, 600 ˚C and 700 ˚C
Time at annealing temperature	1 hour
Heating rate	10 ˚C/min
Cooling rate	Uncontrolled slow cooling inside furnace
Annealing atmosphere	On LCO powder bed in air

The as-deposited film thickness measured using SEM was 1.1-1.3 µm, which means that the average deposition rate was 430-500 nm h^{-1} (reported deposition rates range from ~10 nm h^{-1}

to over 1000 nm h^{-1} [18,21]). Figures 1 a) and 2 show typical XRD patterns and SEM micrographs, respectively, corresponding to these samples. In agreement with several previous studies [19,21,28,32,35,37,47] the as-deposited film possessed some nanoscale crystallinity, as evidenced by the single broad peak at $2\theta \sim 44.8$ ˚. This peak is at a slightly lower angle than the HT-LCO (104) peak in the powder pattern ($2\theta \sim 45.2$ ˚, Figure 1 b)), which could be due to increased unit cell dimensions resulting from structural disruption, as has been reported elsewhere [2]. After annealing at 500 °C, this peak is narrower, more intense, and at a higher angle of $2\theta = 45.3$ ˚, suggesting a transformation to a well-crystallized HT-LCO structure. Furthermore, annealing at 500 ˚C or 600 ˚C caused (101) and (110) reflections to appear, which correspond to favourable orientations for lithium intercalation.

Several features detrimental to cathode performance were evident in the XRD pattern from the film annealed at 700 ˚C. The presence of a (003) peak with high relative intensity compared to the powder pattern indicates that a large proportion of the film grains were unfavourably oriented for lithium intercalation. Furthermore, several peaks corresponding to the electrochemically inactive Co_3O_4 phase are present (signifying the occurrence of lithium loss during annealing at this temperature) while the favourable (110) reflection, which was present after annealing at 500 ˚C and 600 ˚C, is absent. There are also additional substrate peaks at $2\theta \sim 43.3$ ˚ and $2\theta \sim 62.9$ ˚, which may reflect the growth of the native oxide layer on the Waspaloy. In terms of structural properties, the optimum annealing temperature out of those tested is 600 °C.

The area of the as-deposited film surface shown in Figure 2 contained a region of undulating relief. These regions were found to cover only a small fraction of the sample surface and may have been due to local inhomogeneities on the Waspaloy substrates. The microstructure coarsened significantly during annealing at 600 ˚C; however, the large (~500 nm) grains appear to have nucleated at the surface and their coverage was incomplete. This may explain the mostly low X-ray intensities of the film peaks in Figure 1 a).

Several changes were made to the fabrication conditions to improve the structural properties. This new set of conditions is shown in Table 2. The RF power density and annealing duration were both increased to promote crystallization and grain growth; the deposition duration was also increased to encourage the parallel alignment of (104) and (101) planes with the film surface, since these orientations have been reported to reduce the bulk strain energy in thicker films [10,22]. Another key benefit of thicker cathode films is their higher theoretical charge capacities.

Table 2 Refined deposition and post-deposition annealing conditions used in the optimization of the deposition rate and structural properties of LCO films.

Parameter	**Value**
Substrate	Waspaloy foil
Process pressure	0.5 Pa
RF power density	5.5 W cm^{-2}
Deposition duration	4 hours
Annealing temperature	600 ˚C
Time at annealing temperature	2 hours
Heating rate	10 ˚C/min
Cooling rate	Uncontrolled slow cooling inside furnace
Annealing atmosphere	On LCO powder bed in air

The as-deposited film thickness measured using SEM was 2.8-3.2 µm, which means that the average deposition rate was 700-790 nm h^{-1}. The average deposition rate thus increased by ~60 % for a 25 % increase in the power density. It is not clear why the fractional increase of the deposition rate was signifcantly higher than that of the power density.

