

Scientific Report

Concerning the implementation of the project: January – December 2014

During this period the research work was mainly directed towards two distinct objectives: evidencing the effect of the substrate on the oxygen evolution and methanol oxidation reactions (processes that occur at the surface of the deposited platinum particles) and the morphological, structural and electrochemical characterization of hybrid systems Pt-oxide and Pt-BDD (boron-doped diamond). Starting from the most significant results previously obtained, attention was given to the interesting features of Pt-Co₃O₄ composites, although a new approach was also initiated, *i.e.*, the possibility of inducing pre-established electrocatalytic properties by simple modification of the surface chemical composition of the conductive diamond substrate.

The method employed for obtaining the composites (previously described in detail) consisted in the potentiostatic deposition of Co₃O₄ (applied potential, 1.45 V) from a 0.25 M NaHCO₃ + 2 mM Co(NO₃)₂ solution, followed by platinum deposition, from a 1 M NaOH + 4.8 mM H₂PtCl₆ solution, at an applied potential of -0.7 V. Oxide and platinum loadings were controlled by adjusting the deposition time, and the electrodes thus obtained will be further referred as Pt/Co₃O₄/BDD. It should be emphasized that for the study of the oxygen evolution process the use of conductive diamond as substrate is a major asset because this material exhibits an extremely high overpotential for oxygen evolution. This behavior will

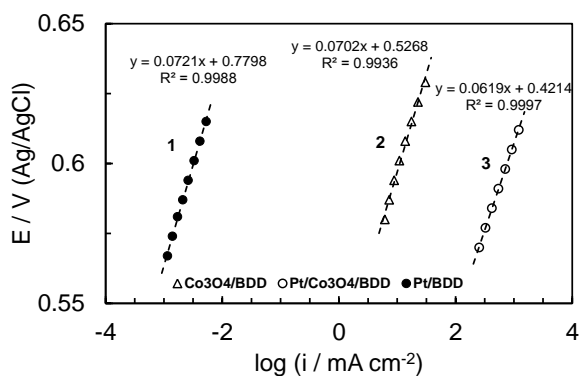


Fig. 1 Tafel representations for oxygen evolution at Pt/BDD (1), Co₃O₄/BDD (2) and Pt/Co₃O₄/BDD (3) electrodes in 1 M NaOH. Oxide deposition charge, 80 mC cm⁻²; Pt loading, 50 $\mu\text{g cm}^{-2}$.

inherently allow avoiding significant interference from the substrate thus ensuring better estimation of the intrinsic electrocatalytic features of the active material. Unlike diamond, cobalt oxide is known to be an excellent electrocatalyst for oxygen evolution, almost as good as platinum. This is why, when a Pt-Co₃O₄ composite is used as electrode material, oxygen evolution will simultaneously occur both on Pt and oxide sites which renders almost impossible quantitative estimation of individual contributions of each electrocatalyst. To overcome this problem, three types of electrodes were

prepared, *i.e.* Pt/BDD, Co₃O₄/BDD and Pt/Co₃O₄/BDD, with similar platinum and cobalt oxide loadings.

Steady-state polarization measurements (the potential was increased in 7 mV steps, then waiting for 1 min for the current to stabilize) were performed with all electrodes within the potential range corresponding to the onset of the oxygen evolution, and typical results are illustrated in Fig. 1 as Tafel representations. It can be observed that the anodic current normalized to the geometric surface area is much lower when the platinum particles were deposited on bare BDD (curve 1), compared to the case of $\text{Co}_3\text{O}_4/\text{BDD}$ and $\text{Pt}/\text{Co}_3\text{O}_4/\text{BDD}$ electrodes (curves 2 and 3). This is because, as already mentioned in previous reports, the surface area of the electrodes is significantly enhanced by oxide coating which inherently leads to an increase of the active surface area of the supported Pt particles. Reliable estimation of the electrochemically active area of the electrodes is a quite difficult task and this is why the performances of the investigated electrodes were compared in terms of Tafel slopes and not based upon the exchange current densities. Thus, close values of Tafel slopes were found for Pt/BDD and $\text{Co}_3\text{O}_4/\text{BDD}$ electrodes (72 and 70 mV decade^{-1} , respectively) indicating that, as expected, the performances of the two types of electrodes are rather similar. It was interesting to observe that for the $\text{Co}_3\text{O}_4\text{-Pt}$ composited deposited on BDD the Tafel slope is with *ca.* 14% lower than that corresponding to each electrocatalyst (Pt or Co_3O_4), demonstrating that the use of an intermediary cobalt oxide layer results in an improvement of the electrocatalytic performances for oxygen evolution of platinum particles and, perhaps, in a more efficient utilization of the noble metal.

