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Use of low-temperature nanostructured CuO thin films deposited by spray-pyrolysis in lithium cells

J. Morales[a], L. Sánchez[a,*], F. Martín[b], J.R. Ramos-Barrado[b], M. Sánchez[b]

[a]*Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Campus de Rabanales, Edificio Marie Curie, Universidad de Córdoba, 14071 Córdoba, Spain*

[b]*Laboratorio de Materiales y Superficie (Unidad Asociada al CSIC), Universidad de Málaga, Spain*

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Abstract

Nanostructured CuO thin films were prepared by spray pyrolysis of aqueous copper acetate solutions at temperatures over 200–300 °C range. The textural and structural properties of the films were determined by scanning electron microscopy, atomic force microscopy, X-ray diffraction spectroscopy and X-ray photoelectron spectroscopy (XPS). Although the sole crystalline phase detected in the film was CuO, XPS spectra revealed a more complex surface structure due to the presence of undecomposed copper acetate that can be easily removed by Ar^+ ion sputtering. The heating temperature was found to have little limited effect on the particle size and thickness of the films, which, however, increased significantly increasing deposition time. The film with the smallest grain size exhibited an excellent electrochemical response in Li battery electrodes and was capable of supplying sustained specific capacity as high as 625 A h kg^{-1} (50% greater than that delivered by bulk CuO and close to the theoretical capacity for the CuO⇔Cu reaction) upon extensive cycling.

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1. Introduction

Copper oxide-based materials are of interest on account of their potential uses in many technological fields. CuO and Cu_2O materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as pn junction diodes [1]. Apart from their semiconductor applications, these materials have been employed as heterogenous catalysts for several environmental processes [2,3], solid state gas sensor heterocontacts [4,5], and microwave dielectric materials [6]. Their use in power sources has received special attention. Thus, in addition to photovoltaic devices [7,8], copper oxides have been used as electrode materials for lithium batteries. The earliest studies in this area focused on their potential use as cathodes in lithium primary cells [9,10]. Recently, their ability to reversibly react with Li ions at low potential values was ascribed to the following reaction [11]:

$$Cu_nO + 2Li \Leftrightarrow nCu + Li_2O \qquad (1)$$

The theoretical deliverable specific capacity of CuO is 675 A h kg^{-1}, which is much higher than that of graphite-based anodic materials (the theoretical gravimetric capacity for which is 372 A h kg^{-1}). For this reason, CuO has been proposed as candidate to replace these carbonaceous materials as negative electrodes in Li-ion batteries. In practice, however, bulk CuO electrodes deliver a sustained reversible capacity of ca. 400 A h kg^{-1} [12], so roughly 40% of the CuO theoretical capacity, referred to its reduction to Cu, is unusable.

Nanostructured materials have emerged as attractive alternatives to conventional materials by virtue of their prominent electronic and chemical properties [13]. Recently, we reported nanostructured PbO_2 and Ag thin electrodes to exhibit excellent electrochemical activity as electrodes in

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* Corresponding author. Tel.: +34 957 218620; fax: +34 957 218621.
E-mail address: luis-sanchez@uco.es (L. Sánchez).

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lead-acid cells [14] and lithium batteries [15], respectively. We extended the methodology used with these electrodes to CuO with the aim of improving its electrochemical response in lithium cells. In this work, we report the preparation and characterization of nanocrystalline CuO thin films by spray pyrolysis of an aqueous solution of copper acetate as a simple preparation method that requires no sophisticated equipment. X-ray diffraction (XRD) spectroscopy, electron and atomic force microscopy and X-ray photoelectron spectroscopy (XPS) were used for characterization purposes. We also explored the activity of a selected film as electrode in lithium batteries. This electrode preparation procedure results increases the electrochemical reactivity of CuO relative to bulk material.

