

Nanostructured Electrochemical Devices for Sensing, Energy Conversion and Storage

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Nanostructured materials are attracting growing interest for improving performance of devices and systems of large technological interest. In this work, the principal results about the use of nanostructured materials in the field of electrochemical energy storage, electrochemical water splitting, and electrochemical sensing are presented. Nanostructures were fabricated with two different techniques. One of these was the electrodeposition of the desired material inside the channels of a porous support acting as template. The other one was based on displacement reaction induced by galvanic contact between metals with different electrochemical nobility. In the present work, a commercial polycarbonate membrane was used as template. In the field of the electrochemical energy storage, the attention was focused on lead-acid battery, and it has been found that nanostructured morphology enhances the active mass utilization up to about 80%, with consequent increase of specific energy and cycling rates to unattainable values for the commercial battery. Nanostructured Ni-IrO₂ composite electrodes showed valuable catalytic activity for water oxidation. By comparison with other Ni-based electrocatalyst, this electrode appears as the most promising anode for electrochemical water splitting in alkaline cells. Also in the field of sensing, the nanostructured materials fabricated by displacement reaction showed performance of high interest. Some new results about the use of copper nanowires for H₂O₂ sensing will be showed, evidencing better performance in comparison with copper thin film. In this work, we will show that nanostructured electrodes are very promising candidate to form different electrochemical setups that operate more efficiently comparing to device with flat electrode materials.

1. Introduction

Nanomaterials are very promising to enhance device performances for sensing, sustainable energy production, and energy conversion and storage, as extensively reported in the literature (Fromer et al, 2013; Zhang et al, 2013; Si et al, 2013). In this field, one of the most severe challenge is to find suitable methods for fabricating nanomaterials. Over the years, numerous preparation methods were proposed in the literature, but not all of them are easily scalable and economically advantageous for industrial application. In this context, electrochemical deposition in template is a facile method for fabricating either two- or one-dimensional nanostructured materials because it allows to easily adjust the fundamental parameters controlling their final features (Li et al, 2013). In addition, electrochemical processes are, usually, cheap and environmental friendly, and they can be easily scaled-up from lab to industrial level. For these reasons, the attention was focused on the synthesis of different type of nanomaterials for application in electrochemical sensing of H₂O₂, in lead-acid and lithium-ion batteries, in solar cells, and in electrochemical water splitting. Here, we will present an electrochemical method for obtaining dimensionally stable nanostructured electrode characterized by the presence of uniform array of nanowires and/or nanotubes with very high surface area. The findings demonstrate that nanotechnology is advantageous for improving device performances. In this work, in addition to the fabrication method, also the performance of different nanostructured materials are presented, and discussed.

2. Fabrication method and characterization of nanostructured materials

One- and two-dimensional nanostructured materials were prepared by electrodeposition, starting from suitable precursors dissolved into aqueous solutions (Inguanta et al, 2013a, Piazza et al, 2013, Farinella et al, 2014). One dimensional nanostructured arrays were obtained by electrodeposition into polycarbonate membrane (Whatman, Cyclopore 47) acting as template. Among the different methods for synthesizing nanostructured materials, electrodeposition is cheap, easy to be conducted and easily scalable. In practice, the electrodeposition can be either direct, when the nanostructured materials is directly deposited on the selected support or inside the channels of the porous template (for instance: deposition of metals, alloys or multi element compounds) (Inguanta et al, 2015), or indirect, when the electrochemical polarization provides the suitable conditions for the formation of the desired compound. It is the case, for instance, of the electrogeneration of bases consisting in the electrochemical generation of hydrogen causing a progressive pH enhancement at electrode interface with consequent precipitation on the electrode surface or inside the template of the desired compound when its solubility limit is achieved (Inguanta et al, 2011). Of course, electrodeposition kinetics is different depending on two- or one-dimensional nanostructure deposition. In the last case, it is important to highlight that, for electrodeposition into a nanoporous template, such as polycarbonate membranes (channels usually 200 nm in diameter and 15-20 μm long), the control of deposition parameters is more challenging, because the mass transport in a confined ambient occurs at different rate than in bulk solution. In particular, electrolyte composition and deposition mode are two fundamental parameters that must be fine collod. The same problems are not present in the case of two-dimensional materials.

