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Synthesis of nano-sized lithium cobalt oxide via a sol–gel method

Guangfen Li[a,b,*], Jing Zhang[a,b]

[a] State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, 300387 Tianjin, PR China
[b] College of Material Science Technology, Tianjin Polytechnic University, 300387 Tianjin, PR China

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ABSTRACT

In this study, nano-structured $LiCoO_2$ thin film were synthesized by coupling a sol–gel process with a spin-coating method using polyacrylic acid (PAA) as chelating agent. The optimized conditions for obtaining a better gel formulation and subsequent homogenous dense film were investigated by varying the calcination temperature, the molar mass of PAA, and the precursor's molar ratios of PAA, lithium, and cobalt ions. The gel films on the silicon substrate surfaces were deposited by multi-step spin-coating process for either increasing the density of the gel film or adjusting the quantity of PAA in the film. The gel film was calcined by an optimized two-step heating procedure in order to obtain regular nano-structured $LiCoO_2$ materials. Both atomic force microscopy (AFM) and scanning electron microscopy (SEM) were utilized to analyze the crystalline and the morphology of the films, respectively.

1. Introduction

Due to the rapid development of micro-device and micro-technology for the past two decades, micro-scale lithium-ion batteries have attracted many attentions [1–3]. Lithium-based layered metal oxides, such as $LiMnO_2$, $LiNiO_2$, and $LiCoO_2$ have been utilized in the micro-device as power sources [4–6]. The disadvantage of layered $LiMnO_2$ is the crystallographic transformation to spinel structure during electrochemical cycling [7,8]. Whereas the layered $LiNiO_2$ has difficulties in preparation a stoichiometric $LiNiO_2$ powders without metal ions mixing and has the structure degradation caused by irreversible phase transition during electrochemical cycling [8]. $LiCoO_2$ has been considered as a prime material for positive electrode in the batteries owing to its predominant characteristics, i.e. high capacity, high specific energy, and material structural stability [9].

Several approaches i.e. plasma vacuum deposition method, radio frequency (RF) sputtering [10,11], pulsed laser deposition (PLD) [12,13], electron cyclotron resonance (ECR) sputtering [14] and the sol–gel method [15–17] have been developed for preparing $LiCoO_2$ thin films. The sol–gel method is a widely applied technique for films preparation because of its well-known advantages, i.e. better stoichiometric control, lower calcination temperature, shorter sintering time, finer particle size with homogeneous distribution and high surface area. These parameters are believed to be crucial for achieving a higher electrode activity and better cell performance. The sol–gel method can also be integrated with either spin-coating or dip-coating process to obtain thin films.

In this study, $LiCoO_2$ thin films were prepared by a spin-coating method. Polycrylic acid was used as chelating agent to prevent the problems of pH controlling in the gel formation and fluffiness during the calcination process. For obtaining dense and homogeneous films with regular nano-sized particles, the experimental conditions as the quantity and the molecular weight of polyacrylic acid (PAA), the calcination temperature, and the multiple-layers prepared by spin-coating process were optimized. The morphology and crystalline of the thin films were characterized by either atomic force microscopy (AFM) or scanning electron microscopy (SEM), respectively.

2. Experiment

$LiCoO_2$ thin films were prepared by a sol–gel process according to the procedure as follows:$LiNO_3$ (A.R., 99%) and $Co(NO_3)_2{\cdot}6H_2O$ (A.R., 99%) were dissolved in de-ionized water and then mixed with PAA (A.R., Mw. 800–1000). PAA acts as chelating agent for a better gel formation. The molar ratio of Li:Co was varied from 1:2 to 2:1, whereas the molar ratio of the total metallic ions charges (M^+) to polyacrylic acid (M^+:PAA) was set as 1:2. The mixture was continuously stirred at 50 °C for a few hours until a homogeneous solution was obtained.

