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ScienceDirect
Journal of Power Sources 162 (2006) 679–684
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Copper–vanadium mixed oxide thin film electrodes

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Received 14 June 2006; received in revised form 4 July 2006; accepted 5 July 2006
Available online 17 August 2006

Abstract

In this work, small amounts of vanadium atoms were incorporated in copper oxide films in order to decrease the charge capacity loss during the electrochemical lithium reaction, mainly in the first cycle. Reactive sputtering was the film deposition technique used to deposit pure copper oxide films, CuO, and copper–vanadium mixed oxides CuO(VO_y). The composition, oxidation state and crystallinity of the deposited films were investigated. Electrochemical studies were performed, and the results demonstrated that the mixed oxides have a better electrochemical behavior with a higher capacity and stability in the charge/discharge processes, when compared to the pure CuO films behavior.

Keywords: Copper oxide; Vanadium; Reactive sputtering; Thin films; Microbatteries; Electrode

1. Introduction

Copper oxide can be found in two different compositions: cupric oxide (Cu_2O), with cubic structure, and cuprous oxide (CuO), which presents monoclinic structure [1,2]. The bulk material density of CuO and Cu_2O is 6.3 and 6.0 g cm^{-3}, respectively [3].

In the battery field, copper oxide has been used as cathode material in primary lithium batteries [4,5], due to its high specific capacity. Li/CuO cells present an energy density of 600 Wh dm^{-3} (300 Wh kg^{-1}) and a theoretical capacity of 4.26 Ah cm^{-3} (670 mAh g^{-1}). The open circuit potential is 2.25 V and the cell operates in an average potential between 1.2 and 1.5 V [4,5]. Copper oxide presents high stability in organic electrolytes, due to its low solubility [6]. This characteristic assures a low self-discharge (<1% per year at ambient temperature) allowing a long shelf life [4,6].

Recently [7–9], it was demonstrated that copper oxide, both in powder (CuO and Cu_2O) and in thin film form (CuO), is capable of react with lithium ions in a reversible way, and is a viable material to be used as electrode in rechargeable lithium batteries. However, the material presents a large capacity loss from the first to the second discharge cycle [7,9,10].

In this work, small amounts of vanadium atoms were incorporated in copper oxide films during the film deposition process, in order to decrease the initial charge capacity loss, and to increase the coulombic efficiency of the lithium reaction process during the successive cycles.

2. Experimental

The oxide films were deposited by d.c. and r.f. sputtering from a copper and vanadium targets, respectively, in an O_2 + Ar atmosphere. The flow of the gases was controlled by two mass flowmeters, and was fixed at 55.0 sccm (Ar) and 5.0 sccm (O_2). The pressure under deposition was 1.0×10^{-2} mbar. A diagram of the sputtering chamber is shown in Fig. 1. The target to substrate distance was ~13 cm. The support of the d.c. target was inclined at 13° due to the position of the substrate on the sample holder. The target diameter (V and Cu) was 5.0 cm. The substrates were indium–tin oxide (ITO, used in electrochemical and X-ray Photoelectron Spectroscopy measurements), glass (used in the X-ray diffraction experiments), carbon or silicon (used in the Rutherford Scattering Spectroscopy experiments). A small part of the substrate was covered with adhesive tape, in order to provide a well-defined step. This step was used in the thickness measurements, by means of an Alpha-Step profilometer.

The presence of crystalline phases was investigated by X-ray diffraction with Cu Kα radiation either under grazing incidence

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doi:10.1016/j.jpowsour.2006.07.011

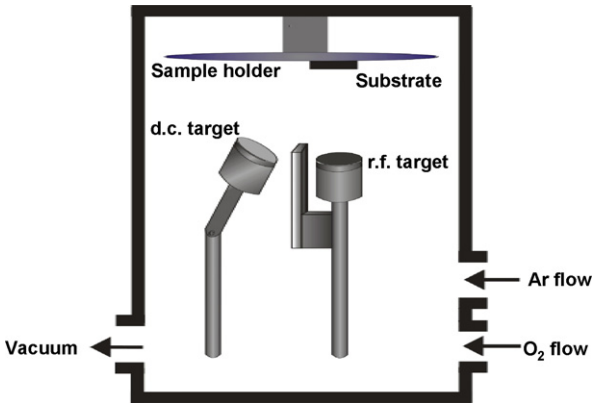

Fig. 1. Diagram of the sputtering chamber geometry.

geometry in the X Pert MRD Philips equipment or in diffractograms with Fe Kα radiation and a graphite monochromator, in a Theta-2Theta Bragg–Brentano geometry. Cu, V and O contents were obtained by Rutherford Back Scattering (RBS) Spectroscopy using a 2.2 MeV He^+ beam.

