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Optimization of 10-μm, sputtered, $LiCoO_2$ cathodes to enable higher energy density solid state batteries

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HIGHLIGHTS

- Developing a process for Li-anode solid state batteries with E_V~750 W-h-L^{-1}.
- Optimization of texture for >5 μm $LiCoO_2$ cathodes.
- Assessment of particle defects on yield of working cells.

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ABSTRACT

An investigation of the morphology of lithium-cobalt-oxide (LCO) films for the production of energy dense, solid-state, thin-film batteries with cathodes in the 10 μm thickness range is described. It was found that, in order to achieve devices with over 80% charge utilization, capable of extended cycling, with cathodes greater than 5 μm, LCO film texture must be actively controlled to maintain orientations preferential to Li diffusion. It was found that the oxygen: argon ratio during sputtering of the cathode plays a critical role in determining the crystallographic texture of LCO films thicker than 5 μm. Specifically, LCO films deposited with an oxygen presence of as little as 4% in Ar showed no detectable (003) peak following anneal. Working cells were fabricated using texture-controlled 10 μm cathodes, exhibiting discharge capacities of 60 μAh/cm^2-μm (600 μAh/cm^2) at C/10, with greater than 95% capacity retention after 100 cycles at a C/5 discharge rate. Cells with 10 μm cathodes and un-controlled (predominantly (003)) texture were capable of achieving similar capacities, however their rate and cycling performance were severely diminished.

1. Introduction

Solid state Li batteries (SSB) offer outstanding volumetric energy density, safety, and cycle performance, relative to conventional liquid-electrolyte based technologies [1–3]. Currently, SSBs are only considered for micro-power applications, i.e. on board chips powering small devices in the μWhr to mWhr range. However, due to recent safety concerns regarding conventional liquid-electrolyte cells in portable electronics [4] there is an excellent case to be made for SSB use in wearable technology, or small device applications (including communications) in the 100 mWhr to 1 Whr range. SSBs offer the following advantages:

1) Due to the absence of a liquid electrolyte, metallic Li anodes can be used without the problems associated with dendrite formation in conventional Li ion cells, thus allowing a higher open cell voltage to be achieved, relative to traditional carbon anodes.
2) There are no side reactions that consume active Li or degrade active materials, and cathode materials that are not feasible in a conventional Li ion cell can be explored (e.g. Ni oxide).
3) Because the cathode and anode are solids, the cell does not fail by decrepitation, and reported results of cells with $>10^4$ cycles with virtually no capacity loss are common [2].
4) Thin film-based LCO cathodes provide potential for higher energy density, from a cathode mass density perspective, relative to LCO particle cathodes, which adhere to particle packing limitations.

One of the more commonly used materials in the solid-state

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battery field is lithium-phosphorous-oxy-nitride (lipon), which has received considerable attention as a candidate for a scalable solid-state electrolyte [5–8]. When integrated with a lithium-cobalt-oxide (LCO) cathode and metallic lithium (Li) anode, lipon -based solid-state batteries can achieve cathode capacities >60 μAhr/μm-cm^2 on discharge [9–11]. However, most reported data is based on relatively thin (<5 μm) single-sided cells. In order for SSBs to increase to the 1 Whr range while maintaining a form factor amenable to mobile/wearable electronics (<20 cm^2), cathode thicknesses approaching 10 μm must be implemented to meet the necessary energy density requirements. For instance, a realistic cost competitive model –assuming a LCO cathode with >80% utilization-involves transitioning to a cell with a form factor of ~10 μm × 10 cm^2, with a battery consisting of ~25 double-sided cells (~10 mAhr per substrate) connected in parallel to give ~ 1 Whr of energy. However, at the time of this publication -to our knowledge-no reports have been issued showing successful cycling of solid-state cells with LCO cathodes in the 10 μm thickness range. Recent reports by Kutbee et al. have demonstrated successful cycling of LCO/LiPON based devices with cathode thicknesses of approximately 6.5 μm, however, these devices were demonstrated on device areas <4 mm^2, and were only capable of achieving cathode utilizations below 40% [12]. One of the primary issues preventing high coulombic efficiency in thick cathodes is the longer diffusion pathways for Li during charge/discharge, which also presents challenges in achieving stable rate performance. Subsequently, in addition to particle mitigation, film uniformity, and film stress concerns, we have found that LCO texture control is essential to maintaining device performance at cathode thicknesses beyond 6 μm. Several other reports have shown development of favorable texture beyond LCO thicknesses of 1 μm, however these reports have only encompassed thicknesses below 5 μm, and typically involve relatively low deposition rate (<1 Å/sec) RF sputtering or pulsed-laser deposition techniques [13–15]. This work will demonstrates a relatively higher deposition rate, pulsed-DC method of cathode deposition capable of achieving stable, high capacity, solid-state cells with cathode thicknesses of 10 μm, by introducing process conditions that promote favorable cathode texturing.

