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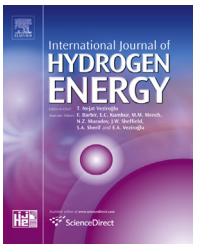

Platinum–carbon electrocatalytic composites via liposome-directed electrodeposition at conductive diamond

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ABSTRACT

A Pt precursor was entrapped in phosphatidylcholine-cholesterol vesicles and the liposomal suspension was used for direct electrodeposition of a Pt-based catalyst on boron-doped diamond (BDD). The average size of the deposited particles (*ca.* 15 to *ca.* 40 nm) is closely related to that of the liposomes and Pt particles are partially embedded into a carbonaceous matrix. Methanol anodic oxidation was used for gauging the electrocatalytic activity of the composites and it was found that the electrodeposition with prior adsorption of the liposomes enables more efficient use of platinum. Without preliminary adsorption, a much higher resistance to fouling was observed for the electrocatalyst. This behavior was ascribed to the presence on the electrodes surface of PtO_2 and of a higher amount of oxygenated carbon states. These species act as oxygen donors contributing to an easier eviction of the adsorbed CO, thus partially regenerating active sites from the electrocatalyst surface.

Introduction

Liposomes, spherical vesicular microscopic systems consisting of one or more amphiphilic lipid bilayers and an equal number of aqueous compartments [1], can fulfill a multitude of functions due to the wide range of possibilities to purposefully modify their surface and/or bulk structure by appropriately adjusting the preparation conditions (see Ref. [2] and references therein). Liposomal systems are currently being studied extensively mainly as delivery systems for various drugs [3,4] and genes [5,6] or for biosensor applications [7], although they also attracted much interest as promising templates for the synthesis of new nanostructured composites with propitious catalytic features [8]. Due to structural similarities, liposomes have also been successfully used as models for cell membranes [9–11] and it was postulated that charge transfer across amphiphilic bilayers takes place both in ways that mimic membrane transfer in living cells [12,13] and through mechanisms involving destructive effects of the electric field on the liposomal membranes [14].

Several electrochemical techniques have been used for the investigation of vesicles or bilayers properties and for the elucidation of the formation mechanisms of self-assembled

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structures on different electrodes [15–18]. Moreover, the electrochemical behavior of liposomes containing various electroactive species, including metal ions (either dissolved in their bulk or incorporated into their membranes), was also sporadically scrutinized [19,20]. It is widely accepted that the interaction between lipid bilayers and solid surfaces is the result of several contributing factors, such as van der Waals forces, double-layer structure, hydration, hydrophobic interactions and thermal undulation, and that its precise nature is related to the specific properties of the involved lipids and solid surfaces [21]. Thus, when interacting with a solid electrode surface, liposomes can generally form either supported lipid monolayers and supported planar bilayers or supported vesicle layers [22,23]. The latter case might be particularly important when dealing with ionic metal species confined to the bulk of liposomes. This is because the electrostatic charge of the vesicles enhances their tendency to be adsorbed on the electrode surface, while cathodic reduction of the entrapped species could facilitate the *in situ* controlled growth of nanostructured metal particles. Although the literature devoted to such an approach is rather scarce, promising results were reported for the electrodeposition of spongy gold particles from a suspension of liposomes containing the plating solution [22].

The present work sought to establish whether or not liposomes can be used as templates for platinum electrodeposition, as well as the extent to which they could assist in regulating the architecture of the deposits. Due to its conspicuous properties (such as high chemical and electrochemical stability, low background current, high overpotential for oxygen and lack of interference with supported metal particles [23,24]), boron-doped diamond (BDD) was used as support for the deposition of the investigated composites. It is worthy of note that electrochemical deposition of platinum seems to be advantageous because it ensures that all of the noble metal is in direct electrical contact with the substrate. This means that all the catalyst can be, in principle, electrochemically active, which might not be the case with other deposition methods [25]. Methanol anodic oxidation was selected as a well-suited test reaction for assessing the electrocatalytic activity of these composites and corresponding preliminary results are also reported.

Material and methods

Liposome preparation

For this study, liposomes were prepared by the lipid film hydration method. The lipid mixture (phosphatidylcholine: cholesterol 10:1 w/w) was dissolved in chloroform, brought to a thin film in a rotary evaporator and then the film was hydrated with a solution of 65 mM chloroplatinic acid. Hand shaking, alternated with periods of brief sonication was applied before leaving the suspension to sit overnight and complete the swelling process. The obtained suspension was sonicated to reduce vesicle size, and materials not entrapped in vesicles were separated through dialysis.

Preparation of Pt-modified BDD electrodes

As-grown boron-doped polycrystalline diamond films were first subjected for 20 min to a mild anodic oxidation treatment (at 2.5 V in a 0.1 M $HClO_4$ solution) and then used as support for Pt electrochemical deposition, carried out at an applied potential of −0.3 V and by using 0.1 M $HClO_4$ as the supporting electrolyte. Two different deposition procedures were adopted. In the first case, in order to allow liposomes adsorption, BDD substrates were kept in contact for 24 h with the as-prepared liposomal suspension then removed, immersed in the 0.1 M $HClO_4$ solution and subjected to cathodic polarization for 30 min. The second procedure consisted in the direct electrodeposition (at the same applied potential and polarization time) from 25 mL of 0.1 M $HClO_4$ solution in which 500 μL of liposomal suspension was added. Chronoamperometric curves were recorded during the deposition process and the integrated cathodic charge was used for the estimation of the platinum loadings. Electrodes obtained by the two methods will be further denoted as ADS and SOL, respectively. After electrodeposition, both types of electrodes were dried in air for 2 h at 25 °C and heated up to 600 °C for 5 h, in order to remove organic residues and to enable platinum exposure to electroactive species from the solution [26]. A slow heating rate of 1 °C min^{-1} was used to avoid sintering problems. Platinum electrodeposition was also carried out from a vesicle-free plating solution (0.1 M $HClO_4$ + 4.8 mM H_2PtCl_6), at the same applied potential, and the electrodes thus obtained were also used in some experiments, for comparison.

Materials, chemicals and apparatus

Non-genetically-modified soy phosphatidylcholine and cholesterol were obtained from Carl Roth GmbH+Co. KG. and Sigma-Aldrich Co. LLC, respectively. Other reagents and solvents were of analytical grade and all the solutions were prepared using doubly distilled water. Working electrodes consisted of highly boron-doped (*ca.* 10^{21} atoms cm^{-3}) polycrystalline diamond films grown on a silicon substrate through microwave plasma-assisted chemical vapor deposition, and the electrochemical measurements were performed at room temperature in a conventional three-electrode glass cell, with a PARSTAT 4000 potentiostat. A high surface platinum foil and a Ag/AgCl electrode (in saturated KCl solution) were used as a counter and reference electrode, respectively.

The morphology of the samples was investigated by scanning electron microscopy (SEM) with a high resolution microscope (Quanta 3D FEG with Everhart-Thornley secondary electron detector), and by atomic force microscopy (AFM) measurements performed in the non-contact mode by means of XE-100 apparatus from Park Systems. AFM images were taken over an area of 8 × 8 μm^2 and for appropriate display XEI (v.1.8.0) program was used. Statistical analysis of the size of superficial particles observed on the topographic AFM images was carried out by Scanning Probe Image Processor software (SPIPTM v. 4.6.0.0) using the threshold method. Surface analysis performed by X-Ray Photoelectron Spectroscopy (XPS) was carried out on Quantera SXM equipment, with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was Al K_α radiation (1486.6 eV, monochromatized) and

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