

## Improved Stability of PtO<sub>x</sub> Sol-Gel-Modified Diamond Electrodes Covered with a Nafion® Film

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Este trabalho descreve a modificação de eletrodos de diamante dopados com boro (DDB), através do depósito de partículas de óxido de platina, pelo método Sol-gel, utilizando-se diversos tipos de pré e pós-tratamentos da superfície. A estabilidade eletroquímica dos recobrimentos catalíticos foi avaliada por voltametria cíclica em meio ácido e mostrou-se superior àquelas já relatadas na literatura, para outros métodos de deposição. Um pré-tratamento térmico da superfície do DDB forneceu eletrodos que retiveram 91,6% do material do recobrimento, após 1000 ciclos voltamétricos, realizados entre as reações de decomposição da água. A aplicação de um filme de Nafion® em cima do recobrimento preservou integralmente o óxido de platina depositado. O uso desses eletrodos modificados em aplicações práticas será possível, utilizando-se as condições experimentais aqui descritas.

The modification of boron-doped diamond (BDD) electrodes with platinum oxide particles deposited by the Sol-gel method and using several pre- and post-treatments of the surface is described. The electrochemical stability of the resulting catalytic coatings was evaluated by cyclic voltammetry in acid medium and was much greater than those previously reported in the literature for others deposition methods. A thermal pre-treatment of the BDD surface yielded electrodes that retained 91.6% of the coated material after 1000 voltammetric cycles carried out between the water decomposition reactions. The application of a Nafion® film on top of the coating preserved integrally the deposited platinum oxide. The use of such modified electrodes for practical applications is now feasible under the present experimental conditions.

**Keywords:** BDD-PtO<sub>x</sub>, Sol-gel, Nafion® film

### Introduction

The boron-doped diamond (BDD) electrode has been the object of intense research activity in recent years particularly in electroanalytical studies<sup>1-4</sup> since it possesses extraordinary chemical stability, low capacitive currents in an extended range of potentials and good reproducibility for analytical studies if properly pre-treated.<sup>5</sup> Taking advantage of these qualities, several authors have used the BDD electrodes to study the complete oxidation or electrochemical combustion of organic compounds for wastewater treatment.<sup>6-8</sup> On the other hand, modifications of the diamond surfaces by metals or metal oxides have been proposed for a variety of applications and using different deposition methods.

Thus, Awada *et al.*<sup>9</sup> have demonstrated that some metals such as Pt, Pb and Hg can be electrochemically deposited on the surface of conductive diamond thin films. In particular, the stability Pt particles deposited on BDD is of great importance since these materials could find

applications in fuel cell systems and sensors. Honda *et al.*<sup>10</sup> and Yoshimura *et al.*<sup>11</sup> studied the electrocatalytic behavior of boron-doped nanoporous honeycomb diamond films modified with Pt nanoparticles using cyclic voltammetry (CV) and electrochemical impedance spectroscopy in acid solution. More recently, Olivia *et al.*<sup>12</sup> developed a glucose biosensor for in vivo monitoring using BDD microfiber electrodes. These electrodes were modified with Pt to detect H<sub>2</sub>O<sub>2</sub> that was enzymatically produced by glucose oxidase immobilized on the electrode surface. The oxidation of methanol was studied by Montilla *et al.*<sup>13</sup> in a Pt-modified diamond electrode where the Platinum particles were deposited on the BDD surface by either chemical or electrochemical methods but the stability of these materials was unsatisfactory and 65% of the Pt was removed from the surface after 1000 voltammetric cycles.

