

Scientific Report

Concerning the implementation of the project: October – December 2011

In this stage of the research efforts have been made in order to put into evidence functional effects of the cobalt oxide substrate on the electrochemical properties of deposited platinum particles. It is widely accepted that the presence on the platinum surface of oxygen-containing functional groups (especially –OH) enhances significantly the electrocatalytic activity for methanol anodic oxidation because they could contribute to CO oxidative desorption. This behavior justifies the selection of the overall electrochemical methanol oxidation process as a test-reaction for evidencing the influence of the substrate. To obtain reliable results, a good electrical contact between the substrate, the intermediary oxide layer and the electrocatalyst (Pt) particles is a prerequisite because it allows avoiding the underestimation of the electrode material performances (which may appear due to the fact that a certain amount of electrocatalyst could be deposited yet electrochemically inactive). In the present case we have a somewhat ideal situation because both the oxide and the electrocatalyst were electrochemically deposited and therefore in direct electrical contact with the substrate.

Pt/Co₃O₄ electrodes were obtained by a two-step electrochemical deposition method by using as primary substrate boron-doped diamond (BDD) polycrystalline films. This is

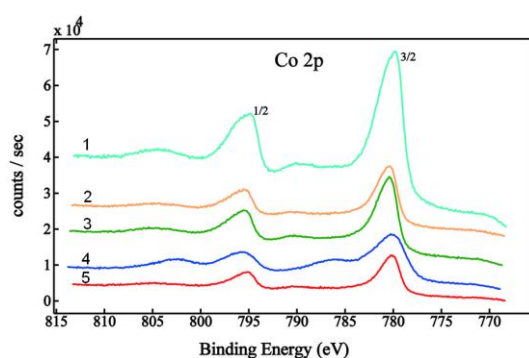


Fig. 1 XPS spectra for Co₃O₄ obtained by thermal (1) and electrochemical (2-5) methods.

because, unlike graphite or glassy carbon, this material allows obtaining oxide films with excellent electrochemical activity and, more importantly, with negligible substrate effects. In a first step Co₃O₄ were electrochemically deposited on the BDD films (surface area, 0.20 cm²) from a 0.25 M NaHCO₃ + 2 mM Co(NO₃)₂ solution, at an applied potential of 1.45 V. The second step consisted in the cathodic deposition of platinum from a 1 M NaOH + 4.8 mM H₂PtCl₆ solution, at an applied potential of -0.7 V. In

order to accurately estimate the amount of deposited Pt, chronoamperometric curves were recorded (under the same experimental conditions) in the absence of the precursor and the electrical charge corresponding to the deposition process was calculated as the difference between the charge recorded in the presence and in the absence of the precursors. The control of these amounts (both cobalt oxide and platinum) was made by appropriately adjusting the deposition time.

Fig. 1 shows XPS spectra obtained for several cobalt oxide deposits obtained electrochemically (2-5) in comparison with that corresponding to a Co₃O₄ layer obtained by

thermal decomposition (1). The excellent agreement between the position of the peaks corresponding to the chemical states of the cobalt species clearly demonstrate that the electrochemical method leads to the formation of Co_3O_4 and not to that of another type of oxide (e.g., $\text{Co}(\text{OH})_2$, CoOOH or CoO_2).

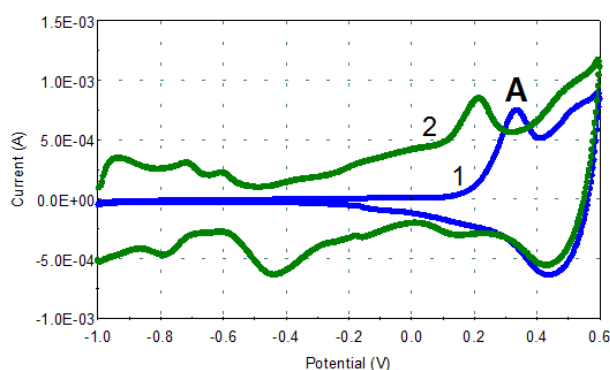


Fig. 2 Cyclic voltammograms in 1 M NaOH for $\text{Co}_3\text{O}_4/\text{BDD}$ (1) and $\text{Pt}/\text{Co}_3\text{O}_4/\text{BDD}$ (2) electrodes.