Unlike sp^2 -type carbon supports, chemical or electrochemical oxidation of diamond leads only to the change of the hydrogen-terminated surface (which inherently appears since the films are grown under hydrogen plasma or in a hydrogen atmosphere) into an oxygen-terminated one, with negligible loss of material. Furthermore, the types of stable C–O surface functional groups, *e.g.*, C–O–C, C=O, and C–OH, that can exist on oxidized diamond may not exist on the graphite surface to the same extent. This feature could be important because it was shown that the presence of oxides or oxygenated functional groups on the carbonaceous substrate can strongly influence both the dispersion level and the activity of the electrocatalysts. Although, due to the high dissociation energy of C–H chemisorbed bonds, hydrogenated as-deposited diamond is generally regarded as stable toward adsorption of atmospheric gases, it was found that, after a more or less prolonged exposure to air, the presence of a certain amount of oxygen on the surface cannot be avoided. Complete removal of oxygenated species requires hydrogen-plasma treatments but more accessible methods, such as strong cathodic polarization in acidic aqueous media or thermal treatments in hydrogen atmosphere, have also been successfully used in order to achieve an overwhelming majority of C–H bonds on the diamond surface. For the present work hydrogen terminated (HT-BDD) and oxygen-terminated (OT-BDD) supports were prepared by annealing BDD samples in hydrogen and oxygen streams, respectively.

Fig. 2 shows characteristic micrographs obtained both for $\text{Pt}/\text{HT-BDD}$ (Fig. 2a) and $\text{Pt}/\text{OT-BDD}$ (Fig. 2b) with similar platinum loadings (40.4 and 40.8 $\mu\text{g cm}^{-2}$, respectively), together with the corresponding voltammetric patterns. It appears that, compared to

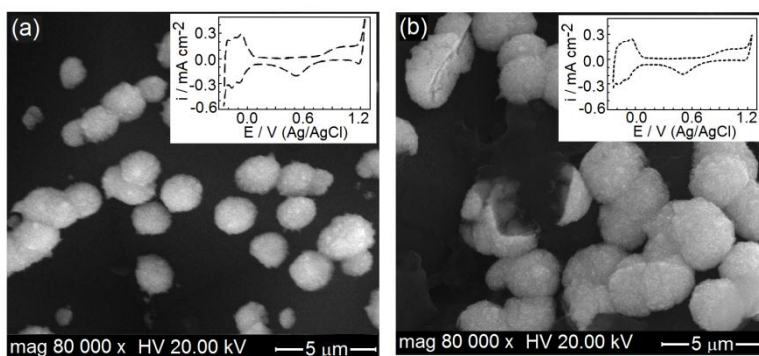


Fig. 2 Characteristic SEM micrographs for Pt/HT-BDD (a) and Pt/OT-BDD (b). Insets: corresponding cyclic voltammograms recorded in 0.5 M H₂SO₄ at a sweep rate of 50 mV s⁻¹. Pt loadings (μg cm⁻²): (a) 40.4; (b) 40.8.

oxidized BDD, the use of a HT-BDD substrate enables a more even spread and a smaller average size (*ca.* 200 nm) of the deposited Pt particles, although the presence of aggregates is also observed. The less uniform distribution of the particles across the surface of OT-BDD and the wider variation range of their size (Fig. 2b) can be plausibly ascribed to the fact that active sites at which PtCl₆²⁻ ions reduction occurs are partially blocked by oxygen-containing groups, as previously postulated for BDD substrates oxidized by prolonged anodic treatments. Due to this blockage, further Pt deposition will take place more readily on already deposited particles which accounts for the higher tendency toward large cluster formation evidenced for Pt/OT-BDD electrodes by SEM measurements (Fig. 2b).