Before spin-coating process, the silicon substrates were cleaned in solvent of ethanol (99.7%) and then acetone (99.5%) in the ultrasonic bath for 2 min to remove dust and organic residue on the silicon surface. Afterwards, the cleaned silicon substrate was placed

* Corresponding author at: Tianjin Polytechnic University, College of Material Science and Technology, State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Xiqing District, Binshui East Road 399, Tianjin 300387, PR China.
E-mail address: liguangfen@tjpu.edu.cn (G. Li).

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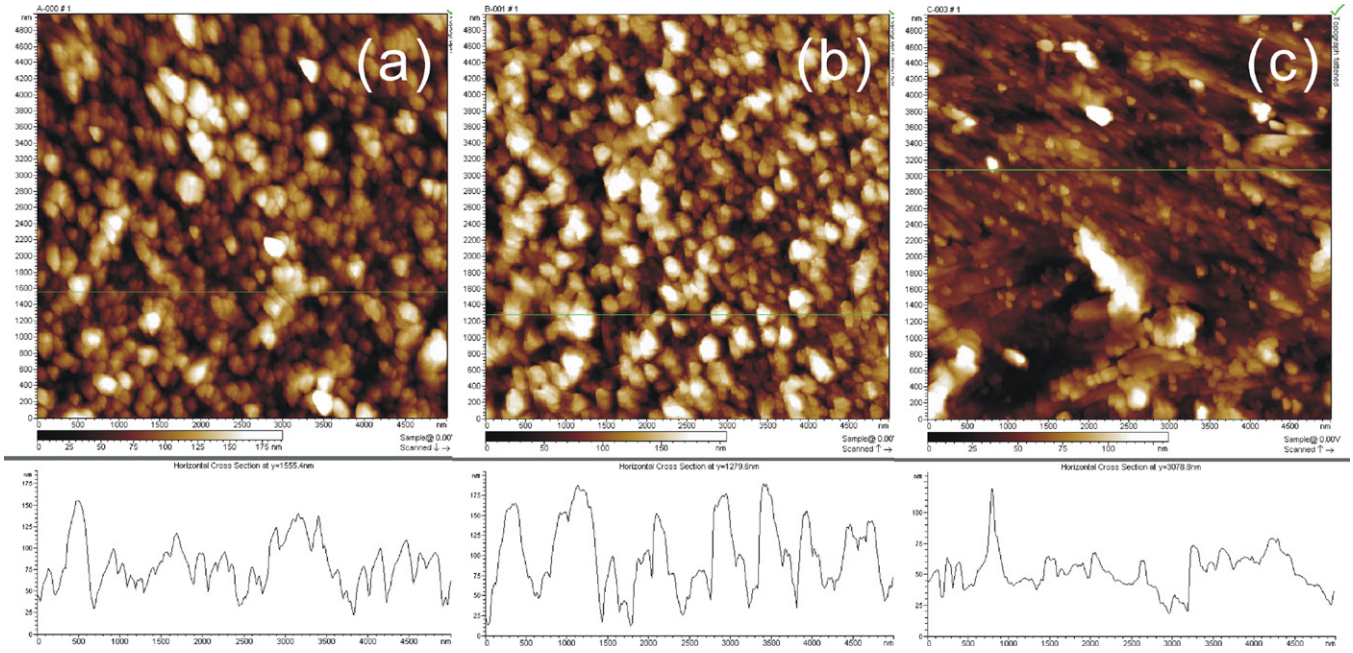

Fig. 1. AFM images of $LiCoO_2$ thin films. The dosage of PAA per 100 ml solution is: (a) 40 g; (b) 60 g; (c) 80 g.

on the holder of the spin-coating equipment, and then a drop of solution was deposited on the substrate surface by a pipette. The formed thin films during spin-coating process were subsequently dried in the oven at 110 °C for 1 h for removing the solvent. Finally, these samples were sintered in the furnace programmed by a two-step calcination process, which will be latter described in details in the study.

