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LETTERS

Electrocatalysis at Conductive Diamond Modified by Noble-Metal Oxides

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In the present work, a generalization of some of the interpretations of heterogeneous catalysis to the case of oxide film electrocatalysts has been attempted, using conductive boron-doped diamond supports. The very high stability of this material allowed the study of the catalytic properties of noble-metal oxide modifications from the level of submonolayer to a few monolayers, avoiding the serious interference of the reactivity of the generally adopted metal supports. A mechanism for the chlorine evolution reaction at submonolayers of oxide electrocatalyst has been proposed, basing on a chlorine radical spillover stage.

The use of supported catalyst films is common practice in heterogeneous catalysis, their properties essentially depending on their chemical nature and their surface texture. Modified electrodes, frequently used in electrochemical experiments, represent a natural development of this conception in the field of electrocatalysis.[1] A wide variety of modifications have been studied, including polymeric, metallic, and metal oxide films, with amounts of deposits varying between submonolayers of adatoms to multilayers, up to several hundreds of nanometer thick films. Modifications have been inserted at the surface of different supports, from carbon to different metal single crystals. Although the thickness of the modifying film is generally sufficiently high, still the interaction with the support may affect its catalytic activity. The strong metal–support interaction described in the particular case of supported metallic films is a typical example of this class of phenomena.[2]

The influence of the support material on the catalytic properties of the film, through changes of its surface composition, is further enhanced when the deposit formation takes place under drastic conditions, and the support itself is involved in the precursor reaction. Oxide film electrodes for anodic electrosynthesis, consisting of IrO_2 or RuO_2, are a typical example in this sense. Their preparation involves several steps leading from precursor salts to the respective oxides, and temperatures on the order of 350–450 °C are required for the transformations to take place.[3] Under these conditions, the synthesis exhibits a poor reproducibility[4,5] and the metal support, generally a valve metal, is partially oxidized.[6] Typically, thin films allowing a better understanding of charging mechanisms cannot be synthesized at usual metal supports such as titanium or tantalum, because of their massive involvement in the oxidation processes: a limiting case of strong catalyst–support interaction. The "model" modifying film in these cases is not available, missing concrete possibilities of reaching better-defined systems.

The recent achievements in the preparation of highly boron-doped diamond (BDD) films with minimal sp^2 carbon contents seem to supply an interesting solution to the above problems. Supported BDD films exhibit very high stability upon different chemical and electrochemical treatments.[7] They can be heated under oxygen up to about 500 °C, undergoing only partial oxidation of surface carbon atoms. Very high stability has been found also under far-positive electrochemical polarization.[8] These features make BDD interesting not only as an electrode film but also as an inert support for electrode films of a different nature. In the present work, the electrochemical properties of deposits of small amounts of RuO_2 and IrO_2 have been studied, exploiting the absence of catalytic activity of Si/BDD besides the above-mentioned high stability. Amounts of oxide electrocatalyst were between 1.2E+13 and 2.65E+16 MO_2 molecules/cm^2, corresponding to a nominal oxide loading between 0.01

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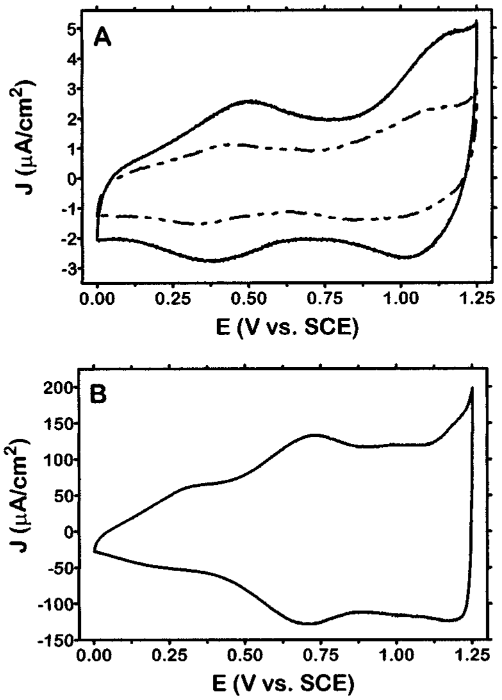

Figure 1. Cyclic voltammograms of two RuO_2-modified BDD electrodes, 1.2E+13 and 6.0E+14 molecules/cm^2 (A), and of a BDD/IrO_2 electrode, 6.0E+14 molecules/cm^2 (B), recorded in 1 N H_2SO_4 at a sweep rate of 0.3 V s^{-1}.

and 10 monolayers. The properties of the BDD support and of modified surfaces were studied in situ by cyclic voltammetry in 1 N sulfuric acid. The ex situ characterization was carried out by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The effect of the modifications on the catalytic activity was tested with the chlorine evolution reaction, making use of quasi-steady potentiostatic curves.