Figure 3 shows typical XRD patterns collected from the as-deposited films and those annealed at 600 ˚C for 2 hours. Corresponding patterns from the films processed using the conditions in Table 1 are also presented for comparison. Moving from the processing conditions in Table 1 to those in Table 2 resulted in a significantly greater (104) peak intensity relative to the other reflections. A combination of factors would have been responsible for this, including a rise in the proportion of grains with (104) planes aligned with the film surface and an increase in crystallinity. Although the unfavourable (003) peak appeared, the intensity ratio of (104) to (003) is over 40 times higher than in the powder pattern, indicating the presence of a strong (104) film texture. It is noteworthy that the absence of oxygen in the process gas did not preclude the formation of the desired film structure, which challenges the belief sometimes expressed that a mixed argon-oxygen process gas is required to develop the desired LCO phase and crystallographic texture [2,3]. This has positive implications for industry, as the deposition process is simplified and raw materials costs are reduced by using argon alone.

Figure 4 shows surface and cross-sectional SEM micrographs of as-deposited and annealed films processed using the conditions in Table 2. The as-deposited film had a columnar structure like the previous as-deposited films, which is consistent with the high degree of crystallographic alignment seen in the XRD patterns in Figure 3. During annealing for 2 hours significant coarsening occurred, and the coalescence of columns (some evidence for which is seen in the cross-sectional view) led to an apparent increase in film surface density. Coarsening and coalescence of columns should increase the areas of the high conductivity transport paths, improving cathode performance. It is possible that the driving force for coalescence (grain growth) was greater than that for the nucleation of new surface grains, which would explain why facetted, equiaxed grains like those seen on the previous annealed film (Figure 2) did not appear. This lack of recrystallization at the film surface preserved the high degree of (104) plane alignment seen in the XRD patterns.

Most literature studies have sought to fabricate LCO films with a high degree of parallel alignment between the (104) or (101) planes and the film surface. The films deposited and annealed using the conditions in Table 2 demonstrated the highest degree of alignment. Furthermore, these conditions resulted in the highest deposition rate. The approximate chemical compositions of films fabricated using these conditions on silicon substrates (Table 3) were determined using ICP-OES and EDX analysis. The as-deposited film was deficient in lithium and showed a slight oxygen deficiency. Surprisingly, the lithium content increased after annealing, which demonstrates the benefit of using an LCO powder bed in the annealing process. Although annealing caused the oxygen content to decrease, the films fabricated on Waspaloy substrates had a stable $R\overline{3}m$ structure (Figure 3). This bodes well for the application of these LCO thin films as cathodes in lithium cells.

Table 3 Approximate compositions of as-deposited and annealed LCO thin films fabricated on <100> silicon wafer substrates using the conditions in Table 2. The Li/Co and O/Co atomic ratios were determined by ICP-OES and EDX analysis, respectively.

Sample	**Overall Composition**
As-deposited	$Li_{0.59}CoO_{1.89}$
Annealed	$Li_{0.76}CoO_{1.74}$

3.2. Characterization of electrochemical performance

The conditions in Table 2 were used to produce thin-film LCO cathodes for electrochemical characterization in coin cells. Figure 5 shows the results of galvanostatic cycling at a rate of

0.1 C between 3.0 V and 4.3 V vs (Li^+/Li) for 50 cycles. Key cathode performance figures are presented in Table 4. Most of the charging curves in part a) of Figure 5 display a "near-plateau" close to 3.9 V, as expected for LCO crystallized in the $R\bar{3}m$ structure. The maximum specific discharge capacity reported here is only slightly lower than the highest published value of 67 μAh $cm^{-2}μm^{-1}$ reported by Tintignac *et al.* [34] for a bias sputtered and annealed LCO film cycled at a rate of 0.2 C. While the discharge capacity loss per cycle achieved by these authors (~0.2 %) was somewhat lower than that reported here, the retention of 70 % of the maximum discharge capacity after 50 cycles compares favourably to most other reports for LCO thin films cycled in organic liquid electrolytes [2,21,25,28,29,35]. It is also noteable that Tintignac *et al.* studied films that were only 500 nm thick, and capacity fading has been found to be more rapid in thicker films like those studied here [7]. Moreover, the maximum areal discharge capacity reported by these authors (33.5 μAh cm^{-2}) is significantly lower than that achieved here (172 μAh cm^{-2}). The discrepancy between the maximum discharge capacity normalized by mass and by film dimensions as percentages of the theoretical values can partly be attributed to the significant error bars expected in the measurements of cathode mass, thickness and area. However, it is not surprising that the capacities normalized by film dimensions are proportionally lower than those normalized by mass, since the actual film density must be lower than the theoretical density of LCO. The causes of reduced density include the presence of some internal porosity and a small amount of film exfoliation in certain regions.