The chemical state of the metals was analyzed by X-ray Absorption Near-edge Structure (XANES). The experiments were performed at the XAS beamline (LNLS—Laboratório Nacional de Luz Síncrotron, Campinas, SP). The photon energy was in the range 8900–9100 eV (copper absorption K-edge) or 5380–5600 eV (vanadium absorption K-edge). The thin film samples were analyzed in the fluorescence mode, and the control samples.

(CuO and V_2O_5 pellets) were measured in transmission mode. The chemical state of the elements was also analyzed by X-ray Photoelectron Spectroscopy (XPS).

Electrochemical cells with the oxide films as the working electrode and two Li metal foils as the reference and counter electrode were used for electrochemical measurements. The electrolyte was 1 M $LiClO_4$ in propylene carbonate. Chronopotentiometric experiments were performed from rest potential to 1 V versus Li, using a current density of 2.0 μA cm^{-2}, by means of a multipotentiostat (VMP system, Biologic) operating in the galvanostatic mode. During the experiments, the cell was maintained inside an Ar dry-box.

3. Results

In this work, copper oxide and mixed vanadium–copper oxides, $Cu_xV_yO_z$, films were deposited and analyzed. The pure copper oxide film (herein called CuV0) was deposited using a d.c. sputtering. The power applied to the copper target was 4 W. For the deposition of mixed oxides this power level at the copper target was maintained and an r.f. sputtering system with a vanadium target was simultaneously actionated. The r.f. power levels were 60, 80 and 100 W, and the obtained thin film samples will be herein denominated CuV60, CuV80 and CuV100, respectively. The composition of all films, deposited onto car-

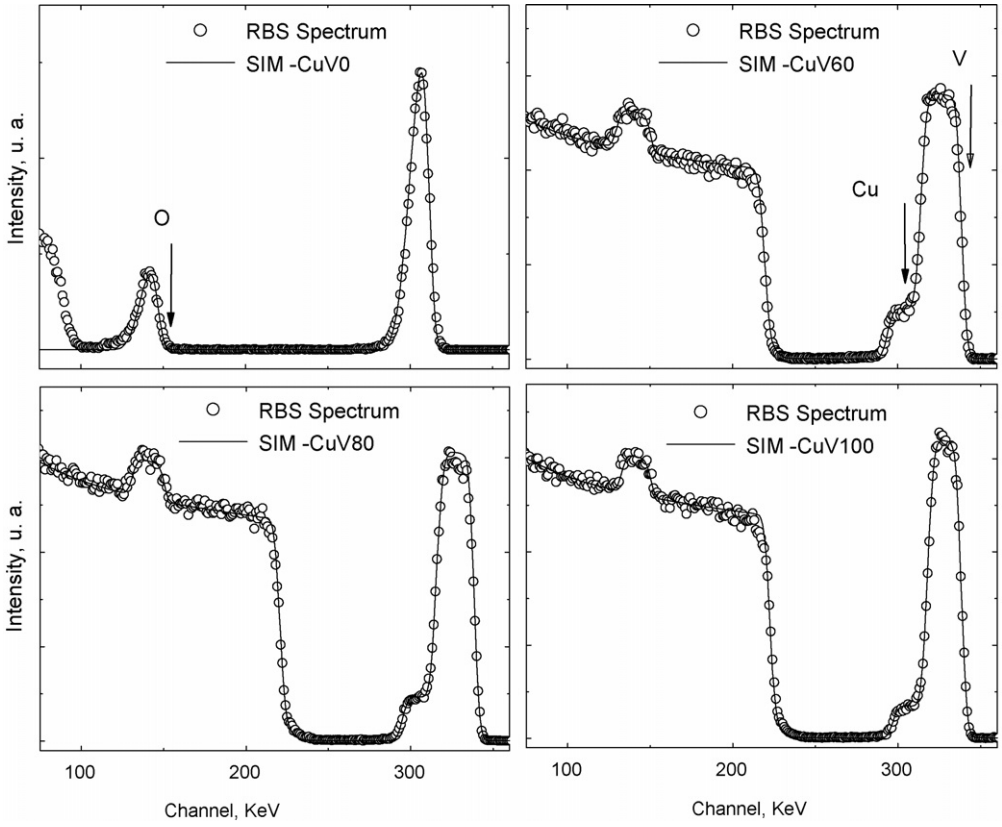

Fig. 2. RBS Spectra and fitting curves. The substrate for films CuV60, CuV80 and CuV100 was Si and for CuV0 film was C.