In the case of one dimensional materials, a gold film was sputtered on one side of the membrane in order to make it electrically conductive. Then, a compact layer of material identical to the nanostructured one was electrodeposited on the gold film in order to give dimensional stability to the nanostructured array and to create also a current collector. Different precursors were used, depending on the desired type of nanostructured material. After deposition, template was dissolved by pure CHCl_3 in order to expose totally the nanostructured mass, as shown by the scheme of Figure 1, where figure 1a shows a scheme of nanowires arrangement to be compared with the real image of Figure 1b showing a firm connection of the nanowires to the support, acting, also, as current collector. Figure 1c shows a top-view of the porous mass evidencing the free space between the nanowires.

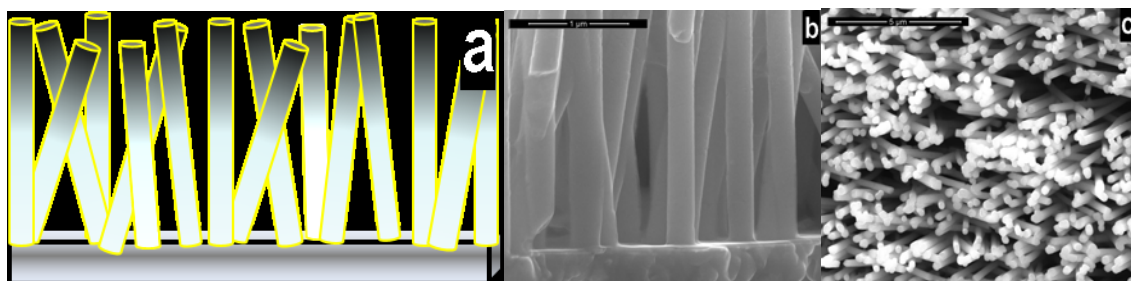


Figure 1 – a): scheme of one-dimensional electrodeposited nanostructures after the template dissolution; b) typical image of nanowires connected to the support; c): top-view of the nanowires

Nanostructures were characterized by XRD, SEM, EDS, RAMAN Spectroscopy, and electrochemical measurements. All these characterization techniques are details in our previous works (Inguanta et al, 2015, Moncada et al, 2014).

3. Electrochemical storage and conversion of energy

In the field of the electrochemical storage and energy conversion, lead-acid battery is a system of great interest owing to the large market penetration. The great success of this battery is due to its safety and cheapness. In addition, its technology, although old, is highly reliable. In lead-acid battery, the active material consists in porous PbO_2 and Pb pressed in the pasted form inside the open space of lead grid. The principal drawback of the lead-acid battery is the low utilization of the active material, essentially due to the significant volume expansion occurring when PbO_2 (cathode) converts into PbSO_4 and, identically, Pb (anode) converts into PbSO_4 too, according to the following cell reaction



In the charge state, sulphuric acid is soaking porous mass. When discharge starts, the conversion reaction proceeds from the electrode surface toward the interior. The volume expansion, during discharge, causes a

