The Use of Conductive Diamond – Supported Platinum as Electrocatalyst for Ethanol Oxidation in Acidic Media

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Boron-doped diamond (BDD) was used as substrate for electrochemical deposition of platinum, with a view to obtain electrodes with catalytic activity for ethanol anodic oxidation. It was found that BDD could be used as a replacement for graphitic carbon that is generally used as support for electrocatalysts in fuel cells applications, which could result in improving the projected lifetime of these devises. Furthermore, an anodic pretreatment of the BDD support, performed before Pt electrodeposition, resulted in an increased resistance to fouling of the electrocatalyst during ethanol oxidation in acidic media.

Keywords: conductive diamond, platinum electrodeposition, ethanol oxidation

It has become common knowledge the fact that, in order to be efficiently used for fuel cells applications, an electrode material must exhibit not only high electrocatalytic activity (usually ensured by the presence of platinum and its alloys), but also reasonably good stability under the severe functioning conditions of these energy conversion devices. High resistance to electrochemical oxidation of the platinum substrate is therefore a prerequisite, mainly because this process could result both in the increase of the ohmic resistance of the electrode and in a loss of the mechanical integrity of its structure. Furthermore, in the case of alcohol fuel cells, another important feature of a possible electrode material should be a low susceptibility to deactivation by the adsorption of various intermediary products of the overall oxidation process.

In the effort of improving the projected lifetime of a fuel cell, a relatively new approach is the use of conductive polycrystalline boron-doped diamond as a replacement for graphitic carbons that are generally used as substrates for noble metals electrocatalysts. This attempt is expected to result in a significant enhancement of the stability of the electrodes, due to the outstanding features of the conductive diamond (such as high electrical conductivity, excellent chemical, electrochemical and mechanical stability, low background current, etc) and to the ability to purposefully modify its surface by electrochemical deposition of metal or metal oxides nanoparticles [1-5]. Thus, a number of recent studies have shown interesting electrochemical properties concerning methanol anodic oxidation on BDD-supported platinum particles [6-8].

Another important feature that has attracted much interest is the structure of the BDD layers surface that affects to some extent the electrochemical processes taking place at the electrode / electrolyte interface. It is important to note that, due to the particular conditions of the diamond films preparation (plasma-assisted chemical vapor deposition), the surface of the BDD is hydrogen-terminated and therefore hydrophobic. However, by a controlled surface oxidation process (chemical, electrochemical, thermal or oxygen plasma treatment) the hydrogen atoms linked to the surface can be replaced by oxygen containing functional groups, resulting in a more hydrophilic surface of the BDD. The oxygen-terminated surface thus obtained is essential for ensuring highly reproducible electrochemical features, which are not available when using conventional carbon electrodes [9].

The present work was aimed at studying the possibility of using BDD-supported platinum as electrode material for ethanol oxidation in acidic media. Preliminary results concerning the influence of an anodic pretreatment of the substrate on the electrochemical behavior of the Pt/BDD electrodes are also reported.

Experimental part

Polycrystalline boron-doped diamond layers were deposited on Si(111) substrate by plasma-assisted chemical vapor deposition, according to a previously described method [10]. The electrochemical experiments were performed in a three electrode glass cell at room temperature, by using a PAR 273A potentiostat. The exposed area of the working electrode was 0.07 cm^2 and a platinum wire (surface area, ca. 5 cm^2) together with a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Nitrogen-purged 0.5 M H_2SO_4 solution was always used as the supporting electrolyte and platinum electrodeposition was carried out potentiostatically (applied potential, -0.1 V) from a 2.3 mM H_2PtCl_6 solution. All the substances were analytical-reagent grade and all the solutions were prepared using bidistilled water.

Results and discussion

In order to study the effect of the nature (hydrogen-terminated or oxygen-terminated) of the diamond surface (BDD_H or BDD_O, respectively) on the electrochemical properties of the deposited Pt nanoparticles, some samples of BDD were anodically treated prior to platinum electrodeposition. The treatment consisted in applying a potential of 3.0 V for two hours in a 0.5 M H_2SO_4 solution, in order to change the as-grown surface of the conductive diamond to an oxygen-terminated one (BDD_O).