It is well established in literature that the Sol-gel method is an excellent alternative for producing stable coatings on different surfaces and this has been used for different purposes. Among others, Mattos-Costa *et al.*<sup>14</sup>

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have constructed stable  $\text{RuIrO}_2/\text{Ti}$  electrodes to be used as anodes in extremely aggressive acid media while Suffredini *et al.*<sup>15</sup> have prepared  $\text{NiCo}_2\text{O}_4/\text{Ni}$  deposits to act as an efficient material for oxygen evolution in alkaline media using the Sol-gel method in both cases. Several other authors have constructed Sol-gel films to be used as sensors<sup>16-17</sup> and, for the first time, carbon powder electrodes were modified by the same method to be used as anodes in direct methanol fuel cells, using a Nafion suspension to fix the  $\text{Pt-RuO}_2/\text{C}$  composite onto a glassy carbon support.<sup>18</sup> A yet unpublished follow-up of that last work has shown that platinum Sol-gel deposits consist of a mixture of Pt, PtO and  $\text{PtO}_2$ , currently described as  $\text{PtO}_x$ .

The aim of this report is to describe the use of the Sol-gel method for the surface modification of BDD electrodes with  $\text{PtO}_x$  particles for the oxidation of methanol as well as the effect of both the electrochemical pre-treatment and the chemical post-treatment of the surface with a Nafion® film on the cyclic voltammetric stability of the coatings.

## Experimental

Electrochemical experiments were carried out in a Pyrex® glass cell provided with three electrodes and degassing facilities for bubbling  $\text{N}_2$ . The working electrode was located in a Teflon® holder leaving an exposed circular area of  $0.63 \text{ cm}^2$ . The reference system was the hydrogen electrode in the same solution (HESS) and the auxiliary one was a  $2 \text{ cm}^2$  Pt foil. The boron-doped working electrodes ( $1.2 \times 1.2 \text{ cm}$  plates) were purchased from the Centre Suisse d'Electronique et de Microtechnique SA (CSEM), Neuchâtel, Switzerland, having final boron content of the order of 800 ppm.

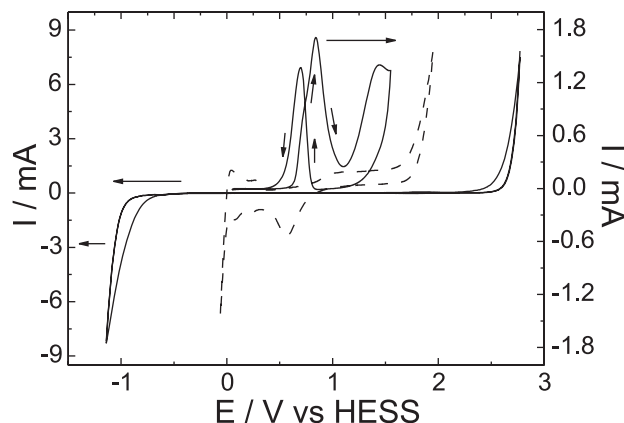
A Pt (II) acetylacetonate Sol was applied to BDD surfaces by the painting technique and the solution was evaporated in 5 minutes at a temperature of  $400 \text{ }^\circ\text{C}$  in an oven with an Argon atmosphere. This procedure was repeated eight times and at the end the electrode was subjected to a thermal densification treatment at  $400 \text{ }^\circ\text{C}$  for 1 hour. Three different BDD electrodes were prepared following that routine. On the first one, the coating was applied after a cathodic pre-treatment at  $-3.0 \text{ V}$  for 30 min. For the second one, a thermal pre-treatment at  $400 \text{ }^\circ\text{C}$  for 30 min was used prior to the coating deposition. The last one was produced as the second one and then wetted with  $40 \mu\text{L}$  of a 0.5% Nafion® solution that was evaporated on the electrode surface using a hot air stream. This rendered a well-adhering film that increased the stability of the coating.

All reagents used in this work were Merck P.A. quality and water was purified by the Milli-Q system from

Millipore. The  $0.01 \text{ mol L}^{-1}$  Sol-gel solution was prepared with Pt (II) acetylacetonate following published procedures.<sup>14-15</sup> Cyclic voltammeteries were performed in a  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution using a Mod. 283 EG&G PARC electrochemical instrument while a LEO series 440 microscopy was used for the SEM and EDX analyses.

