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Influence of the ZnO nanoarchitecture on the electrochemical performances of binder-free anodes for Li storage

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ABSTRACT

Zinc oxide nanoarchitectures may be employed as binder-free, high specific capacity anodes for lithium batteries. By means of simple and low-impact wet chemistry approaches, we synthesized 1D (nanorods), 2D (single- and multi-layered nanosheets), and 3D (nanobrushes) ZnO arrays. These nanoarchitectures were compared as far as concerns their electrochemical properties and the structural modifications upon lithiation/delithiation. The best results were offered by 2D nanosheets, which showed reversible capacity of the order of 400 mAhg^{-1} after 100 cycles at 1 Ag^{-1}. This was due to: i) small nanoparticles, with average diameter of about 10 nm, which maximize the array specific surface area and favor the formation of the LiZn alloy; ii) the presence of a mesoporous texture, which allows larger space for accommodating the volume changes upon lithiation/delithiation. However, also these 2D structures showed large irreversible capacity losses. Our work highlights the need for more efficient buffering solutions in ZnO binder-free nanostructured anodes.

1. Introduction

Lithium-ion batteries still have insufficient energy density, power density and lifetime for massive use in electric vehicles, and also suffer of serious safety problems [1,2]. Efforts to improve battery performances are directed to improve materials and architectures of both the electrodes and the electrolyte compartments. As far as the anode is concerned, in particular, the main task is to substitute graphite with materials more performing in terms of specific capacity, structural and chemical stability. A help in this sense can come from nanotechnology, which allows exploring a wide range of architectures able to improve electrode kinetics and to control harmful strains.

Recently, innovative nanoarchitectures of different semi-metals, metals or metal oxides were reported, which showed good properties, e.g. high surface area, short Li$^+$ diffusion path lengths and high rate of electron transport [3,4]. These moieties included carbon- and silicon-based materials, alloys, and transition metal oxides, obtained in form of 1D (e.g. nanorods) and 2D (e.g. nanosheets) nanostructures. Most of these architectures may be also grown as nanostructured films on metal substrates, and directly used as binder-free electrodes, which offer easier electrode processing, faster ions and electrons diffusion, and better accommodation of the strains deriving from lithium (de)/intercalation, or (de)/alloying reactions [5]. In this frame, nanostructured ZnO was recently investigated as anode for LiBs for its high theoretical capacity (978 mAh g^{-1}) and good chemical stability [6]. In addition, it is a low-cost material with a reduced environmental impact, which is a relevant aspect to be considered in the development of Li-ion and post-Lithium batteries. In contrast, it suffers of poor kinetics and a drastic volume change during cycling, which determines large capacity fading during the initial cycles and reduced life cycle.

Li storage in ZnO anodes includes two reversible reactions, namely the formation and decomposition of Li_2O, accompanied by the Zn/Li alloying steps [7]. Several ways to improve the ZnO electrochemical performances were tried: i) coating with carbon-based materials, which increases cycling stability and rate capability [8–12]; ii) doping with transition metals, like Co or Fe, which resulted in a remarkable enhancement of the specific capacity [6]; iii) switching from bulk to nanostructures. Following this last approach, many nanoarchitectures were explored ranging from micro- and nanorods [7,13–15] to nanotubes [16], needles, nanowires [17,18] and nanosheets [19–22]. Recently, MOF-based ZnO@ZnO quantum dots/C nanorods arrays showed good properties in terms of capacity retention at relatively high currents [23]. We recently reported ZnO nanosheets covered with a graphite layer, which showed capacity of 600 mAh g^{-1} after 100 cycles at a specific current as high as 1 Ag^{-1}[24].

However, significant results variability is found in the literature about the electrochemical performances of similar ZnO anodes. In fact, the functional properties strictly depend on synthesis procedures, anode preparation technique (binder-free vs. ink-based), and morphological features (porosity, particle dimensions, etc.). In spite of the

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several ZnO architectures proposed so far, a full evaluation of the nanostructure stability as a consequence of the electrochemical reactions involving ZnO as anodes is still lacking. Drastic morphology degradation phenomena, such as nano-amorphization, nano-cracking or disordering of the porous network, were proved only in the case of one-dimensional nanostructures [12,23].

Here, we investigated the electrochemical properties of 1D, 2D and 3D ZnO nanoarchitectures directly grown on the current collector as binder-free electrodes. In detail: a) nanorods (NR), b) nanosheets (NS), c) multi-layer nanosheets (NS-ML), and d) 3D hierarchical nanobrushes (NB) were prepared by means of a versatile hydrothermal synthesis, which was properly optimized in order: i) to be suitable for non-specific substrates; ii) to maximize the film surface area by modulating the film porosity; iii) to obtain finer morphological features.

2. Experimental Section

2.1. Synthesis

All the samples investigated in this study were deposited on stainless steel (SS) disks (diameter: 10 mm, thickness: 0.5 mm, AISI 304, Goodfellow), used as both the substrate and the current collector for subsequent electrochemical characterization. Prior to deposition, the as-received disks were subjected to a careful mechanical polishing (employing first P600 and then P2500 abrasive papers), and subsequently washed with high purity acetone. After evaporation of the solvent, the disks were covered with a 200 nm-thick layer of platinum. The Pt coating, besides protecting the steel during the synthesis and preventing its potential oxidation during the annealing step, had the scope to improve oxide layer adhesion and to ensure optimal electrical contact between the oxide layer and the SS current collector. The oxide layers were deposited by means of a simple and low-cost hydrothermal procedure. In the following, details of the hydrothermal synthesis and calcination treatments were reported separately for each nanoarchitecture.

