



## Zinc oxide nanostructures by chemical vapour deposition as anodes for Li-ion batteries



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### ABSTRACT

ZnO nanostructures are grown by a simple chemical vapour deposition method directly on a stainless steel disc current collector and successfully tested in lithium cells. The structural/morphological characterization points out the presence of well-defined polycrystalline nanostructures having different shapes and a preferential orientation along the *c*-axis direction. In addition, the high active surface of the ZnO nanostructures, which accounts for a large electrode/electrolyte contact area, and the complete wetting with the electrolyte solution are considered to be responsible for the good electrical transport properties and the adequate electrochemical behaviour, as confirmed by cyclic voltammetry and galvanostatic charge/discharge cycling. Indeed, despite no binder or conducting additives are used, when galvanostatically tested in lithium cells, after an initial decay, the ZnO nanostructures can provide a rather stable specific capacity approaching  $70 \mu\text{A h cm}^{-2}$  (i.e., around  $400 \text{ mA h g}^{-1}$ ) after prolonged cycling at 1 C, with very high Coulombic efficiency and an overall capacity retention exceeding 62%.

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### 1. Introduction

In the last decade, intense efforts of the scientific community have been devoted to the development of high energy density rechargeable batteries to be used in demanding portable electronic devices and green technologies like electric/hybrid-electric vehicles [1]. In such a scenario, Li-ion batteries (LIBs) have emerged as power sources of choice thanks to their superior characteristics, such as high capacity, long life and fast rate capability [2]. However, all these aspects are strictly related to the accurate balance between the lithium storage capacity and reversibility of the electrode materials [3]. Regarding the negative electrode, to increase LIBs performances, conventional carbon-based anodes must be replaced with materials providing higher energy as well as power densities [4]. Indeed, graphite is the most commonly used anode material, mainly because of its low cost, high yield and long life cycle. Nevertheless, its performances are limited by a relatively low capacity, theoretically predicted to be  $372 \text{ mA h g}^{-1}$ , as well as

low rate capability [5]. This aspect has driven to investigate innovative anode materials with improved characteristics.

Depending on their reversible reaction mechanism vs. lithium, anode materials may be divided into three main groups: (i) intercalation/insertion materials (e.g., graphitic and carbonaceous materials, titania and titanates), (ii) alloying materials (e.g., Si, Sn, Ge,  $\text{SnO}_2$ ), (iii) conversion materials (e.g., transition metal oxides, metal sulphides and phosphides). In particular, the class of metal oxides (MO) is considered to be an interesting alternative to graphite [6,2]. These mainly include tin oxide or tin-based composite oxides and 3d transition-metal oxides, where the most investigated metals are Fe, Co, Ni, Cu and Zn [7], both in their nanostructured form as well as in the form of thin films. Another MO material deeply investigated in the last years is titanium dioxide ( $\text{TiO}_2$ ), which is characterized by a theoretical specific capacity of about  $330 \text{ mA h g}^{-1}$ , and a volume change upon lithium insertion/deinsertion process lesser than 4%. Both these aspects envision the preparation of  $\text{TiO}_2$  outstanding stable structures with an extremely long cycling performance in LIBs [8–14].

ZnO is a well-known wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV) and a proven capability for reversible electrochemical Li storage [8,9]. It has a theoretical capacity of  $978 \text{ mA h g}^{-1}$  as an anode material for LIBs [15–18]. Among other MO, ZnO has some advantages, being easy to prepare, chemically stable and low-cost [19]. However, it generally exhibits low reversible capacity, poor kinetics and severe capacity fading