Table 4 Key performance figures for the LCO thin-film cathodes.

Film mass (with standard error)[a]	(2.3 ± 0.1) mg
Film thickness (with standard error)[b]	(2.77 ± 0.02) μm

Current to achieve 0.1 C cycling rate	31 μA
Maximum discharge capacity	304 μAh (6^{th} cycle)
Maximum areal discharge capacity[c]	172 μAh cm^{-2}
Maximum specific discharge capacities (% of theoretical for 0.5Li extracted)[d]	132 mAh g^{-1} (96 %) 62 μAh $cm^{-2}$$\mu m^{-1}$ (90 %)
50^{th} cycle specific discharge capacities[d]	92 mAh g^{-1} 43 μAh $cm^{-2}$$\mu m^{-1}$
Percentage of maximum discharge capacity remaining in the 50^{th} cycle	70 %
Average discharge capacity decrease from maximum per cycle	0.69 %

[a]Mass measurements were made on the as-deposited film since the Waspaloy substrate underwent a mass gain during annealing that could not be determined reliably.

[b]The thickness is the mean value of five measurements made on other LCO films fabricated in the same deposition.

[c]The area of the cathode was assumed to be equal to the area of the Waspaloy substrate.

[d]LCO film thickness and mass measurements were used to normalize the absolute capacity values.

Although the overall cycling performance is encouraging, certain aspects were less favourable and require examination. The first cycle charging curve in Figure 5 a) shows that the initial charge capacity was anomalously high (634 mAh g^{-1}, normalized by cathode mass), while the plot of capacity versus cycles in part b) suggests that the subsequent four cycles were erratic: zero discharge and charge capacities were recorded in cycles 3 and 4, respectively, and the maximum discharge capacity was not reached until the 6^{th} cycle.

Furthermore, the charge capacity remained significantly above the discharge capacity during the early stages of cycling, and the coulombic efficiency only rose above 95 % after the 13th cycle. After this point in the cycling, the charge and discharge capacities were similar and proceeded to diminish at approximately the same rate. The plot of $\delta Q/\delta V$ vs V for these data (Figure 6) shows peaks at ~3.9 V on charging and discharging. The separation between these peaks increases with cycle number, indicating an increase in the internal resistance of the cell over cycling. There is an additional peak on charging in the first cycle between 3.9 and 4.0 V, which accounts for some of the very high first-cycle charge capacity.

It is usual for the charge capacity to be significantly higher in the first cycle than in subsequent cycles, since charge is consumed in the reduction of electrolyte at the lithium metal anode, forming a passivating solid electrolyte interphase layer. However, this explanation is unlikely to account fully for the behaviour seen here. One possibility is that the excess charge capacity was provided by oxidation of the Waspaloy substrate, occurring most rapidly at the beginning of cycling and diminishing as the surface became passivated by the growing oxide layer. Fragnaud *et al.* [30] noticed a rapid drop in capacity and an increase in impedance during the early stages of cycling an LCO thin-film cathode deposited on aluminium. The authors proposed that this behaviour was due to the oxidation of the aluminium substrate by reaction with delithiated CoO_2, which in turn was reduced to electrochemically inactive Co_3O_4. They attributed the observed capacity drop to the loss of active material in this reaction. An explanation along these lines does not fit the behaviour seen here: the charge capacity fell from an abnormally high level to a more normal level over the first few cycles, which is more indicative of a diminishing excess charge current due to Waspaloy oxidation and passivation than of active material loss. This is also a reasonable explanation for the erratic behaviour near the beginning of cycling, since the growth of the oxide layer could have created spikes in impedance such that the upper and lower voltage limits were reached almost instantaneously without any detectable charge transfer through the cell. Subsequent lithiation of the oxide layer may have reduced the impedance and allowed charge transfer to resume. To understand the contribution of the Waspaloy substrate to the overall electrochemical properties, the Waspaloy-LCO interface was studied further.