2. Experimental procedure

2.1. LCO deposition

All cell stacks consisted of a 10 μm LCO/2 μm lipon/5 μm Li arrangement, and were deposited on 150 μm thick CoorsTek alumina substrates. Prior to current collector deposition, bare alumina substrates were sonicated in an IPA bath for 15 min. Following sonication, the substrates receive an evaporated film stack of 100 nm of Au on a 10 nm Ti adhesion layer, through a custom shadow mask geometry designed by Intermolecular, Inc. (IMI). LCO deposition was performed using pulsed-DC sputtering in a Semicore SC943 in-line sputtering tool. LCO targets were provided by Umicore. Target geometry consisted of three $LiCoO_2$ tiles, comprising a total target area of 5 inches by 17.5 inches. LCO tiles were hot pressed from a powder source material, to produce a $LiCoO_2$ composition of 99.999% purity with an average grain size of 5 μm, and density of 4.9 g/cm^3.

Sputtering gas during LCO deposition consisted of an Ar or Ar + O_2 mixture, with total flow rate controlled to 50 sccm, and a working pressure of 5 mTorr. Sputtering power was maintained at 1500 Watts (~2.75 W/cm^2). Target to substrate spacing was fixed at 38 mm. For the LCO studies outlined below, the deposition rate was varied between 2.9 Å/sec–3.7 Å/sec. No active substrate heating was employed, however, a customized in-situ temperature probe was utilized to determine the evolution of temperature throughout LCO deposition. For the outlined conditions, substrate temp reached a maximum steady state value of approximately 110 °C. After LCO deposition, samples were sonicated in IPA bath for 5 min to remove particles, and subsequently annealed in air for 1 h at 800 °C in a box furnace. The anneal temperature was ramped from room temperature to 800 °C, at 5 °C per minute. Passive cooling down to 300 °C was followed by active cooling by opening the furnace door until the substrates were cooled to room temperature.

2.2. Lipon deposition

Following LCO deposition, lipon was deposited in a separate, custom-designed, IMI P-30 sputtering system with three independent Li_3PO_4 targets, sputtering simultaneously. Li_3PO_4 targets were 2 inches in diameter, 0.25 inches thick, and also supplied by Umicore. Targets were hot pressed from powder source material, to produce a Li_3PO_4 composition of 99.9% purity with a density of 2.35 g/cm^3. Sputtering gas during lipon deposition consisted of 80% N_2 in Ar, with total flow rate controlled to 40 sccm, at a working pressure of 5 mTorr. Sputtering power was maintained at 200 Watts per target (~1.2 W/cm^2). Target to substrate spacing was set to 75 mm, and total lipon deposition rate was 0.7 Å/sec. All samples were deposited at room temperature.

For all devices, lipon thickness was targeted at 1.5–2 μm, in order to ensure sufficient uniformity without “pinhole” features, and maintain sufficient cell yield, as devices with relatively thinner lipon layers showed increased shorting behavior. Prior to use in devices, lipon composition was characterized by XPS analysis of 2 μm films deposited on SiO_2. According to XPS, films consisted of roughly 6% at. N, 13% at. P, 38% at. Li, and 43% at. O, giving an N/P ratio of approximately 0.5. Fig. 1 a) shows the XPS core level N1s spectra, showing nitrogen bonding to consist roughly of 30% triple-coordinated (>N-) bonding states. Transport quality of lipon films was characterized by impedance analysis on devices structures consisting of Au/lipon/Au deposited on boro-silicate glass. The active area for each device was 1 cm^2, with a 2 μm lipon thickness. Fig. 1 b) shows the resulting Bode response, from which ionic conductivity of the lipon was calculated to be approximately 3E-6 S/cm. Impedance spectroscopy was measured with an Ametek Parstat 4000 A.

2.3. Li deposition and final cell assembly

The Li anode was evaporated from a tantalum crucible, in a cryo-pumped chamber, located within an Ar-filled glove box. Li films were 5 μm in thickness, deposited at roughly 25 Å/sec. A Li anode thickness of 5 μm of lithium was chosen based on considerations of both uniformity and first cycle loss considerations. Following anode deposition, each alumina substrate consisted of 10 independent SSB devices. The active area of each cell was 1 cm^2, as dictated by LCO footprint, with total active cell volume calculated using profilometry on 10 witness cells per cathode run. Fig. 2 shows a picture of a typical multi-cell substrate. Electrical contact for device testing was established through soldered connections to the device perimeter. In order to achieve a stable connection, copper pads were deposited by e-beam evaporation, prior to lithium deposition, to provide soldering points for testing leads. Testing of cell arrays was either carried out in an Ar-filled glovebox (MBraun), or devices were packaged in the glove box, sealed in a tri-layer pouch, and tested in ambient conditions. All cell testing was performed on an Arbin Instruments 40 channel tester. It was observed that the open circuit voltage (V_{OC}) of the cell (once the Li anode was deposited) was an effective screening criteria. It was found, and was related by other workers in the field, that an open circuit voltage (V_{OC}) of >1.5 V ensured that a cell would cycle at least 5 cycles with normal behavior, enough to evaluate steady state capacity and impedance. Cells meeting this V_{OC} criteria advanced to receive rate-testing and