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upon cycling, even at low current regimes, arising from the low electronic conductivity and large volume variation of ZnO active material particles [15,20]. In fact, its capacity may drop to below 200 mA h g<sup>-1</sup> after just few cycles [17]. To overcome some of these drawbacks, nanostructures with various dimensions and morphologies started to be taken into account [15–18], as they might provide large electrolyte/electrode contact area and short diffusion paths for Li ions and electrons [16,18]. In this respect, core-shell ZnO nanostructures, like C-coated and TiO<sub>2</sub>-coated ZnO nanorods [15,16], and flower-like ZnO–NiO–C films [20] are reported in the literature as promising solutions for improving the electrochemical properties of ZnO anodes. Despite some improvements have been achieved in these cases, the effective reduction of the volume variation as well as the increase of the electronic conductivity still represent a severe drawback [20]. One-dimensional nanorods (NRs) present a considerably higher surface area than bulk or thin film structures, providing a greater number of sites for the electrochemical reaction [16]. It has been also proven that these nanostructured electrodes often exhibit better electrochemical characteristics than those made of common granular powders [17,21,22] and may enhance both lithium storage capacity and cyclability of ZnO anodes [20].

In this scenario, this work deals with an interesting approach, which is the fabrication of highly porous thin film ZnO nanostructured electrodes, grown by a simple two-step process involving a chemical vapour deposition (CVD) onto stainless-steel substrates. CVD has been selected as it is a low-cost, low maintenance and effective process for depositing uniform films exhibiting good adhesion to the growing substrate; moreover, the easiness in controlling the growth rate allows a high reproducibility of the samples. The as-prepared ZnO nanostructured films were tested in lab-scale lithium cells showing interesting ambient temperature performance, particularly if one considers that they have been obtained in the absence of foreign ingredients such as binders and conductivity enhancers, which would affect the overall energy density output.

## 2. Experimental

ZnO nanostructures were grown on commercial stainless steel discs, following a two-step procedure. Firstly, a ZnO seed layer, acting as the nucleation site for the nanostructures, was deposited on the substrate by means of sol-gel/spin-coating technique [23,24]. Then, ZnO nanostructures were grown by chemical vapour deposition (CVD) method [25,26], using a thermal CVD reactor working at atmospheric pressure [27,28].

### 2.1. Synthesis of ZnO seed layer

Before the seed layer deposition, the stainless steel substrates (1 cm diameter, Alloy SS-316, AISI-316 (Fe/Cr18/Ni10/Mo3) disc, Goodfellow Cambridge Ltd.) were cleaned with acetone and ethanol in an ultrasonic bath for 10 min, and successively dried under nitrogen flow. In order to increase the surface wettability of the steel substrate, a plasma treatment in Ar was carried out prior to the seed layer deposition. ZnO seed layers were synthesized according to the sol-gel/spin-coating technique previously reported by Natsume et al. [29,30]. Firstly, a 10 mM concentrated solution of zinc acetate di-hydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>, 98%, Aldrich) in ethanol was prepared. A drop of this solution was deposited onto the cleaned substrates and spin-coated for 10 s at 1000 rpm plus 30 s at 3000 rpm. This process was repeated five times. Finally, to achieve the crystallization of the seed layer, the substrates were calcined in a furnace at 350 °C in air for 20 min.

### 2.2. CVD growth of ZnO nanostructures

ZnO nanostructures were grown on seeded substrates into a three-zone tubular furnace (Carbolite, UK) equipped with an alumina tube placed horizontally, operating at atmospheric pressure. The alumina tube had a section of 80 mm in diameter and was 1.5 m long. The samples were arranged on a flat alumina holder and placed in the central zone of the tube. A 125 μm-thick metallic Zn foil (99.99%, Goodfellow) was used as the source and placed on the holder, in close proximity to the substrate, in order to maximize the transport efficiency of material towards the substrate surface during growth. After sealing the tube, the residual air was removed from the

chamber by fluxing 4000 sccm of argon gas at atmospheric pressure for a few minutes. The growth temperature was set to 650 °C using a heating ramp of 10.5 °C min<sup>-1</sup>, allowing partial evaporation of the zinc source. During the temperature ramp and the deposition step, argon (flow rate of 1500 sccm) was used as carrier gas to transport vapours from the source to the substrate, while oxygen (flow rate of 75 sccm) was introduced into the chamber at the deposition temperature to oxidize the metallic Zn. After a deposition step of 20 min, all gases were closed and the system cooled down to ambient temperature.