It was observed that the anodic pre-treatment of the diamond substrate results in an increase of the overpotential corresponding to Pt(IV) reduction. This is most likely due to a repelling effect induced by the presence on the BDD_O surface of oxygen-containing functional groups, such as carbonyl, ether or hydroxyl [11]. Furthermore, these functional groups could hinder to some extent the platinum deposition process by blocking a certain number of reaction sites.

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In order to study the electrochemical behaviour of platinum particles deposited both on hydrogen-terminated and oxygen-terminated diamond, Pt/BDD_H and Pt/BDD_O, respectively, electrodes were obtained and figure 1 shows typical chronoamperometric curves recorded during potentiostatic Pt deposition (deposition potential, -0.1 V) on BDD_H and BDD_O substrates (curves 1 and 2, respectively). The variation of the deposition current as a function of time illustrated in figure 1 is also in line with the results of the linear sweep experiments, proving that platinum is less efficiently deposited on the highly oxidized BDD_O surface.

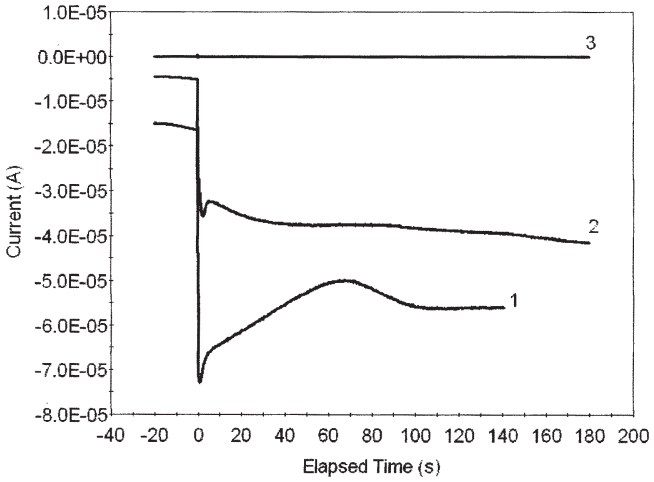

Fig. 1. Chronoamperometric curves recorded during platinum deposition at BDD_H (1) and BDD_O (2) and in the absence of Pt(IV) species (3). Applied potential, -0.1 V

Based upon the chronoamperometric curves recorded during Pt(IV) reduction, the deposition time was adjusted in order to obtain Pt/BDD_H and Pt/BDD_O electrodes with comparable platinum loadings, corresponding to a value of the deposition charge of 8.11 mC and 7.13 mC for Pt/BDD_H and Pt/BDD_O, respectively. It is important to note that at potential values higher than ca. -0.2 V the hydrogen evolution is negligible and a current efficiency close to 100% is expected for Pt electrodeposition [12]. This feature enabled us to calculate, starting from the above deposition charges, platinum loadings of 4.10 μg for Pt/BDD_H and 3.60 μg for Pt/BDD_O. After platinum electrodeposition, the electrodes were thoroughly rinsed with bidistilled water, transferred into fresh 0.5 M H_2SO_4 deaerated solution, and cyclic voltammograms were recorded within the -0.3 to 1.1 V potential range, at a scan rate of 20 mV s^{-1}, until a stable response was obtained (ca. 15 cycles). Figure 2 shows voltammograms recorded after stabilization for Pt/BDD_H (curve 1) and Pt/BDD_O electrodes (curve 2), and it can be observed that, in both cases, the shape of the voltammetric response is characteristic of platinum behaviour in acidic media.