As insets from Fig. 2 demonstrate, the shape of the voltammetric response recorded for both types of electrodes after stabilization is typical for the behavior of platinum in acidic media, which enables the estimation of the active surface area of the electrocatalyst from the charge associated with hydrogen adsorption, corrected for that of the double layer. Thus, integration of the cathodic charge within the potential range -0.2 to 0.1 V yielded values of the hydrogen adsorption charge of *ca.* 90.7 and *ca.* 74.4 μC cm⁻² for Pt/HT-BDD and Pt/OT-BDD, respectively. By assuming a value of 0.21 mC cm⁻² for smooth platinum surface and by taking into

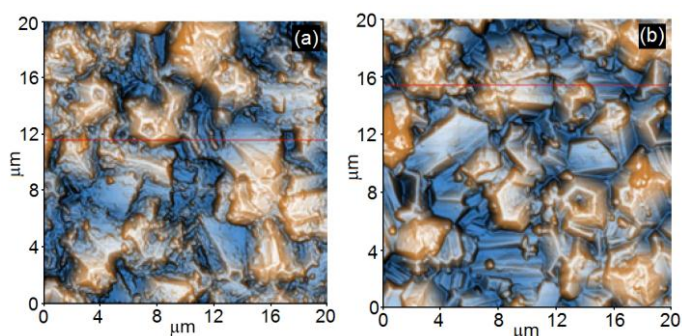


Fig. 3 AFM images of Pt/HT-BDD (a) and Pt/OT-BDD (b) electrodes recorded after stabilization of the voltammetric response. Pt loadings (μg cm⁻²): (a) 40.6; (b) 40.3.

consideration the corresponding values of the platinum loading, specific surface areas of *ca.* 1.07 and *ca.* 0.87 m² g⁻¹ can be roughly estimated for Pt particles supported on HT-BDD and OT-BDD. These values are well below those required for practical applications, which is obviously the result of the relatively low specific surface area of the diamond film. However, the above findings are noteworthy because they indicate that, in terms of efficiency of noble metal utilization, HT-BDD is better suited to be used as support for the electrocatalyst.

The effect of the substrate pre-treatment on the morphology of the platinum deposit was also examined by AFM and, as typical images from Fig. 3 illustrate, the results corroborate the conclusions of the SEM investigation suggesting that the use of a hydrogenated BDD substrate enables more uniform distribution of electrodeposited Pt particles. Interestingly, statistical analysis of the AFM results yielded for the two types of electrodes different kurtosis (R_{ku}) parameters. Thus, a value of 3.16 was found for Pt/HT-BDD, very close to that corresponding to a perfectly random surface ($R_{ku}=3$), indicating a rather Gaussian surface distribution. Conversely, the higher value observed for Pt/OT-BDD ($R_{ku}=5.11$) attests preferential agglomeration of electrocatalyst particles, in agreement with the proclivity towards cluster formation evidenced by SEM.

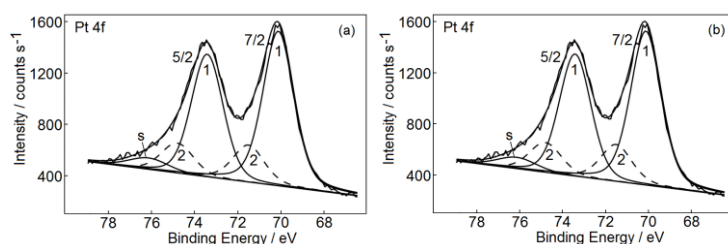


Fig. 4 XPS spectra in the Pt 4f region for Pt/HT-BDD (a) and Pt/OT-BDD (b) electrodes. Doublets were ascribed to Pt clusters (1) and Pt particles (2).

XPS was employed in order to analyze the surface of the Pt-modified pre-treated BDD electrodes and Fig. 4 shows narrow-scan spectra in the Pt 4f region, for Pt/HT-BDD (a) and Pt/OT-BDD (b). In both cases only elemental platinum was found and it was observed that,

as expected, the surface concentration of Pt clusters was higher for Pt/OT-BDD (*ca.* 80%) than for Pt/HT-BDD electrodes (*ca.* 65%).