progressive pore shrinkage with possible complete occlusion, determining interruption of the electrolyte continuity. Consequently, the interior part of the active mass remains unreacted. Usually, the level of unreacted PbO_2 can reach a value close to 50%, whilst 65% is the typical value for Pb electrode (Pavlov, 2011). The low level of active mass utilization determines low energy density that reaches a maximum value of 40 Wh Kg^{-1} in SLI batteries rated at 20h (Pavlov, 2011). Really, for maximizing the specific energy is mandatory to discharge at low rate in order to slow down the pore shrinkage. For this reason, thin plates are used for applications requiring high discharge rate. The nanostructured PbO_2 electrodes prepared in our lab by electrodeposition in template provides a satisfactory solution to this problem. Nanostructured electrodes were obtained by a two-step procedure from an aqueous solution of $1\text{M Pb(NO}_3)_2$ and 0.3M HNO_3 . In the first step, a current collector of PbO_2 was electrodeposited onto the Au-coated side of the membrane at constant current, 0.01 A cm^{-2} . During the second step, growth of PbO_2 nanowires inside template channels was conducted at constant potential, $1.5 \text{ V vs. calomel standard electrode}$ (Moncada et al, 2015a, Inguanta et al, 2013b). In these deposition conditions XRD and Raman analyses showed that nanostructures consist of a pure β phase. Their morphology, investigated by SEM, is similar to that presented in Figures 1b and c. The free space between the nanowires accommodates the volume expansion without interruption of the electrolytic continuity. In addition, being each nanowire completely immersed into sulfuric acid 5M and owing to the nanometric size (200 nm diameter), conversion reaction encompasses totally the mass of the nanowires. As consequence, the energy density, referred to the PbO_2 mass, is 80% of the theoretical one, as evidenced in Figure 2. In particular, the most significant results shown in this figure are the high discharge capacity and efficiency at as a high cycling rate as 2C for about 1,000 cycles. During the charge/discharge process of electrode, several unintentional interruptions of power supply occurred (marked with * in Figure 2). Nevertheless the recovery of efficiency after the interruptions was significantly high at values between 85-87%. This reveals that nanostructured electrodes adapt quite well to discontinuous operational conditions of battery.

Such performances are unattainable by commercial lead acid batteries that must be cycled at low rate (usually 0.05C) for obtaining long life time (Moncada et al, 2014, Moncada et al, 2015b). Further work on the fabrication and characterization of nanostructured Pb is in progress, in order to assembly lead-acid battery at lab-scale with both electrodes having nanostructured morphology.

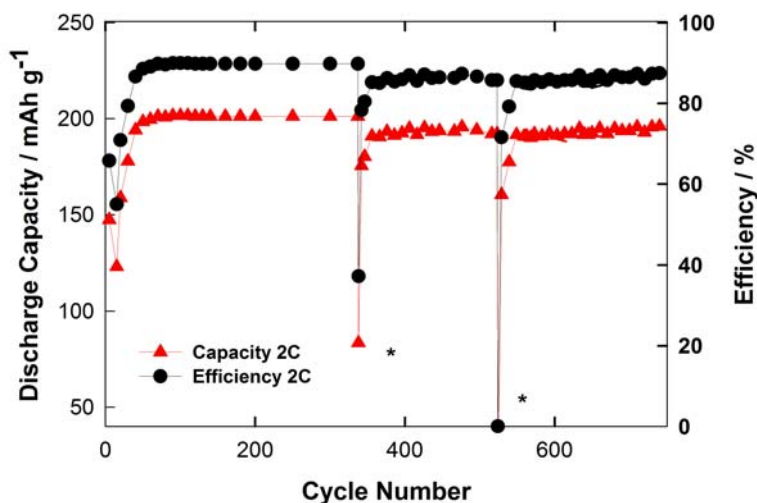


Figure 2 - Discharge capacity and efficiency at 2C vs. numbers of cycles

4. Ni-IrO₂ nanowires for electrochemical water splitting

Composite Ni-IrO₂ nanowires were prepared by electrodeposition in nanoporous polycarbonate membranes acting as template. The potential application of this material can be envisaged in the field of the electrochemical water splitting, where Ni-IrO₂ could act as anode for oxygen evolution, which is a highly hindered reaction. The challenge was the fabrication of a nanostructured electrode with better electrocatalytic activity than electrodes of the same materials but with different morphology and either with or without IrO₂. The innovation was the increase of catalytic activity due to the combination of Ni nanowires with IrO₂ nanoparticles (Battaglia et al, 2014). A water splitting cell can be considered a system for energy storage, because

the principal product is hydrogen, which is a high value energy carrier. For the fabrication of the composite electrode, Ni was initially electrodeposited, then nanoparticles of IrO₂ catalyst were electrodeposited on the Ni nanowires after the template dissolution. Deposition of the catalyst was carried out either under constant current or by cyclovoltammetry at 10 mV s⁻¹. A typical morphology of the composite electrode is shown in Figure 3, where the deposition of IrO₂ was conducted at 1 mA cm⁻² for 3 h. XRD showed the presence of peaks of only Ni, thus it is possible to conclude that iridium oxide was deposited in an amorphous phase.