The electrochemical behavior of the cobalt oxide coatings was checked by cyclic voltammetry under typical experimental conditions (1M NaOH, sweep rate 50 mV s^{-1}) for better comparison with the data reported in the literature for Co_3O_4 obtained by thermal methods. Fig. 2 illustrates typical voltammetric responses obtained for an electrode coated with cobalt oxide (deposition charge, 500 mC), both before (curve 1) and after the deposition of 0.22 mg cm^{-2} Pt (curve 2). It was observed that the shape of the voltammogram for the $\text{Co}_3\text{O}_4/\text{BDD}$ electrodes is quite similar to that obtained for spinel cobalt oxides prepared by non-electrochemical methods. It is known that the peak occurring at potential values around 0.35 V (labeled A in Fig. 2) is ascribed to the redox transition between Co_3O_4 and CoOOH . By integrating the charge corresponding to this peak it was therefore possible to estimate the surface concentration of Co species (Γ_{Co}). The results of the cyclic voltammetric experiments shown in Fig. 2 also put into evidence interesting features of $\text{Pt}/\text{Co}_3\text{O}_4/\text{BDD}$ electrodes (curve 2). Thus, it appears that at potential values below ca. -0.2 V, the shape of the voltammogram is characteristic for the behavior of platinum in alkaline media, suggesting that, when deposited on the cobalt oxide support, Pt particles largely maintain their typical electrochemical properties. Nevertheless, the cathodic shift of peak A demonstrates the presence of a certain interaction between the electrocatalyst particles and the Co_3O_4 layer, which seems to facilitate the transition between the two oxide forms.

The first result of the oxide layers deposition is the enhancement of the specific active surface area of the electrodes, obviously ensuring also a higher specific surface area of the subsequently deposited electrocatalyst. On the other hand, it is known that the cobalt oxide (Co_3O_4) is somewhat less electrically conductive compared to other oxide electrocatalysts (RuO_2 , IrO_2). It was therefore necessary to establish the most suitable thickness of the intermediary oxide layer which would ensure the highest active surface area and avoid the presence of significant ohmic drop. To this end, electrochemical impedance spectroscopy (EIS) measurements were performed and by correlating the results with the theoretical response of an appropriate equivalent circuit the main parameters of the coatings were established. Fig. 3 shows the effect of the increase of the Co_3O_4 loading on the specific resistance (R_{ox}) and on the specific capacitance (C_{ox}) of the oxide layer. It was found that the minimum value of the resistivity (and the lowest loss by ohmic drop) is

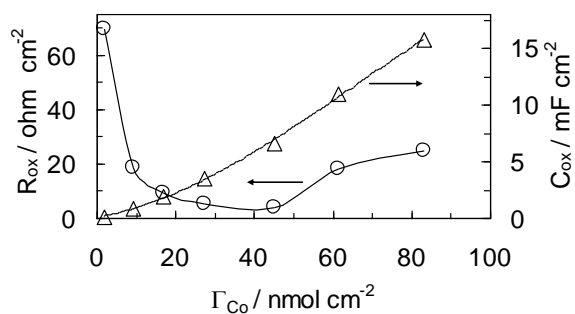


Fig. 3 The variation of the specific resistance and specific capacitance of the Co_3O_4 layer as a function of the oxide loading.

F g^{-1}) suggesting the possibility of using such materials for supercapacitor applications. Furthermore, subsequent deposition of platinum on the intermediary Co_3O_4 layer results in an important enhancement of the potential range suitable for this kind of applications (curve 2 in Fig. 2).