Figure 7 shows the results of cyclic voltammetry (CV) on a bare Waspaloy disc that had been annealed using the conditions in Table 2 and placed in a coin cell with lithium metal on the negative side and the same liquid electrolyte as used previously. The experiment consisted of five scans performed between 3.0 V and 4.3 V vs (Li^+/Li) at a nominal scan rate of 0.033 mV/s. Immediately after assembling the cell, the OCV was found to be ~0 V; however, the cell was left for 13 days before starting the CV tests, by which time the OCV had risen to 2.57 V, as seen at the beginning of the first forward voltage scan in Figure 7. This increase in the OCV suggests that a reaction occurred between the Waspaloy and the electrolyte, and that the reaction product had a potential of ~2.6 V vs (Li^+/Li).

The CV results show that on the first forward scan the oxidation current started to increase rapidly once the voltage had passed 3.4 V, reaching an initial peak at 3.94 V before dropping slightly and then rising again to the maximum value of 5.44 μA between 4.24 V and 4.26 V. On the reverse scan the current dropped rapidly from its maximum value, reached a small peak around 3.8 V, then continued to fall. It became negative below 3.47 V and levelled off at a maximum reduction current of 0.18 μA (only 3.4 % of the maximum oxidation current). The peak at 3.94 V may correspond to the peak seen between 3.9 V and 4.0 V in the first cycle on the differential capacity plot for the cycling of the LCO cathode (Figure 6), which suggests that Waspaloy oxidation was responsible for this peak and hence a significant proportion of the excess first cycle charge capacity. The current measured over most of the scan range was significantly lower in the second scan (the highest value was 2.81 μA) and continued to drop in subsequent scans, but by smaller amounts each time. This shows that the Waspaloy oxidized at the highest rate in the first scan, forming a passivating layer that significantly decreased the oxidation current in subsequent scans. Thus, the CV data confirm that the Waspaloy substrate oxidizes in the voltage range used for galvanostatic cycling and that the oxide formed provides protection against further oxidation, which explains the gradual improvement in coulombic efficiency seen in the early stages of cycling in Figure 5 b). It is also significant that after the first CV scan, subsequent scans show peaks in oxidation current around 4.3 V. This suggests that oxidation of the Waspaloy accelerates near the upper potential limit and continues through the early stages of cycling. This progressive growth of the Waspaloy layer may be partly responsible for the increase in internal resistance of the cell over cycling.

To improve the cycling performance, the upper voltage limit was decreased to 4.2 V for the rate test experiments, the results of which are shown in Figure 8. Additionally, the native oxide layer on the Waspaloy was removed by grinding prior to LCO film deposition to see whether the oxidation of the Waspaloy would be slower and steadier if less oxide were present on the substrate at the start of cycling. An upper limit of 4.2 V for LCO cycling is more commonly reported than the 4.3 V limit used in the previous experiment, but it does come at the cost of a small reduction in maximum discharge capacity (117 mAh g^{-1} compared to 132 mAh g^{-1} in the previous cycling experiment). It is noteworthy that this maximum discharge capacity was attained in the first cycle at 0.1 C in this experiment, whereas in the previous experiment the maximum discharge capacity was not reached until the sixth cycle due to the erratic early cycling behaviour. The initial cycling at 0.1 C (calculated from the film mass of (2.1$\pm$0.2) mg and corresponding to a current of 29 μA) was much less erratic than seen in the previous experiment: the initial charge capacity was significantly closer to the initial discharge capacity, and the coulombic efficiency rose to 96 % in the second cycle. The differential capacity plot (Figure 9) of the data in Figure 8 a) does not show a peak between 3.9 V and 4.0 V during the initial cycling at 0.1 C, which suggests that removing the native oxide layer from the Waspaloy substrate significantly limited further substrate oxidation during cycling. Despite this, the average discharge capacity decrease from the maximum per cycle during the first 10 cycles was 0.63 %, which is very similar to the value achieved in the previous cycling experiment and may indicate that the capacity loss is principally due to structural changes within the LCO layer rather than impedance growth due to Waspaloy oxidation.