This feature enabled us to estimate the active surface area of the electrocatalyst from the charge associated to hydrogen adsorption [13]. Thus, by integrating the electric charge within the potential range 0.1÷-0.25 V, and tacking into account the charge corresponding to the double layer charging, average values of 56 μC and 110 μC were calculated for Pt/BDD_O and Pt/BDD_H electrodes, respectively. It is known from the literature [14, 15] that the value corresponding to hydrogen adsorption on smooth platinum is 0.21 mC cm^{-2} which allowed us to calculate a specific active surface area of the Pt particles of 7.5 m^2g^{-1} for Pt/BDD_O and 12.7 m^2g^{-1} for Pt/BDD_H. It appears that the use of hydrogen-terminated conductive diamond as

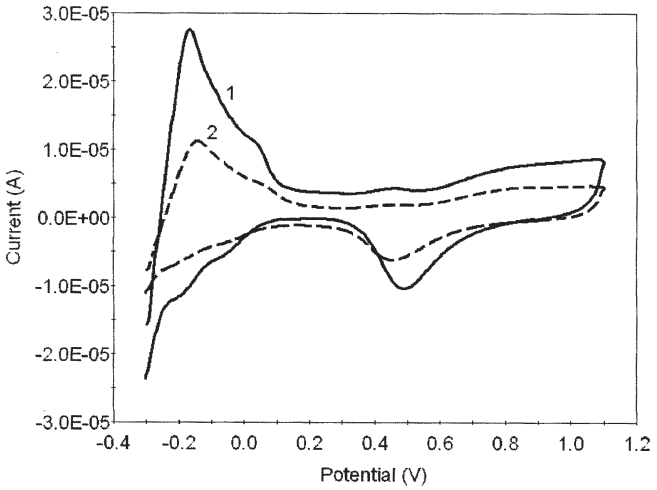

Fig. 2. Cyclic voltammograms recorded at 20 mV s-1 in 0.5 M H_2SO_4 deaerated solution at Pt/BDD_H (1) and Pt/BDD_O (2) electrodes. Platinum loadings: (1), 4.10 μg; (2), 3.60 μg

substrate for Pt electrodeposition will ensure, at least in principle, better utilization of the catalyst because compared to oxidized BDD, noted BDD_O, it enables obtaining higher active area of the electrodes. This is probably due to the fact that the surface of the BDD_O substrate exhibits a small number of active sites for Pt deposition, resulting in a larger size of the platinum particles and therefore in a lower active surface area.

In order to assess the electrocatalytic activity for ethanol oxidation of the two types of electrodes cyclic voltammetric experiments were performed in a 0.5 M H_2SO_4 + 1.3 M C_2H_5OH solution, and typical results are illustrated in figure 3.

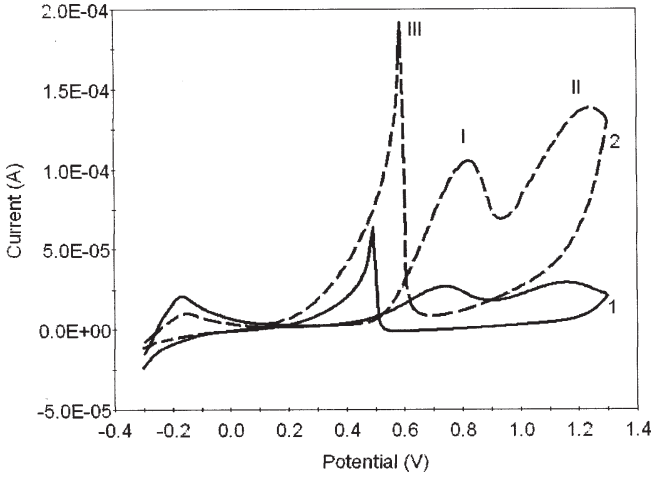

Fig. 3. Cyclic voltammograms recorded in 0.5 M H_2SO_4 + 1.3 M C_2H_5OH (scan rate, 20 mV s^{-1}) at Pt/BDD_O (1) and Pt/BDD_H (2) electrodes. Platinum loadings: (1), 3.60 μg; (2), 4.10 μg

The shape of the voltammograms from figure 4 is characteristic of ethanol oxidation at platinum electrodes in acidic media, and the nature of the associated voltammetric peaks is discussed in detail in the literature. Thus, the peaks occurring within the potential range 0.6÷0.8 V (labeled I) during the anodic scan were ascribed to the adsorption of the ethanol, followed by its oxidation. At higher potential values, the surface of the Pt particles is oxidized and further oxidation of ethanol (that takes place within the range of peak II) is hindered by the presence of platinum oxide on the electrocatalyst surface. During the reverse scan, the oxide is reduced and the occurrence of peak III is due to ethanol oxidation on the clean surface of the platinum particles [16, 17].