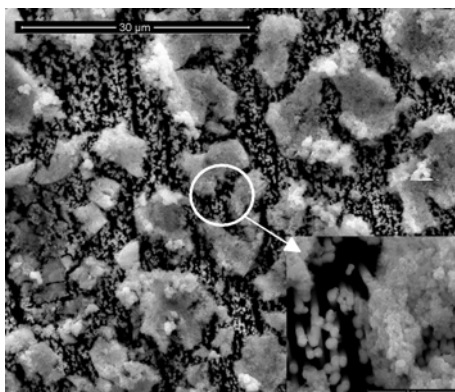


Figure 3 - SEM image, with high magnification inset, of iridium oxide on Ni nanowires after amperostatic deposition at 1 mA cm⁻² for 3 h.

Cell potential vs. $\ln i$ (where i is the current density referred to the geometrical area) plot of the composite electrode in comparison with Ni nanowires, with Ni film, and with Ni sheet is shown in Figure 4.

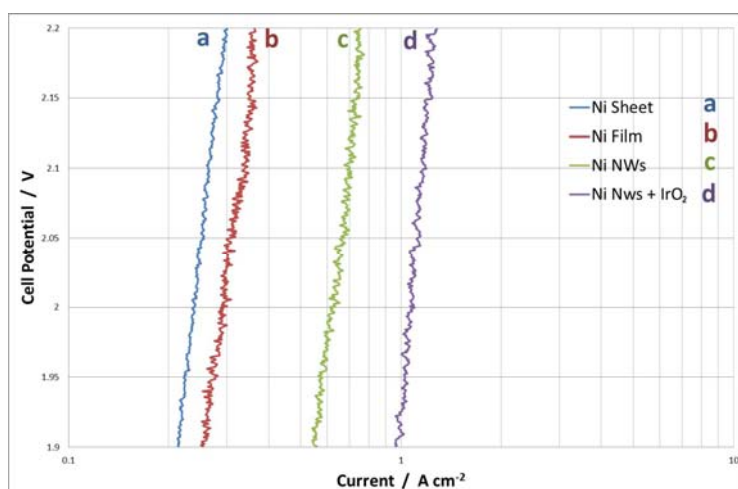


Figure 4 - Quasi-steady-state polarization curves (0.01 V min⁻¹) measured for different electrodes in 1 M KOH at room temperature.

This Figure clearly evidences the beneficial effect of the IrO₂ addition. Really, the best performance in terms of electrode potential vs. $\ln i$ is exhibited by Ni-IrO₂ nanostructured electrode. In particular, IrO₂ was also deposited on carbon paper (CP) and it was found that the combination of Ni nanowires with IrO₂ exhibits a higher catalytic activity than the CP-IrO₂ composite electrodes. It was also found that, in otherwise identical conditions, a cell for water splitting works at lower potential and for very long time with Ni-IrO₂ electrodes than with Ni film or pure Ni nanowires. This means that Ni-IrO₂ composite electrode is very stable in alkaline solution and able to work for long time without fading. In conclusion, we can say that it is possible to improve significantly the kinetics of electrochemical water oxidation in alkaline solution by using Ni nanowires modified by partial coverage with IrO₂ particles. More work is in progress for fabricating a nanostructured electrocatalyst acting as cathode for hydrogen evolution. This reaction is kinetically easier, but noble metals of Pt group are

necessary. On the contrary, taking advantage from the nanostructured morphology, new composite materials are under investigation.

