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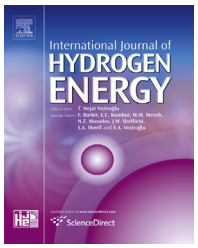

Facile electrochemical synthesis, using microemulsions with ionic liquid, of highly mesoporous CoPt nanorods with enhanced electrocatalytic performance for clean energy

A. Serrà, E. Gómez, E. Vallés *

Grup d'Electrodeposició de Capes Primes i Nanoestructures (Ge-CPN), Departament de Química Física and Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Catalonia, Spain

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ABSTRACT

We have established a facile and generalizable electrochemical synthesis of metallic mesoporous nanorods in the nanochannels of commercial polycarbonate membranes using microemulsions containing ionic liquids. Herein, we report the preparation of magnetic CoPt nanorods with various meso or nanopores distributions, depending on the microemulsion type (ionic liquid –in-water (IL/W), bicontinuous (β) or water-in-ionic liquid (W/IL)). The synthesized porous nanorods show a much enhanced electrocatalytic activity for methanol oxidation in comparison with compact Pt nanorods (up to 12 times) or Pt/C electrocatalyst (Pt nanoparticles or commercial black platinum). Therefore, the synthesized CoPt mesoporous nanorods could be excellent catalysts in direct methanol fuel cells (DMFC's), as they have high surface areas, large pore volumes and high corrosion stability, and they exhibit promising catalytic properties.

Introduction

In the past decade, a wide range of proposals have been devoted to synthesizing different nanomaterials as nanoparticles [1–3] or nanorods [4–6], due to their potential applications, particularly in the areas of catalysis, adsorption, fuel cells and biomaterials.

Nowadays, nanomaterials arouse an enormous interest as regards in energy conversion and storage devices, due to their effectiveness as electrocatalysts for Methanol (DMFCs) or Ethanol (DEFCs) Fuel Cells [7,8]. However, the disadvantages of the high cost and low supply of Pt-based catalysts, the crossover effect, as well as their poor durability, seriously limit their commercial availability. Currently, significant improvements in the DMFCs have been made by combining different tactics, but several problems still remain unsolved. The major advances focus on enhancing their durability and their electrocatalytic activity by increasing both the surface –volume ratio and the catalytic performance [9–12].

* *Corresponding author.*
E-mail address: e.valles@ub.edu (E. Vallés).
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The use of nano or mesoporous structures has been proved to be an effective approach to lowering the loading of Pt and improving its catalytic activity as a consequence of their high surface-volume ratio. Mesoporous nanomaterials can be prepared through several methodologies including the traditional hard-templating [13,14], phase separation [15,16] and alloy-dealloying approaches [17–19], amongst others. In the last years, soft-template systems like liquid crystals have been proposed as a new synthetic route [20–23]. Nevertheless, these approaches are not very simple enough, so trying to find new facile and successful pathways to produce nano or mesoporous nanomaterials of metals and alloys has become a new challenge in the fabrication of nanocatalysts.

Recently, surfactant micelles have been demonstrated as a useful tool to synthesizing mesoporous Pt nanorods in the confined space of polycarbonate membranes [24]. This method, however, has only been used to fabricate platinum nanorods with a single pore size and in very specific conditions.

The preparation of bimetallic platinum catalysts with 3d-transition metals (Fe, Co, Ni, among others) is another widely applied strategy to enhance the electrochemical activity for methanol oxidation (reduction of poisoning by adsorbed intermediates) and to reduce the catalyst costs [25,26].

Lastly, magnetic nanostructures have emerged as a new type of promising multi-functional architectures for potential applications in data storage, magnetic carriers for biomedical devices or magnetic catalysts [27,28]. The manipulation and recyclability of the catalytic material would be easier with magnetic catalysts, because their magnetic behaviour facilitates the anchoring or recovery of the material by applying an external magnetic field [29,30]. Magnetic CoPt alloys permits combining both characteristics. Moreover, the CoPt alloys are generally more stable than other platinum alloys (with Ni, Fe or V), due to the higher degree of alloying of the cobalt with the platinum [31,32].