As expected, the discharge capacity extracted from the cell decreased notably with each increase in the cycling rate. However, reasonable performance was still achieved at a rate of 0.5 C: the discharge capacity of the 11th cycle was 98 mAh g^{-1} (83 % of the maximum discharge capacity) and the average rate of capacity decrease from this value per cycle was not significantly higher at 0.88 % over the 5 cycles. Even at a rate of 1 C, a discharge capacity of 78 mAh g^{-1} was achieved in the sixteenth cycle, which is 67 % of the maximum discharge capacity, although the average capacity decrease per cycle was somewhat higher at 2.4 % over the five cycles. The cell still displayed some discharge capacity at a rate of 2 C (41 mAh g^{-1} in the 21st cycle), but the average capacity decrease per cycle increased significantly to 4.9 % over the 5 cycles. At a rate of 5 C, almost no charge could be inserted into or extracted from the cell, and the discharge capacity was <1 mAh g^{-1} for each of the five cycles. It is significant that on decreasing the cycling rate to 0.l C for the final five cycles of the experiment, the discharge capacity increased to approximately the level that would have been expected from an extrapolation of the trend set by the initial ten cycles at 0.1 C and roughly followed the trendline to the end of the experiment. It is also significant that the overall average capacity fade per cycle was only 0.39 %, which is much lower than the value for the first ten cycles. This indicates that very little structural degradation of the cell was induced by the segments of high-rate cycling, further supported by the high values of coulombic efficiency seen at most stages of the experiment. The differential capacity plot (Figure 9) shows increasing separation of the single oxidation and reduction peaks with increasing cycling current and no additional peaks present on the plots, suggesting that most of the decrease in capacity was due to polarization by the internal resistance of the cell and was thus temporary. The fact that the peaks for the 35th cycle have a greater separation than those for the 10th cycle shows there was some permanent structural degradation within the cell that led to an increased internal resistance. Nevertheless, the retention of 86 % of the maximum capacity after 35 cycles, despite the periods of high-rate cycling, is a promising result and shows that this cell design is capable of providing high current bursts with little or no additional structural degradation as a consequence.

3.3. Structural and chemical characterization of the Waspaloy-LCO interface

The Waspaloy-LCO interface in the cell cycled at 0.1 C for 50 cycles was observed directly by milling trenches into cycled and uncycled film samples using a PFIB followed by SEM and EDX characterization of glancing trench surfaces. Figure 10 shows secondary electron SEM images and EDX line scans across the layers of a) an uncycled sample and b) the sample cycled at 0.1 C for 50 cycles (Figure 5). A platinum layer was deposited before milling to protect the surface of the LCO film from damage by xenon ion irradiation.