2.2. 1D- Nanoarchitecture: synthesis of ZnO nanorods (NRs)

ZnO nanorods were synthesized by means of a simple all-solution strategy based on an optimized hydrothermal growth of long NRs onto a patterned ZnO seed-layer. The synthetic conditions of both the seed-layer and the NRs were taken from our previous works [25,26] and modified, due to the switch to a different substrate (Pt-coated SS instead of glass slides or Si substrates), in order to obtain good deposition and adhesion of the oxide seed layer and successful growth of the 1D-nanoarchitecture. The ZnO seed-layer was obtained by starting from a hydrogel-based precursor, through three main steps: i) deposition of the hydrogel onto the substrate by spin-coating; ii) photo-polymerization of the film via UV radiation; iii) thermal degradation of the organic components at 500 °C in air. The hydrogel-precursor solution was prepared mixing 350 μL of a solution containing a source of Zn^{2+} cations (hereby called “A”) with 1.0g of a polymeric solution (hereby called “B”). “A” was prepared dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (32 wt%) in MeOH (68 wt%); “B” was obtained by mixing poly(ethylene glycol) dimethacrylate (70 wt%), 2,2-dimethoxy-2-phenylacetophenone ‘DMPA’ (13 wt%), used as photo-initiator, and MeOH (17%). All the employed reagents were purchased from Sigma-Aldrich. On each substrate, 10 μL of the hydrogel-based precursor were spin-coated (SPIN150, Single Substrate Spin Processor, SPS) employing the following conditions: step 1) v=500 RPM, t=15 s; step 2) v=4000 RPM, t=30 s; acceleration=350 RPM s^{-2} for both steps. Subsequently, photo-polymerization of the film was carried out during 2 h of UV-irradiation (2 UV lamps, P=15 W, λ_{max}=310 nm). The hydrogel layer was treated for 30 min at 500 °C in static air, with a heating rate of 5 °C/min, in order to remove the organic components and achieve the crystallization of the ZnO seed-layer. The ZnO NRs were hydrothermally grown onto the seed layer according to the procedure below reported. The solution was directly prepared into a 100 ML-Duran® GL45 glass laboratory bottle, mixing at room temperature and under magnetic stirring hexamethylenetetramine (HMT) 2.4 M, NH_4OH (28.0–30.0% NH_3 basis) and polyethylenimine (PEI), used as surfactant, previously diluted 1:3 (by weight) in distilled water and finally, adding drop-wise and under a vigorous magnetic stirring 40 mL of a 50 mM $Zn(NO_3)_2 \cdot 6H_2O$ solution. The concentration of chemicals in a 80 mL solution for the hydrothermal growth, were: 25 mM HMT, 610.5 mM NH_4OH, 2.24 mM PEI, 25 mM Zn^{2+}. Three Pt-coated SS substrates were vertically introduced in the bottle, being each one fastened with PTFE tape to a 2.5 cm x 2.5 cm-microscope glass slide (previously cleaned with high purity acetone), and the bottle was then sealed with a PTFE cap. The hydrothermal synthesis was carried out in a heater at 90 °C for 5 h. The substrates, now uniformly covered with ZnO NRs, were rinsed several times with distilled water and dried at room temperature for at least 48 h, before performing the characterization and the electrochemical tests.

2.3. 2D- Nanoarchitecture: synthesis of ZnO nanosheets (NSs)

The ZnO NSs were grown directly on the SS substrates following the procedure described in our previous work [24]. In detail, using the same type of laboratory bottle employed for the NRs growth, a 80 mL-solution for the hydrothermal growth of the NSs was prepared by mixing, at room temperature and under magnetic stirring, the following aqueous solutions: hexamethylenetetramine (HMT) 2.4 M, sodium citrate dibasic sesquihydrate 0.1 M and $Zn(NO_3)_2 \cdot 6H_2O$ 160 mM. The concentration of the chemical in the final solution were: 80 mM HMT, 1.8 mM citrate, 80 mM $Zn(NO_3)_2 \cdot 6H_2O$. As already described for the synthesis of NRs, the substrates were introduced in the bottle that was then sealed with a PTFE cap. The hydrothermal synthesis was carried out in a heater at 60 °C for 6 h. As the result of this step, a non-porous metal-organic phase was produced, which needed further thermal treatment. The films were then rinsed with distilled water and dried at room temperature for at least 24 h, before the annealing step, which was performed in a tubular oven at 350 °C for 1 h, with a heating rate of 5 °C/min.

2.4. 2D- Nanoarchitecture: synthesis of ZnO multi-layer nanosheets (ML-NSs)

Triple-layer ZnO nanosheets (ML-NSs) were prepared performing the hydrothermal synthesis of the NSs array (as discussed in section 2.1.2), layer by layer, consecutively for three times, with a calcination treatment after each deposition step.

2.5. 3D- Nanoarchitecture: synthesis of hierarchical ZnO brushes (NBs)

The ZnO NBs structures were obtained by carrying out the NR and NS syntheses described above in sequence, with no variation in the procedures. First, ZnO NRs were hydrothermally grown on the ZnO seed-layed previously deposited on the conductive substrate. After washing with distilled water and subsequent drying for at least 48 h, the substrates were tightened again to a slide glass with PTFE tape, and the nanosheets were synthesized directly on the NRs by the hydrothermal process described above.

2.6. Characterization

The polycrystalline film and the various ZnO nanoarchitectures, grown on Pt-covered SS substrates, were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (HiRes-SEM) and profilometry. XRD measurements were carried out by means of a