The morphologic structure of the oxidic and metallic deposits obtained by the above electrochemical methods was investigated by SEM and Fig. 4 shows typical micrographs obtained for $\text{Co}_3\text{O}_4/\text{BDD}$ (a), Pt/BDD (b) and $\text{Pt}/\text{Co}_3\text{O}_4/\text{BDD}$ (c) structures. It was observed that, for a surface concentration of Co species higher than ca. 40 nmol cm^{-2} , the oxide coating is rather continuous, with uniform thickness, although some preferential deposition

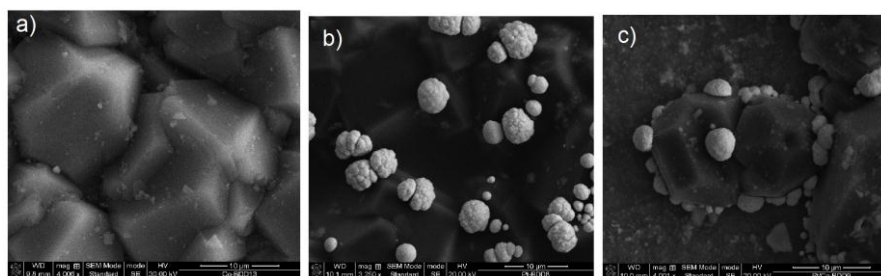


Fig. 4 SEM images obtained for electrodes $\text{Co}_3\text{O}_4/\text{BDD}$ (a), Pt/BDD (b) and $\text{Pt}/\text{Co}_3\text{O}_4/\text{BDD}$ (c). Γ_{Co} (nmol cm^{-2}): a) 63; c) 48. Pt loading, 0.23 mg cm^{-2} .

appears at the boundaries between the crystals and on their edges (Fig. 4a), probably due to a higher current density in these zones. We should emphasize that from the standpoint of possible practical applications of cobalt oxide (e.g. supercapacitors, or oxygen evolution activity) there is no need for a continuous layer of oxide to be deposited because the diamond substrate does not interfere with the overall electrochemical features for such applications. Nevertheless, in view of the scope of the present project, a continuous, uniform, Co_3O_4 layer is suitable because it avoids that platinum particles are deposited directly on the bare BDD surface. This feature will enable the assessment of the influence of the oxide substrate on the electrocatalytic performances of the platinum particles by simply comparing the electrochemical properties of Pt/BDD and $\text{Pt}/\text{Co}_3\text{O}_4$ electrodes.

By comparing SEM results for electrodes with similar loadings of platinum, deposited on the diamond support both with (Fig. 4c) and without (Fig. 4b) an intermediary oxide layer,

ensured by an amount of Co_3O_4 corresponding to a surface concentration of Co species within the range 15 to 50 nmol cm^{-2} . At the same time, such loading will also ensure a reasonably high specific surface, as indicated by the corresponding value of the specific capacitance. It is also important to note that the results of the cyclic voltammetry and EIS experiments exhibited a significant value of the specific capacitance of the oxide coating (ca. 2×10^3

mF cm^{-2})

it was found that the presence of the Co_3O_4 results into a better dispersion of the Pt particles. A possible explanation for this behavior is provided by the fact that the hydrophobic character of the BDD surface leads to the presence of a small number of active sites for hydrated Pt(IV) species. Obviously, the hydrated oxide layer will ensure a much larger number of such sites. This hydrated structure is also responsible for the somewhat high specific capacitance of the coatings because it leads to a more or less amorphous structure which is less rigid and allows protons to be incorporated three-dimensionally.