The apparent difference in LCO film thickness between the samples may be explained by the different local deposition rates that the substrates experienced, since they were mounted at different lateral positions with respect to the target even though the vertical displacement was constant. In both samples, the compositions measured at the centres of each layer are very similar, and the LCO film shows an O/Co ratio of ~2, as expected. Furthermore, the SEM images suggest that the LCO films were well-bonded to the Waspaloy substrates before and after cycling, which is essential for optimal cathode performance. The EDX line scans of the uncycled samples in a) indicate that elemental diffusion between the Waspaloy and LCO layers during annealing was marginal, although some nickel diffusion into the LCO layer may have occurred. Small peaks in the titanium and aluminium concentrations are present in the Waspaloy-LCO interfacial region. Along with chromium, these elements are known to form oxides on the surface of Waspaloy, providing it with protection from corrosion in extreme environments [48]. This layer may have helped to limit the interdiffusion of elements between the Waspaloy and LCO layers during annealing, minimizing any negative impact on the electrochemical performance. Several of the element concentration profiles across the Waspaloy-LCO interface are somewhat different in the cycled sample, as shown in Figure 10 b). The key difference is the greater width of the interface region, indicated by the shoulders in the nickel and oxygen profiles, a significantly higher aluminium peak and a slightly higher titanium peak. The SEM images also appear to show a thicker Waspaloy-LCO interfacial region in the cycled sample. Furthermore, this region is rougher than that in the uncycled sample. These observations indicate that the oxide layer on the surface of the Waspaloy grew during cell cycling, supporting the interpretation of the galvanostatic cycling and CV data.

While the removal of the native oxide layer prior to cell fabrication appeared to improve the performance in the early stages of cycling, the overall performances of both sets of cells compare favourably to previous reports. For example, most studies report the fabrication of significantly thinner LCO films, which have much lower areal capacities [17,19, 22–26,28,33,34,36,49]. In terms of fabrication conditions, mixed argon-oxygen process gases at high pressures, costly Pt/Au-coated substrates with heating or a potential bias applied during deposition and longer, higher temperature, or more complex post-deposition annealing processes are frequently reported [21,34–36]. Thus, the fabrication, structural, and electrochemical properties reported here for LCO thin films prepared by a rather simple process are very promising.

4. Conclusions

Thin films of $LiCoO_2$ were fabricated under conditions chosen to achieve an optimal balance between manufacturability and cathode performance. The use of a pure argon process gas, unsintered sputtering target, lower process pressure (0.5 Pa), and higher power density (5.5 W cm^{-2}) than commonly used in the literature reduced materials costs, simplified the processing and increased the deposition rate by a factor of around four. Further, these processing conditions resulted in LCO films with structural and electrochemical properties that compare favourably with the best results reported elsewhere, challenging a number of widely-held assumptions regarding optimum processing conditions for LCO thin films. The use of Waspaloy substrates – previously uninvestigated for LCO – allowed the development of these desirable structural properties, in particular a high degree of parallel alignment of the (104) planes with the film surface and volume fractions of deleterious secondary phases such as Co_3O_4 so low as to be undetectable by XRD. The maximum specific and areal discharge capacities of 132 mAh g^{-1} / 62 μAh $cm^{-2}μm^{-1}$ and 172 μAh cm^{-2} measured for cycling at 0.1

C are among the best values reported, and can be attributed to the good structural properties of the LCO film and its interface with the Waspaloy current collector over the majority of the cycling experiment. The poor initial cycling performance in the first cycling experiment was attributed to oxidation of the Waspaloy substrate, which occurred at a high rate until the oxide layer passivated the surface. Nevertheless, the discharge capacity retained after 50 cycles (70% of the maximum value) is comparable with most values reported for LCO thin films cycled in organic liquid electrolytes. Cycling stability and efficiency were greatly improved by removing the native oxide layer from the Waspaloy substrate prior to LCO deposition and reducing the upper cycling cutoff voltage from 4.3 V to 4.2 V; this avoided rapid passivation of the substrate and reduced the rate of structural degradation of the LCO film. Although this led to a lower maximum discharge capacity (117 mAh g^{-1}), the average discharge capacity loss per cycle from the maximum value was reduced significantly to 0.39 % over 35 cycles, even though the cycling included segments performed at C-rates of up to 5 C. Furthermore, the cells were found to demonstrate reasonable cycling performance up to a rate of 1 C and were capable of providing short bursts of current at a rate of 2 C, which may prove useful in certain applications. Future studies may look at applying the approach used here to production line sputtering equipment and further optimizing the processing parameters to achieve a low-cost, high productivity manufacturing process. An important parameter that has not received sufficient attention thus far is the target to substrate distance, which must be carefully optimized in manufacturing processes to achieve the best balance between deposition rate and film uniformity.