5. Nanostructured electrochemical sensors for H₂O₂ detection

Certainly, sensing is one of the preferential application of nanostructured materials, because the high specific surface (real surface to geometrical one) favours the achievement of low detection limit, which is a fundamental parameter qualifying a sensor. Therefore, in order to ascertain the possible advantages in terms of selectivity, resolution, and sensitivity, copper nanowires were fabricated and characterized for the sensing of H₂O₂. Although hydrogen peroxide is known as a cytotoxic molecule, in recent years, it has been found that, in air-living organism, has important roles as a signalling molecule in the regulation of a variety of biological processes. A valuable review about the H₂O₂ formation mechanism, and its roles can be found in (Weal et al, 2007). In the present case, the nanowires were grown inside the channels of a template consisting in polycarbonate membrane, by a displacement reaction induced by galvanic contact between metals with different electrochemical standard potentials (Battaglia et al, 2013, Inguanta et al, 2013c, Larosa et al, 2012)). The galvanic contact was established between a sacrificial anode (usually Al) immersed in 1M KCl, and the gold film covering one side of the template, which is in contact with solution containing precursor of the nanowires, that in this case is 0.1M CuSO₄·5H₂O with 0.05M H₃BO₄ at pH 2. The scheme of the experimental apparatus is shown elsewhere (Inguanta et al, 2008). The potential difference between the two metals is the driving force for the deposition of the nanowires, according to



With this method an array of ordered and uniform nanowires was obtained with a morphology very similar to that showed in Figures 1b and c. XRD results showed that nanowires consist of polycrystalline copper, while by EDS spectroscopy we have observed the formation of a pure phase. A typical calibration curve for detection of H₂O₂ by copper nanowires is shown in Figure 5. It was taken from stepped amperometric curve after a controlled amount of H₂O₂ solution was added to phosphate based electrolyte. A linear response from 60 μM to 3700 μM of H₂O₂ was obtained with a R² coefficient greater than 0.999 and with sensitivity of about -0.509 μA/μM cm², which is a very satisfying value. In addition, a LOD (Limit Of Detection) of 13.8 μM was measured, which is better than 19.4 μM featuring copper film sensor. In general, it has been found that the nanostructured morphology greatly improves the sensing parameters for hydrogen peroxide in comparison with copper film. The strong difference is likely due to the large real surface of the nanowires in comparison with that one of thin film, which is about 70 fold less. A drawback in the use of the nanowires is the low wettability, hindering the porous mass permeation by aqueous solution.

This disadvantage, determining a low utilization of the sensible mass, can be limited or removed, decreasing the solution surface tension by addition either of ethanol or of suitable surfactants. Moving from these satisfying findings, more work is in progress for investigating other nanostructured materials for sensing.

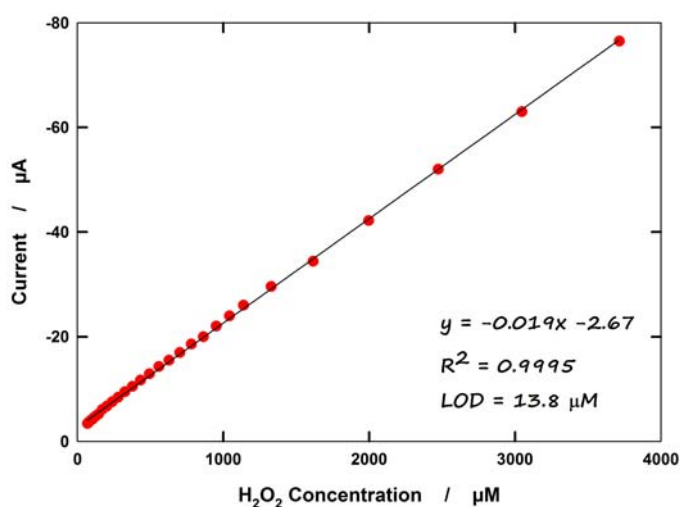


Figure 5: Calibration line of Cu nanowires for detection of hydrogen peroxide

6. Conclusions

Nanostructured material can be synthesized either by electrochemical deposition or by displacement reaction due to the galvanic contact between metals with different standard electrochemical potential. In both cases, a porous polycarbonate membrane was used as template, which was chemically dissolved after deposition exposing the nanostructures whose morphology was conformal to the template. In the case of the displacement reaction, the growth of the nanostructures occurred spontaneously without supplying external energy. We presented three application fields where the nanostructured materials can be used successfully. They concern electrochemical energy storage, electrochemical water splitting, and electrochemical sensors. For each of these applications, satisfying results were found, encouraging to conducting further investigations for both overcoming some drawbacks still existing, and checking the possible use of these materials for other applications.

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