Thin Solid Films 661 (2018) 46–52

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Characterization of low-temperature solution-processed $LiCoO_2$ thin-film cathode with molecular weight control of polyvinylpyrrolidone

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ARTICLE INFO

Keywords:
Lithium cobalt oxide
Thin film
Nanoparticles
Solution process
Solid-state thin film battery

ABSTRACT

Numerous $LiCoO_2$ cathode thin-films have been prepared for all-solid-state thin-film battery applications. Preparation methods include sputtering, pulsed laser deposition, electron beam evaporation, screen printing, and spin coating. When compared to vacuum deposition methods, the solution-processed fabrication methods could result in significant cost savings and large-area production. Unfortunately, high-temperature annealing ($T_{anneal} > 700\,^{\circ}C$) of $LiCoO_2$ cathode thin film is usually crucial for achieving a high performance layered phase. Here, we report on phase control of spin-coated $LiCoO_2$ thin film by varying the molecular weight of polyvinylpyrrolidone (PVP) at low temperature. We could achieve thick and smooth film morphology by optimizing the PVP molecular weight. This method could be a promising cathode layer for low-cost thin-film batteries.

1. Introduction

Rechargeable lithium ion batteries have been used in a wide variety of electronic applications, including handheld devices and electric vehicles. In recent years, human-friendly flexible or stretchable micro-thin-film batteries have been attracting much attention due to their potential applications as next generation power sources. Electronic applications include flexible and wearable electronic devices, implantable health care applications, and ubiquitous sensor arrays [1–6]. Compared to conventional lithium ion batteries with thick active layers and flammable liquid electrolytes, all-solid-state thin-film batteries (TFBs) with solid-electrolyte films have many advantages such as a long cycle life, mechanical flexibility, capability of integration with large area electronics, and excellent explosion safety [7–10]. For high performance all-solid-state TFBs, research on materials and processing for cathode films is of great importance. There have been intense investigations into thin-film deposition of cathode, anode, and electrolyte materials. In particular, cathode thin-film materials have been demonstrated with layered or spinel structure transition metal oxides, such as $LiMn_2O_4$, $LiNiO_2$, $LiCoO_2$, and $LiFePO_4$ [11–21].

$LiCoO_2$ has been the most common cathodic material for commercial Li-ion batteries due to its high specific capacity and operating potential. The $LiCoO_2$ cathode for all-solid-state TFBs has been fabricated primarily by physical vapor deposition (PVD) techniques, such as sputtering and pulsed laser deposition, which tends to be costly and low throughput [22–27]. Moreover the limited substrate shape with line-of-sight deposition methods makes PVD techniques incompatible with advanced device structures for high density or free form factor design [9, 28, 29]. Recently, chemical vapor deposition and atomic layered deposition methods have been demonstrated with more flexible substrate choice [29–33].

As an alternative to high cost and low-throughput vacuum deposition methods, solution processing allows low-cost, high-throughput, and large-area fabrication by roll-to-roll manufacturing [34–36]. Various soluble precursors, such as nanoparticle-ink coating, electrodeposition, and sol-gel coating, have been investigated for fabrication of the cathode layer [37–39]. The disadvantages of solution-processed $LiCoO_2$ cathode films include the rough surface morphology and low crystallinity in as-prepared film without high temperature post-annealing [40–42]. The rough surface of the solution-processed $LiCoO_2$ film results in poor contact with the solid-electrolyte layer, leading to an increase of interfacial Li diffusion resistance between the active materials. In addition, the rough surface of these films weakens their adhesion to the substrate, which is responsible for crack formation and

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https://doi.org/10.1016/j.tsf.2018.07.011
Received 29 December 2017; Received in revised form 4 July 2018; Accepted 11 July 2018
Available online 20 July 2018
0040-6090/