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Figure Captions

Figure 1 a) Typical XRD patterns from as-deposited and annealed LCO films fabricated using an initial set of conditions chosen to optimize the deposition rate and structural properties (Table 1). HT-LCO and substrate peak labels are abbreviated to 'HT' and 'S' respectively. b) XRD pattern of the LCO powder used to produce the LCO targets.

Figure 2 Surface and cross-sectional secondary electron micrographs of as-deposited and 600 ˚C annealed LCO films fabricated using an initial set of conditions chosen to optimize the deposition rate and structural properties (Table 1). The blue arrows on the cross-sectional micrographs point to the top surfaces of the films. Detachment of the films from the substrate occurred during sectioning for cross-sectional characterization due to deformation of the metallic Waspaloy.

Figure 3 Typical XRD patterns from as-deposited and 600 ˚C annealed LCO films fabricated using conditions chosen to optimize the deposition rate and structural properties. '1st' refers to the initial set of conditions (Table 1), while '2nd' refers to the second, improved set of conditions (Table 2). HT-LCO and substrate peak labels are abbreviated to 'HT' and 'S' respectively.

Figure 4 Surface and cross-sectional secondary electron micrographs of as-deposited and 600 ˚C annealed LCO films fabricated using the second, improved set of conditions chosen to optimize the deposition rate and structural properties (Table 2). The blue arrows on the cross-sectional micrographs point to the top surfaces of the films. Detachment of the films from the substrate occurred during sectioning for cross-sectional characterization due to deformation of the metallic Waspaloy.

Figure 5 Charge-discharge cycling performance of a cell with an LCO thin-film cathode fabricated using the conditions in Table 2 and cycled between 3.0 and 4.3 V vs (Li^+/Li). Cycling was performed at a constant current corresponding to an initial C-rate of ~0.1 C. a) Charge-discharge curves recorded at several different stages of the cycling experiment; b) plot showing the charge and discharge capacities and the coulombic efficiency over the course of the cycling experiment. The anomalously large first cycle charge capacity has been removed to allow for the use of a more appropriate scale.

Figure 6 Differential capacity plots calculated for the cell fabricated with the native oxide layer left *in situ* on the Waspaloy substrate and tested at 0.l C for 50 cycles (Figure 5).

Figure 7 CV plots for bare Waspaloy annealed using the conditions in Table 2 and tested between 3.0 V and 4.3 V vs (Li^+/Li) at a nominal scan rate of 0.033 mV s^{-1}.

Figure 8 Charge-discharge cycling performance of a cell with an LCO thin-film cathode fabricated using the conditions in Table 2 and cycled between 3.0 and 4.2 V vs (Li^+/Li) at a series of different currents corresponding to C-rates of 0.1 C, 0.5 C, 1 C, 2 C and 5 C (calculated from the theoretical capacity). The native oxide layer was removed from the Waspaloy discs prior to LCO deposition. a) Charge-discharge curves recorded at several different stages of the experiment; b) plot showing the charge and discharge capacities and the coulombic efficiency over the course of the experiment. A blue curve has been drawn to extrapolate the trend set by the first 10 cycles at 0.1 C to the end of the experiment.

Figure 9 Differential capacity plots calculated for the cell fabricated after the native oxide layer had been removed from the Waspaloy substrate. The cell was tested at a series of different cycling rates from 0.1 C to 5 C (Figure 8).

Figure 10 Secondary electron micrographs of the glancing trench surface produced by PFIB sectioning and the results of EDX line scans performed across this surface for **a)** an uncycled LCO thin film fabricated using the conditions in Table 2 and **b)** the LCO film cycled at 0.1 C for 50 cycles (Figure 5 and Table 4). The Pt layer was deposited prior to sectioning to protect the top sample layer (the LCO film) from xenon ion irradiation. As EDX is unable to detect lithium, the atomic concentrations of each element plotted do not account for the presence of lithium in the samples.