

High efficiency electrodes based on nanostructured materials for energy devices

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Abstract

In the last years we have focused our attention on the electrochemical synthesis of nanostructured materials for energy. The synthesis procedure is a typical bottom-up procedure and it is based on the electrodeposition of metals, alloys, pure and mixed oxides inside the pores of nanostructured membranes acting as templates [1-4]. After dissolution of the template, a more or less ordered array (in dependence on the template) of either nanowires or nanotubes is obtained. Their aspect ratio (length/width) can be adjusted by controlling the electric charge passed during the synthesis and high values can be achieved.

Both anodic alumina and polycarbonate membranes are currently used as templates in dependence of the desired morphology. Anodic alumina membranes can be produced by anodizing aluminum in aqueous solutions where the anodic oxide is scarcely soluble. In these conditions, well ordered structures are formed with cylindrical channels perpendicular to the surface and located at the centre of an array of hexagonal cells. The diameter of channel and the size of cell depend on the nature of the anodizing solution, applied voltage and temperature, while the thickness can be changed with the passed electrical charge. Consequently, it should be possible to tailor membranes with morphological features suitable for every specific applications. Track-etch polycarbonate membranes are constituted by circular pores with uniform diameter which are randomly distributed. The smallest pore diameter may reach 5 nm while pore population is about $10(7\div 11)$ pores m^{-2} . In general, the pores show a cigar-like structure and are not perpendicular to the surface.

As regard the morphology of nanostructures its depends on that of template, in particular for the case of anodic alumina membrane, ordered arrays of parallel nanowires are obtained, while interconnected structures are fabricated by polycarbonate templates. In this last case, the advantage consists in a better mechanical stability of the nanostructures, in particular at high aspect ratios. Tubular structures can also be obtained by electrodeposition into the pores of anodic alumina membranes. The tubular structures of nano/microcrystalline materials hold great potential for various applications due to their high porosity, large specific surface-to-volume ratio. For instance, the development of new functional materials with high porosity is required for optimized performances of dye-sensitized photovoltaic cells, dimensionally stable anodes, metal-ion batteries, electrochemical supercapacitors, hydrogen storage devices, bio-sensors, and gas sensors. In contrast to randomly orientated nanotubes, high density and well-aligned nanotube arrays may provide enhanced and smart functionality.

Different types of materials were fabricated with attention toward those useful for energy applications [5-12]. For instance, for photovoltaic solar energy conversion, nanowires of CIGS (copper, indium, gallium selenide) were deposited and the procedure for in-situ growth of the p-n junction CIGS/ZnS is currently investigated. For electrochemical storage of energy, SnCo alloy was synthesized and tested as anode of Li-ion batteries, while nanostructures of $LiFePO_4$ were fabricated for application as cathodes. Also Pb and PbO_2 nanowires were fabricated for new generation of lead-acid batteries, featured by high utilization degree of active material and a very high charge and discharge rates (up to 10C). In addition, new electrolytes for both Li-ion and lead-acid batteries are under development. Nanostructured materials of interest in the field of water electrolyzers were also fabricated and characterized. In particular we have developed nanostructured electrodes, with very large active area, constituted of PdCo alloys (cathode) and RuO_2 (anode), to be used for H_2 and O_2 evolution reaction respectively. In fact, PdCo alloy is a valid alternative to Pt for H_2 evolution, whilst ruthenium oxide is one of the most active catalysts for O_2 evolution.

Here, we describe the electrochemical deposition of different nanostructures into nanoporous template, leading to regular arrays of either nanowires or nanotubes. In particular the attention will be focused on nanomaterials for batteries (Figure 1). Scanning electron microscopy was used in order to characterize the morphology of the different nanostructures, consisting of perfectly cylindrical wires or tubes, with an having uniform diameter throughout length. Crystallographic structure and chemical composition were also investigated by energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy. The influence of different parameters, like temperature, solution composition and pH of solution, on growth and morphology of metal oxide nanostructures was studied, whilst nanostructures length was controlled by the electrodeposition time.

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Figures

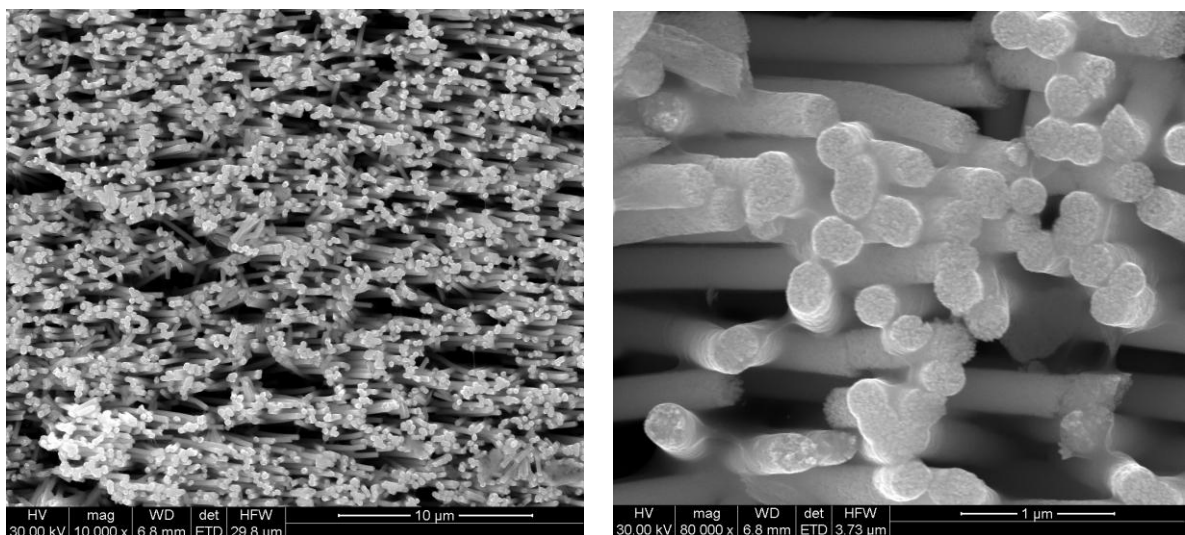


Fig. 1 Nanostructured lead dioxide electrode.