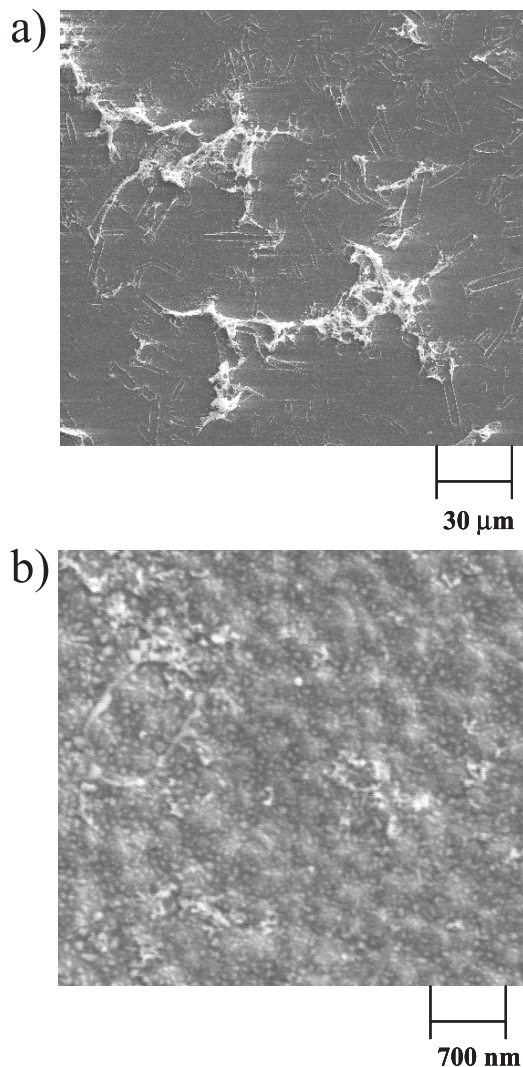
## Results and Discussion

The electrochemical characterization of the electrodes was initially made by cyclic voltammetry in acid media ( $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution) and the response of BDD before and after modification with  $\text{PtO}_x$  clusters (thick-solid and dashed lines, respectively) is presented in Figure 1. After the BDD surface was modified, both the oxygen (OER) and the hydrogen evolution reactions (HER) become very rapid due to the Pt catalytic effect in clear contrast to the low activity of the surface towards water decomposition as already reported in a previous publication.<sup>19</sup> Moreover, the dashed-line curve presents the typical polycrystalline Pt surface processes such as adsorption/desorption of hydrogen and the oxide formation and reduction. This demonstrates that the particles have a good electrical contact with the diamond surface and high purity. In addition, the effectiveness of the modified electrode for methanol oxidation is illustrated by the thin-solid line curve in the same figure.



**Figure 1** - Cyclic voltammograms of the BDD surface without modification (thick full line) and after modification with  $\text{PtO}_x$  clusters (dashed line) in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution ( $v = 0.5 \text{ V s}^{-1}$ ). The thin full line corresponds to methanol oxidation on the modified BDD surface after addition of  $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$  ( $v = 0.02 \text{ V s}^{-1}$ ).

Figure 2 shows the SEM images of coatings deposited on thermally pre-treated BDD by the Sol-gel method. The distribution of the clusters is irregular on the diamond surface with sizes varying between  $10 \text{ e } 100 \mu\text{m}$  (clear regions in Figure 2a). A micrograph recorded on the dark part of Figure 2a with a higher magnification (Figure 2b)