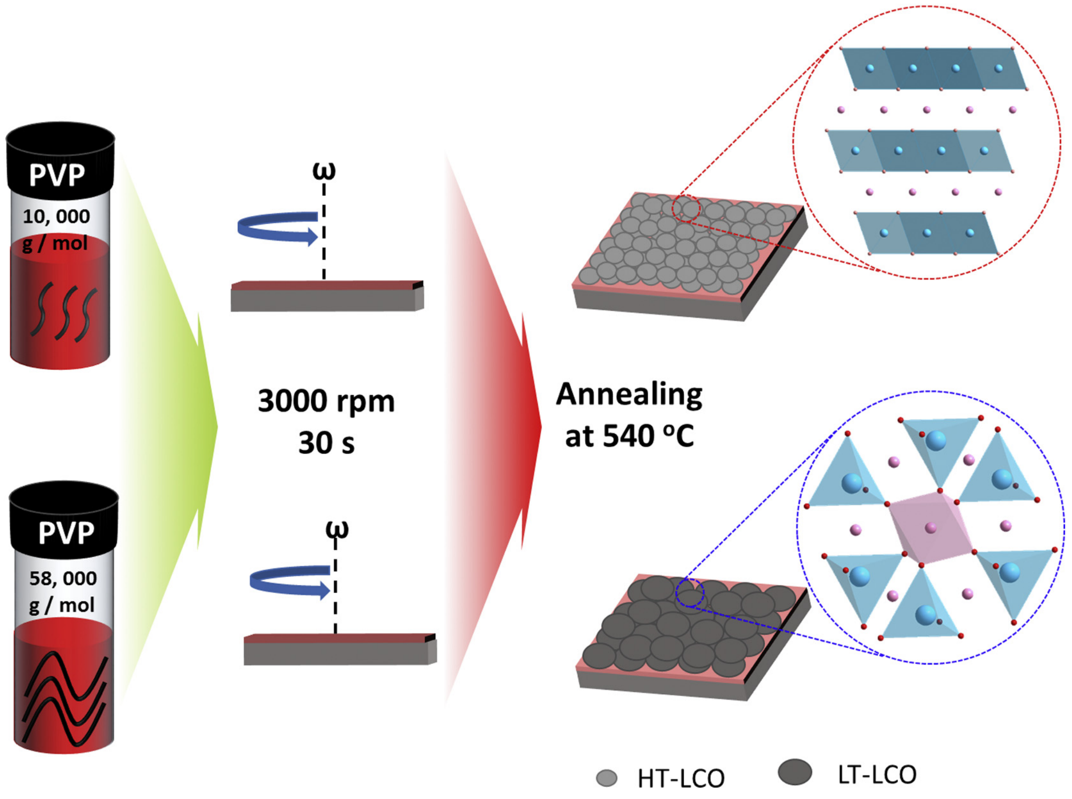

Fig. 1. Schematic representation of the solution processing of $LiCoO_2$ thin film cathode.

detachment from the substrate when the films are bent. In order to improve the crystallinity, contact, and adhesion of the films with their neighboring layers, $LiCoO_2$ cathode films are normally post-annealed near 700 °C. However, it is desirable to lower the required post-annealing temperature because high-temperature annealing limits the use of many substrate materials for flexible TFB applications. It also limits the integration of batteries with other devices.

Here, we report that the nanoparticle crystal phase and size of solution-processed $LiCoO_2$ cathode thin-films can be controlled for high performance TFBs by varying the molecular weight of polyvinylpyrrolidone (PVP) with post-annealing at a mild temperature of 540 °C [43–45]. The spectroscopic and electrical characterization of $LiCoO_2$ cathode thin-films confirm that the small particle size could reduce the phase transformation temperature. The successful implementation of $LiCoO_2$ cathode thin-films shows discharge capacities of 19.15 μAh/cm and retained capacity of 82.65% after 100 cycles.

2. Experiment

2.1. $LiCoO_2$ precursor preparation

The precursor solution for $LiCoO_2$ film was prepared using lithium nitrate ($LiNO_3$, 98.0%, Junsei chemical) and cobalt nitrate hexahydrate ($(Co(NO_3)_2{\cdot}6H_2O$, 98.0%, Aldrich) as the Li and Co sources, respectively. The [Li]/[Co] molar ratio was 1.05 in order to compensate for possible lithium loss during heat treatment. 0.720 g of $LiNO_3$, 2.910 g of Co $(NO_3)_2{\cdot}6H_2O$ and 0.500 g of PVP were dissolved in 20 ml 2-methoxyethanol. Solutions were formed using two different molecular weights of PVP (10,000, and 58,000 g/mol, Aldrich). The precursor solution was stirred for 24 h at room temperature to form a homogeneous solution.

2.2. Thin-film deposition

A heavily n-doped silicon wafer (2 cm × 2 cm) with its native oxide was used as the substrate for characterization of the $LiCoO_2$ thin film. The substrates were cleaned with acetone and isopropyl alcohol for 10 min. The cleaned films were dried with N_2 and treated with oxygen plasma for 10 min. The $LiCoO_2$ precursor solution was spin-coated onto Si wafers at 3000 rpm for 30 s and then annealed at 500 °C for 10 min under ambient air to prepare the first $LiCoO_2$ layer. After annealing, oxygen plasma treatment was carried out once again to enhance the adhesion of the second layer of $LiCoO_2$ solution precursor. These processes were repeated five-times to achieve sufficiently thick films. Finally, the 6th layer was annealed at 540 °C (ramp rate of 10 °C/min from 400 to 540 °C) for 1 h under ambient air to improve the crystallinity. For electrochemical characterization of the thin films, aluminum foil was used as a substrate to assemble a 2032 coin cell.

2.3. Thin-film characterizations

The prepared thin films were analyzed using grazing incidence X-ray diffraction (GIXRD) with X'pert Pro (PANalytical, Netherlands). The system used a step size of 0.043° at a scan rate of 0.45 s/step with Cu Kα radiation. The vibrational modes observed by Raman spectroscopy with LabRAM HV Evolution (HORIBA, Japan) operating at a 532 nm wavelength from a frequency-doubled Nd:YAG laser (Cobolt). The surface morphologies and thin film cross sections were observed with a field emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss, Germany) at a 5 kV accelerating voltage. The root mean square (rms) roughness of as deposited thin films was determined using atomic force microscopy (AFM). The AFM images under non-contact mode were obtained with a XE-120-AFM (Park Systems, Korea) that used Al-coated non-contact tips (Nanosensors, PPP-NCHR, Switzerland, 42 N/m force constant, 330 kHz resonance frequency, and 1.0 Hz scan rate.).

2.4. Electrochemical characterization

All electrochemical measurements were carried out on the 2032 coin cells as assembled in an Ar-filled glove box. A $LiCoO_2$ thin film