The crystalline and morphology of the thin films were mainly analyzed by either scanning electron microscope (SEM, Quanta 200, FEI company, U.S.A.) or atomic force microscopy (AFM, AFM-STM5500, Agilent, U.S.A.).

3. Result and discussion

3.1. The crystalline and morphology of the thin films in dependent of the quantities of polyacrylic acid

PAA is primarily used as chelating agent for a better dispersion of metal ions in the gel film. The quantities of PAA have impacts on the rheological properties of the solution, the gel film thickness, and then $LiCoO_2$ crystallization process. An appropriate addition of PAA can improve the film quality and favor $LiCoO_2$ crystallization. In this study, the solution consists of lithium and cobalt in proportion of 2:1, whereas the total metallic ions concentration (M^+) is 0.3 mol/l. The quantities of PAA varying from 40 g/100 ml, 60 g/100 ml, to 80 g/100 ml were chosen for the investigation. The calcination procedure is performed as (i) increasing the temperature from room temperature to 300 °C with a speed of 1 °C/min, and keeping for 2 h, (ii) increasing temperature from 300 °C to 600 °C with a speed of 5 °C/min, and keeping for another 2 h. The purpose of setting the initial temperature as 300 °C is to expel H_2O and CO_2 from gel film produced during the organic materials decomposition. The AFM analyses of the thin films were revealed in Fig. 1.

For obtaining the thickness of the various films, the film surface was scratched by a sharp needle and then the depth of the scratch was measured by AFM. The film thickness was in the range from 10 nm to 100 nm. As the quantities of PAA in 100 ml solution are 40 g, the thin films with thickness of 20 nm are resulted. The fine particles size is about 200 nm, and the particle *z*-height varies from 75 nm to 155 nm. As the PAA content increases to 60 g, the thin films appear more homogeneous. The particles *z*-height ranges from 105 nm to 185 nm, and the particles sizes are uniform with a narrow size distribution. When further increasing the PAA content to 80 g, the average *z*-height of the particles decreases extremely, and particles morphology can hardly be identified by AFM analysis. The reason why the crystalline and the morphology of thin film changes with the quantity of PAA can attribute to the combustion heat created by PAA decomposition, which is necessary for the synthesize of $LiCoO_2$. However, it has disadvantage for the formation of $LiCoO_2$, especially when excessive PAA is used in the process. The CO and CO_2 generated by thermal decomposition of PAA lead to void formed in the $LiCoO_2$ phase, which is unfavorable for the crystal formation.

3.2. The influence of calcination process on the morphology of the thin films

The investigation of the influence of two-step calcination process on the morphology of thin film was carried out by extending the calcination time from 2 h to 4 h for each step. At second step, we reduced the heating speed to 2 °C/min. The SEM micrographs of $LiCoO_2$ thin films calcined at temperature of 700 °C, 800 °C, and 900 °C in air, are given in Fig. 2.

When $LiCoO_2$ thin films were calcined at 700 °C, a smooth and less dense thin film was formed on the substrate surface, where the particles grew in parallel with the substrate surfaces. The rod-like particulates scattered with a broad size distribution, shown in Fig. 2a. However, when the calcination temperature increased to 800 °C, $LiCoO_2$ thin film became homogenous, which consists of extremely dense layers and monodispersed rod-like particulates with an average particle size of about 5 μm. The particulates size distribution is rather narrow, shown in Fig. 2b. As the calcination temperature increased to 900 °C, less dispersed irregular particulates are observed, the particles tends to aggregate and the surface congeries appears porous. The combination effects of the fast growth of $LiCoO_2$ particles at high calcined temperature, and the rapid releases of CO_2 gas from the decomposition of PAA under higher temperature cause the substantial particulates agglomeration, which hinders the formation of $LiCoO_2$ crystals, in Fig. 2c. These observations suggest that $LiCoO_2$ thin films calcined at an