Herein we report a new, facile and successful approach for synthesising CoPt magnetic nano or mesoporous nanorods in a single pot. These are grown, by means of electrodeposition method, in the nanochannels of commercial polycarbonate membranes, using water-in-ionic liquid (W/IL) as well as bicontinuous (β) and ionic liquid-in-water (IL/W) microemulsions. The bimetallic nanostructures synthesized with this procedure show much enhanced activity, strong methanol tolerant capability and corrosion resistance in comparison with compact CoPt nanorods, commercial Pt/C catalysts or other recent state-of-the-art Pt-based nanostructures.

Experimental

Materials

Non-ionic surfactant p-octyl polyethylene glycol phenyl ether a.k.a. Triton X-100 (Acros Organics, 98%), ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate a.k.a bmimPF_6, Arcos Organics, >98%), chloroform (Sigma–Aldrich, +99%), boric acid (Merck, 99.8%), Co(II) chloride (Carlo Erba, >98.0%), sodium hexacloroplatinate (IV) hexahydrate (Aldrich, 98%), ammonium chloride (Fluka, >99.5%), boric acid (Merck, 99.8%), and deionized water (Millipore Q-System) with a resistivity of 18.2 MΩ cm^{-1}.

Microemulsion preparation

Microemulsions were prepared by mixing a CoPt aqueous solution (2.5 mM $CoCl_2$, 1.2 mM Na_2PtCl_6, 0.1 M NH_4Cl, 10 g dm^{-3} H_3BO_3 and pH = 4.5) (W), an ionic liquid (bmimPF_6) (IL) and a surfactant (Triton X-100 (p-octyl polyethylene glycol phenyl ether)) (S) at 25 °C in different proportions, to define different kind of microemulsions. According to the bibliography [33], a 66.5 wt. % of water, 5.0 wt. % of bmimPF_6 and 28.5 wt. % of Triton X-100 forms an ionic liquid-in-water microemulsion (IL/W), a 55.8 wt. % of water, 7.0 wt. % of bmimPF_6 and 37.2 wt. % of Triton X-100 forms a bicontinuous microemulsion (β) and a 26.7 wt. % of water, 11.0 wt. % of bmimPF_6 and 62.3 wt. % of Triton X-100 forms a water –in-ionic liquid microemulsion (W/IL). We use these proportions for preparing the microemulsions, but substituting the pure water for the CoPt electrolytic solution. Electrodeposition will take place from the aqueous component of the microemulsion.

Electrosynthesis of CoPt nanorods

20 μm-thick commercially available polycarbonate (PC) membranes (Millipore Co., USA) with 200 nm pore size diameter, metalized by sputtering with gold (100 nm-thick) on one side, were used to synthesize the nanorods. The electrochemical fabrication was performed at room temperature (25 °C) using a three-electrode electrochemical system with a platinum wire, PC membrane, and an Ag/AgCl (3 M KCl) electrode as counter, working and reference electrodes, respectively, by applying a constant potential of −1.05 V (controlled by potentiostat/galvanostat Autolab with PGSTAT30 Equipment and GPES software) at 25 °C. Prior to the electrodeposition, the PC membranes were immersed 12 h in the different media to assure a uniform filling of the pores.

Nanorods characterization

In order to analyse the morphology and structure of the nanorods, the sputtered gold layer was etched with I_2/I- solution and the polycarbonate membrane was dissolved with chloroform and washed with chloroform (x3), ethanol (x3) and water (x2). The nanorods morphology was analysed by using Field-Emission Scanning Electron Microscopy (Hitachi 800 MT) and High-Resolution Transmission Electron Microscopy (Jeol 2100). An X-ray analyser incorporated in a Leica Stereo Scan S-360 Equipment was used to determine the elemental composition. Furthermore, to test the electrocatalytic activity for the methanol oxidation and the corrosion behaviour, a glassy carbon electrode was used as a support in which to deposit the nanorods by means of an ink with water and 5 wt. % of Nafion solution.

Results and discussion

The manufacturing procedure of the CoPt nanorods implies the electrodeposition of the CoPt in the interior of the channels of the polycarbonate membranes. Therefore, different CoPt nanorods (nano/mesoporous or compact as a reference)