### 2.3. Characterization techniques, lithium cell assembly and testing

Sample morphology was characterized by Field Emission Scanning Electron Microscopy (FESEM) on a ZEISS Supra 40. X-ray Diffraction (XRD) patterns were obtained on a PANalytical X'Pert PW1140–PW3020 (Cu Kα source), then fitted and compared with the database pattern reported for hexagonal wurtzite ZnO. Optical Contact Angle (OCA) measurements were performed using a OCAH200 equipment (DataPhysic Instruments GmbH) under ambient conditions. The sessile drop method was implemented employing 1:1 w/w mixed ethyl carbonate–diethyl carbonate solution droplets having a volume of 1.5 μL.

The electrochemical response of the as-prepared films was tested in three electrodes polypropylene T-cells assembled as follows: an as-prepared ZnO film supported on SS-316 (0.15 mg of estimated active material) as working electrode, a 1.0 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in a 1:1 w/w mixture of ethylene/diethyl carbonate (EC:DEC, Solvionic) liquid electrolyte soaked on a Whatman GF/A separator and a Li metal foil (Chemetall) as counter electrode. For cyclic voltammetry (CV), a second Li foil was added at the third opening of the cells, acting as reference electrode. Galvanostatic discharge/charge cycling tests (cut off potentials: 0.02–3.0 V vs. Li) and CVs (0.02–3.0 V vs. Li, at 0.1 mV s<sup>-1</sup>) were carried out at ambient temperature on an Arbin Instrument Testing System model BT-2000. Discharge/charge cycles were set at the same current of 0.1 mA (i.e., estimated to be 1 C rate based on a ZnO theoretical specific capacity of 978 mA h g<sup>-1</sup>). Clean electrodes and fresh samples were used for each test. Procedures of cell assembly were performed in the inert atmosphere of a dry glove box (MBraun Labstar, O<sub>2</sub> and H<sub>2</sub>O content <0.1 ppm) filled with extra pure argon (6.0).

Note that samples weight was measured through a high precision scale balance (±0.00001 g). Each measurement was repeated at least two times on five different samples and the average was considered as the estimated value. Then, active material thin film weight was determined by the difference between the weight of the ZnO-coated substrate and the uncoated substrate. Nevertheless, as a significant capacity error can be associated with this kind of measurement, the specific capacity values might be overestimated. Thus, the estimated active material weight was used only to calculate the current regime (C rate) to be adopted, while the specific capacity values were reported in μA h cm<sup>-2</sup>.

## 3. Results and discussion

### 3.1. Structural/morphological characterization

The FESEM analysis at different magnification which gives an overview of the ZnO nanostructures grown on the steel disc substrate is shown in Fig. 1. The coverage of the surface was not definitely uniform and homogeneous. Depending on the region considered, the presence of different types of ZnO nanostructures was pointed out. Most of the material was clearly composed of homogeneously distributed nanowires (NWs, see images c and d of Fig. 1). From Fig. 1e the average diameter (90 ± 27 nm) and length (564 ± 150 nm) of ZnO NWs were estimated (the tilt correction factor was applied to compute the length of the wires). In the most external regions, near the edges of the support, particularly those being close to the Zn source during CVD, nanocombs (NCs) directly deposited onto the underlying NWs were found to be present (see images b and c of Fig. 1). It is believed that these nanostructures started to form at the end of the CVD process, when the gas flow was closed and the sample started to cool down. For this reason, NWs were not always clearly visible in top-view FESEM scans. The inner regions of the samples were not covered as much as the edges, and the growth of nanostructures was more limited in height (see image f of Fig. 1), probably due to a not very efficient transport of the vapour-phase material from the source to the substrate. Indeed, in these regions nanostructures with low aspect-ratio, more similar to nanorods (NRs), were observed.

The crystal structure and orientation of ZnO nanostructures were evaluated by means of X-ray Diffraction measurements. The

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