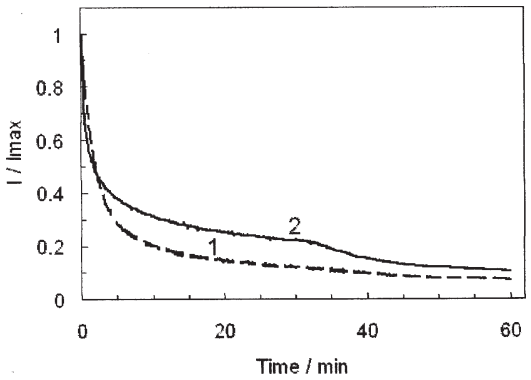

Fig. 4. Chronoamperometric curves recorded in 0.5 M H_2SO_4 + 1.3 M C_2H_5OH solution at an applied potential of 0.6 V at Pt/BDD_H (1) and Pt/BDD_O (2) electrodes. Platinum loadings: (1), 4.10 μg; (2), 3.60 μg.

As figure 3 shows, the ethanol oxidation current at the Pt/BDD_H electrodes (curve 2) is much higher than that recorded for the same process when oxidized diamond was used as substrate for Pt (curve 1). This behavior is most likely due to the higher active area of the electrocatalyst from the Pt/BDD_H structures. It is interesting to note, however, that the voltammograms from figure 3 also suggest that at the Pt/BDD_O electrodes ethanol oxidation occurs more readily, despite their lower active area. Thus, at Pt/BDD_H (curve 2) the peak potentials of peaks I and II are 0.82 and 1.24 V, respectively while on the voltammograms recorded at the Pt/BDD_O electrodes (curve 1), the same peaks occur at potential values of 0.74 and 1.16 V. A possible explanation for this behaviour is provided by assuming that, when deposited on oxidized diamond substrate, platinum particles are less susceptible to deactivation via CO poisoning, compared to platinum on hydrogen-terminated BDD. This could result in an lower overpotential of the overall anodic process and therefore in a cathodic shift of the voltammetric peaks evidenced during ethanol oxidation at Pt/BDD_O electrodes.

In order to put into better perspective these results, long term polarization measurements were also performed in a 0.5 M H_2SO_4 + 1.3 M C_2H_5OH solution at an applied potential of 0.6 V, and the results are illustrated in figure 4, both for Pt/BDD_H (curve 1) and Pt/BDD_O electrodes (curve 2).

It should be noted that, although the two types of electrodes have comparable platinum loadings, they are quite different in terms of active surface area, which results in different instantaneous values of the oxidation current. This is why, for better comparison, in figure 4 the instantaneous ethanol oxidation current (I) was normalized by its maximum value (Imax). It can be observed that for short-time electrolysis (ca. 3 min), the decrease of the current was slower for the Pt/BDD_H electrodes (curve 1 in fig. 5) probably due to their higher active area. However, after ca. 30 min of continuous polarization, the oxidation current of the Pt/BDD_O reached ~22% of its initial value, while that for Pt/BDD_H decreased to ~12%. This is further proof that the presence of oxygen-containing functional groups on the BDD surface renders the deposited Pt particles more resistant to poisoning during ethanol anodic oxidation.

Conclusions

The unique electrochemical features of polycrystalline conductive diamond prompted us to investigate the possibility of using BDD as a substrate for platinum electrodeposition in view of ethanol fuel cells applications. It was observed that Pt electrodeposition on hydrogen-terminated BDD resulted in obtaining electrodes with good electrocatalytic activity for ethanol oxidation in acidic media. It is expected that, due to the robustness of the BDD, the use of diamond-supported platinum as electrode material will greatly enhance the projected lifetime of alcohol fuel cells. It was also found that strong oxidation of the BDD substrate prior to platinum deposition allows obtaining electrodes with increased resistance to fouling during ethanol oxidation, although Pt/BDD_O exhibited lower active area of the electrocatalyst.

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