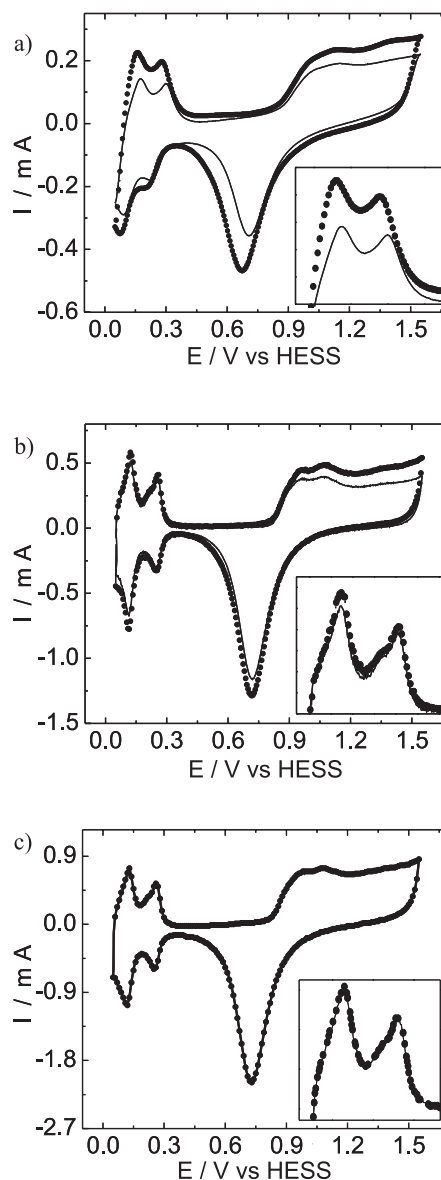
**Figure 2** - SEM images at two different magnifications of the BDD-PtO<sub>x</sub> electrode surface prepared by the Sol-gel method. Picture (b) was taken in one of the dark areas of the picture (a).

shows nanoparticles with spherical form and sizes around 50 nm. Table 1 presents the atomic percentages obtained by EDX on this modified electrode as well as on a clean BDD surface. The increase in oxygen content after the Sol-gel modification confirms the presence of PtO<sub>x</sub> on the surface. It also shows that minute amounts of Pt have a very significant effect on the electrode behavior, as presented in Figure 1, suggesting an excellent distribution of the particles.

**Table 1** –Atomic percentages obtained by EDX on the BDD and the BDD-PtO<sub>x</sub> electrodes

	BDD	BDD-PtO <sub>x</sub>
Carbon	98.05	95.02
Oxygen	1.95	4.91
Platinum	—	0.07

The stability of the different Sol-gel deposited electrodes was tested by comparison of the initial electrode response with that observed after 1000 potential cycles between the HER and the OER in the H<sub>2</sub>SO<sub>4</sub> solution at 500 mV s<sup>-1</sup>. Figure 3 illustrates the increasing stability of the PtO<sub>x</sub> clusters deposited on the BDD surface as a function of the pre- and post-treatments of the surface. A quantitative evaluation on the H-desorption charge for each electrode (inserts in Figure 3) shows variations of 33.6% (a), 8.4% (b) and negligible (c) for the corresponding Pt active surface area due to dissolution and detachment during the 1000 cycles.



**Figure 3** - Cyclic voltammograms for the first cycle (points) and after 1000 cycles (full lines) for the BDD-PtO<sub>x</sub> electrode in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution recorded for electrodes prepared after: cathodic pre-treatment (a), thermal pre-treatment (b) and thermal pre-treatment plus deposition of a Nafion® film on the surface (c). The inserts are enlargements of the H-desorption region for each case.  $v = 0.5 \text{ V s}^{-1}$

## Conclusions

These results clearly indicate that the Sol-gel method produces more stable PtO<sub>x</sub> deposits on BDD surfaces than other reported techniques even when only a cathodic surface pre-treatment is used. Moreover, the use of a thermal pre-treatment considerably increases the stability while covering the surface with a Nafion® film makes the clusters detachment/dissolution become negligible. Thus, the simple and low cost reported methodology produces stable catalytic electrodes that should find useful applications in sensors and fuel cells anodes, among others.

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