2. Experimental details

A spray pyrolysis method described elsewhere [16] was used to prepare the CuO thin films. An aqueous solution of 0.05 M $Cu(CH_3COO)_2$ was used as precursor. The solution was pumped into the air stream in the spray nozzle at a rate of 50 ml h^{-1} by means of a syringe pump, for a preset time of 30, 60 for 80 min. An air stream of 25 l min^{-1}, measured at 1.25 bar, was used to atomize the solution. Circular disks of commercial 304 stainless steel (0.4 mm thick and 7.5 mm in diameter) were used as substrates. The disks were kept at temperatures over the range 200–300 °C. The amount of oxide film attached to the substrate was determined by weighting the electrode before and after deposition, using a Sartorius microbalance with ± 1 μg sensitivity.

X-ray diffraction patterns were recorded on a Siemens D5000 X-ray diffractometer, using Cu Kα radiation an a graphite monochromator, in steps of 0.02° and 1.2 s. Scanning electron microscopy (SEM) images were obtained on a Jeol JMS-5300 microscope. Topographic atomic force microscopy (AFM) examinations were performed by using a Nanoscope IIIa contact-mode AFM (Digital Instruments). Type NP cantilevers (Digital Instruments) with Si_3N_4 tips and a spring constant of 0.58 N/m were employed.

X-ray photoelectron and X-ray excited Auger spectra were obtained with a Physical Electronics PHI 5700 spectrometer using non-monochromated MgKα radiation ($h\nu$=1253.6 eV) and a hemispherical analyser operating at constant pass energy of 29.35 eV. The spectra were recorded with the X-ray generator operating at 15 kV and 20 mA. The energy scale of the spectrometer was calibrated using the Cu 2p3/2, Ag 3d5/2 and Au 4f7/2 photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. The vacuum in the analysis chamber was better than 10^{-9} mbar.

Binding energies were corrected using the binding energy values for C 1s of adventitious carbon (and for the methyl group) at 284.8 eV. Samples were mounted on a holder without adhesive tape and kept under high vacuum in the preparation chamber overnight before they were transferred to the analysis chamber of the spectrometer. Survey spectra over the range 0–1200 eV were recorded at a 187.85 pass energy, each region being scanned several times to ensure an adequate signal-to-noise ratio. A 3×3-mm sample area was sputtered with 4 keV Ar^+; the sputter rate was assumed to be ~0.3 nm min^{-1} as determined for Ta_2O_5 under identical sputter conditions. Spectra were processed using PHI-Access V.6 and Multipak software, both from Physical Electronics. High-resolution spectra were fitted upon Shirley background correction and satellite subtraction. Surface atomic concentrations were determined from peak areas, using Shirley background subtraction and sensitivity factors provided by the spectrometer manufacturer (Physical Electronics, Eden Prairie, MN). Data for the Cu 2p region were acquired at short times in order to minimize the reduction of copper oxide by X-rays.

Electrochemical measurements were carried out in two-electrodes cell, using lithium as counter-electrode. The electrolyte used was Merck battery electrolyte LP 40, which consists of 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate in 1:1 w/w ratio. Circular disks of stainless steel coated with the active material were used as working electrodes. Cells were galvanostatically charged and discharged at a current density of 0.075 mA mg^{-1}. SPES curves were recorded at 75 mV h^{-1} per step. All electrochemical measurements were controlled via a MacPile II potentiostat−galvanostat.

3. Results and discussion

The experimental conditions used to prepare films are shown in Table 1. The amount of film deposited increased with increasing deposition time; no clear-cut correlation with the deposition temperature was observed, however. All samples thoroughly coated with substrate; however, film uniformity varied with temperature, as revealed by the SEM images. Fig. 1 shows selected typical images for the samples. Samples A, B and C were rougher than the other because the small amounts of deposited material allowed the wrinkled morphology of the substrate surface to be distinguished. Increasing the time of deposition (samples E and F) led to a dense, compact homogeneous film coating and the formation of some cracks in parallel to the increase in the amount deposited. However, sample D, which was

Table 1
Preparation conditions and selected properties of CuO thin films

Film	Temperature (°C)	Time (min)	Mass deposited (mg cm^{-2})	Thickness[a] (nm)
Sample A	200	30	0.36	660
Sample B	250	30	0.30	475
Sample C	300	30	0.17	420
Sample D	200	60	0.58	1100
Sample E	250	60	0.56	1150
Sample F	300	80	0.73	1250

[a] Values estimated from SEM images.