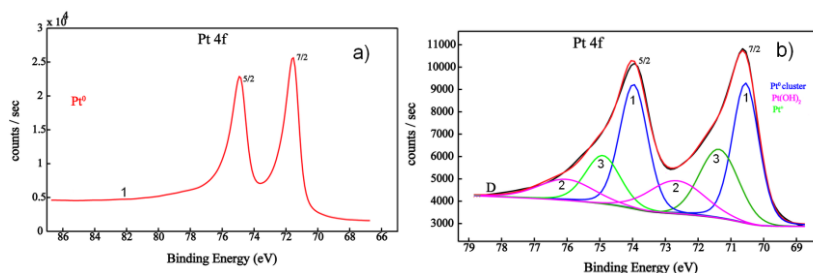


Fig. 5 Deconvoluted XPS spectra for Pt/BDD (a) and Pt/Co₃O₄/BDD (b): 1) elemental Pt; 2) Pt(OH)₂; 3) platinum suboxides.

The nature of the platinum chemical species was investigated by XPS, both on the BDD and on the Co₃O₄ substrate and Fig. 5 shows typical results corresponding to the Pt 4f region. It was found that, when deposited on bare BDD, platinum is present

only in the metallic form, although the presence of clusters was also evident (Fig. 5a). For the platinum deposited on the oxide layer, the spectra were fitted by three overlapping Gauss-Lorentz curves (Fig. 5b), ascribed to the presence on the Pt/ Co₃O₄/BDD surface of metallic platinum (curve 1), Pt(OH)₂ (curve 2) and platinum suboxides (curve 3).

In order to assess the extent to which the presence of these species of platinum affects the overall electrochemical properties of the electrodes anodic oxidation of methanol was chosen as test-reaction. Fig. 6 shows cyclic voltammograms recorded in a 1 M NaOH + 4.9 M CH₃OH solution, at a sweep rate of 50 mV s⁻¹ for Pt/BDD (curve 1) and Pt/ Co₃O₄/BDD

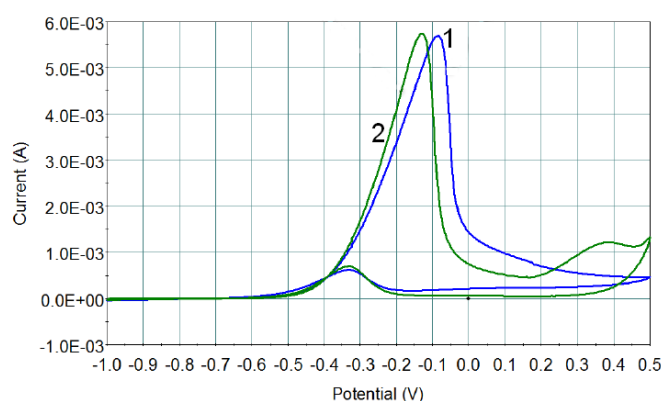


Fig. 6 Cyclic voltammograms recorded for methanol oxidation at Pt/BDD (1) and Pt/Co₃O₄/BDD (2) electrodes

(curve 2) electrodes, with similar platinum loadings (0.23 mg cm⁻²). It was found that in the presence of the intermediary layer the main anodic peak ($E_p \sim -0.1$ V) shifts with ca. 54 mV towards lower values (curve 2 from Fig. 6), indicating that methanol oxidation is facilitated to some extent. The better performances of Pt/ Co₃O₄/BDD electrodes can be ascribed to the presence on the surface of -OH

species that may exert a certain co-catalytic effect on the overall oxidation process by assisting in the desorption of the intermediates. It was also interesting to observe that the height of the anodic peak on the reverse scan ($E_p \sim -0.35$ V) is higher for Pt/ Co₃O₄/BDD

electrodes, although the height of the main peaks is the same. This behavior suggests that the presence of the oxide substrate improves to a certain extent the resistance to CO-poisoning of the Pt particles, also as a result of the functional effects induced by the presence on the surface of oxygenated functional groups.

Some of the results obtained in this stage of the research were reported in a paper submitted to Japanese Journal of Applied Physics, for an issue devoted to polycrystalline diamond.