Oxygen evolution was chosen as a test-reaction, very well suited to the investigation of whether the chemical termination of the BDD substrate has any effect on the electrocatalytic features of the deposited Pt particles, or not. To this end, steady-state

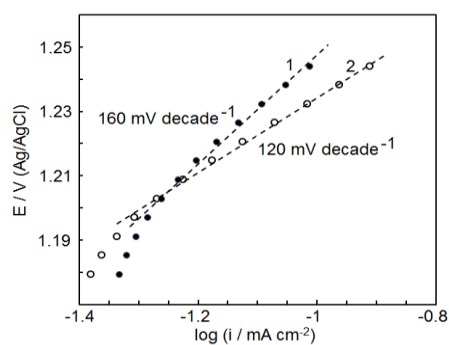


Fig. 5 Steady-state polarization results obtained in 0.5 M H_2SO_4 for platinum-modified OT-BDD (1) and HT-BDD (2) electrodes. Pt ($\mu g\ cm^{-2}$): (a) 40.9; (b) 40.5.

polarization measurements were carried out in acidic solution by applying increasingly positive potentials in 6 mV steps and then waiting for 1 min for the current to stabilize. To put the results into better perspective, the measured current was always normalized to the active surface area of the Pt deposits, estimated as above from the corresponding cyclic voltammograms. Fig. 5 shows Tafel plots for oxygen evolution, typical of the behavior observed for the platinum deposited on the two types of substrates. It was found that, when HT-BDD was used as support, the Tafel slope ($\sim 120\ mV\ decade^{-1}$) was lower than in the case of Pt deposited on OT-

BDD ($\sim 160\ mV\ decade^{-1}$). We should emphasize that the above values of the Tafel slope cannot be used directly to infer mechanistic details, because the electrocatalyst deposits are rather inhomogeneous in terms of particle size, and it was previously demonstrated that the

Tafel slope for oxygen evolution depends on this parameter. Thus, the slopes can only be compared on a relative basis. On this basis, however, it is possible to conclude that the slope for oxygen evolution is lowered by the use of the HT-BDD substrate (with *ca.* 25%), which is a slight, but nonetheless significant, inherent advantage of the hydrogen-terminated diamond. The higher Tafel slope observed for OT-BDD-supported platinum could plausibly be ascribed to the presence on the diamond substrate surface of oxygen-containing functional groups. Due to their close proximity to Pt particles, these groups might create less favorable conditions (by steric hindrance and/or electrostatic repulsion) for the adsorption of hydroxyl species on the active sites from the electrocatalyst surface, with detrimental effects on the oxygen evolution overall process.

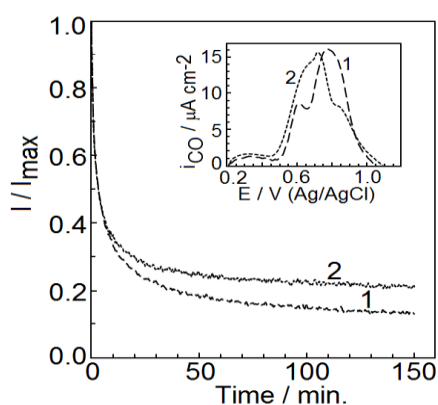


Fig. 6 Chronoamperograms in a 0.5 M H_2SO_4 + 2.46 M CH_3OH solution at Pt/HT-BDD (1) and Pt/OT-BDD (2) electrodes (applied potential, 0.55 V). Inset: corresponding stripping voltammograms of adsorbed CO.

BDD. Thus, after 150 min of continuous polarization, the oxidation current at Pt/HT-BDD electrodes reached *ca.* 13% of its initial value while that for Pt/OT-BDD decreased only to *ca.* 21% (curves 1 and 2, respectively). This is an indication of the fact that, when deposited on oxidized diamond, platinum is less sensitive to deactivation (*e.g.* via CO poisoning) during methanol oxidation in acidic media.

The results obtained in this stage of the research were published in the following papers:

- Influence of electroformation regime on the specific properties of cobalt oxide platinum composite films deposited on conductive diamond (*Thin Solid Films* **556** (2014) 81-86.)
- Effect of the chemical termination of conductive diamond substrate on the resistance to carbon monoxide-poisoning during methanol oxidation of platinum particles (*Journal Power Sources* **261** (2014) 86-92.)

In order to better put into evidence the effect of BDD pre-treatments on the electrocatalytic activity of supported platinum, methanol anodic oxidation in acidic media was also investigated. Long-term polarization measurements were performed in a 0.5 M H_2SO_4 + 2.46 M CH_3OH solution and Fig. 6 shows typical chronoamperometric curves recorded for electrodes with similar platinum loadings at an applied potential of 0.55 V. For a more straightforward comparison of the results on a relative basis, the oxidation current (I) was normalized by its maximum value (I_{max}). It was found that for short-time electrolysis (*ca.* 3 min) the time dependence of the current exhibits a rather sharp decrease for both types of electrodes, although after *ca.* 5 min this decrease becomes slower at Pt/OT-