BDD films of 1 μm thickness were grown on low-resistivity (1 mΩ cm) Si wafers, according to an elsewhere described procedure.[9] RuO_2 and IrO_2 modifications were deposited by a traditional sol−gel method,[10] pyrolyzing the precursor salts at 400 °C for 30 h. Blank experiments with Si/BDD electrodes showed that the above thermal treatment does not modify the electrochemistry of the support.

In all cases, the preparation led to stable modifications, unaffected by anodic polarization under chlorine evolution. Cyclic voltammograms obtained at as-prepared electrodes reached a stable shape after a limited number of cycles. Typical CV data are shown in Figure 1. The main features of the voltammogram (Figure 1A) are already present for the lowest oxide deposit. They remain unchanged at electrodes with higher oxide loading, whose only effect is the increase of voltammetric current. Different solid-state redox couples between 0.00 and 1.25 V (vs SCE) for the RuO_2-H_2O and IrO_2-H_2O systems are clearly identified. As shown in Figure 1, two well-resolved peak pairs are observed, possibly related to the same oxidation state transitions ($M^{II}-M^{III}$ and $M^{III}-M^{IV}$). The voltammogram in Figure 1B, relative to the IrO_2 film, also exhibits weaker signals due to higher oxidation state transitions. The more positive one, partially superimposed with the oxygen evolution onset, could be associated with the $Ir^{V}-Ir^{VI}$ transition. The existence of the above redox couples has been discussed in the literature, in relation with the mechanism of oxygen evolution reaction.[3] The present results are a clear-cut in situ evidence of distinct oxidation state changes, as the cyclic voltammograms at RuO_2 and IrO_2 thick-film electrodes exhibit poorly resolved peaks, which convolute into broad flat maxima.[3,11]

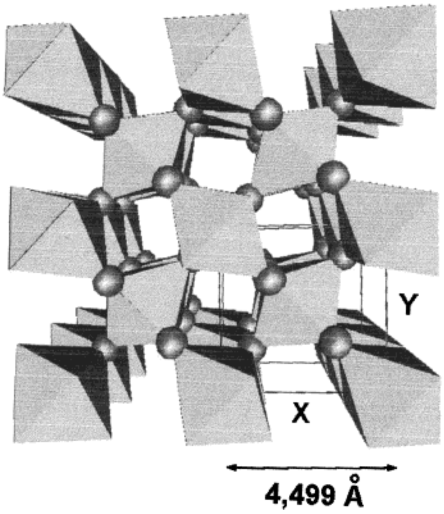

Figure 2. Three-dimensional array of distorted octahedra in the rutile structure. View along the 001 direction.

The latter feature has possibly justified an overestimation of the purely capacitive contribution to the charge-storage capacity of oxide electrodes. Data in Figure 1 indicate that the complementary faradaic contribution could be the most important one. Equilibria of the type:[3,12]

$$MO_x + H^+ + e \rightleftharpoons MO_{x-1}OH$$

involving two or more oxidation state changes can better account for the very high capacities measured, the proton exchange being much faster than double-layer rearrangements caused by changes of electrode potential.

The three-dimensional array of distorted RuO_6 octaedra, on which the rutile structure of RuO_2 is based, presents void channels normal to the 001 plane (Figure 2). As the inner walls of these channels are oxygen-based, the above electrochemical ion (proton)-exchange equilibria may extend several Ångstroms below the oxide surface through, e.g., a Grotthus-type mechanism.[13] The intergrain−interparticle boundaries, often considered the reason for the large capacities of the RuO_2 films, would rather magnify an intrinsic property of the structure of this oxide.

Voltammetric (anodic) charge relative to the lowest oxide loading, 1.2E+13, indicates that 2.28 electrons are exchanged per oxide molecule. Assuming an electronicity of 2 for the global charging process, this is in agreement with the expectation that, at very low coverage, most of the noble-metal sites can undergo oxidation state changes. With increasing the oxide loading to 6.0E+14, which approximately represents one oxide monolayer, the voltammetric charge increases up to only 6.77 μC, almost twice the previous value (3.44 μC). The efficiency of the charge storage is considerably decreased, possibly due to accumulation of oxide in the deeper parts of the polycrystalline diamond surface, which can incorporate even higher amounts of oxide without exposing larger external surfaces. The coating containing 2.65E+16 molecules/cm^2 exhibits an anodic voltammetric charge of 50.62 μC, which is still lower than 224.34 μC, the value calculated for a complete monolayer of RuO_2 molecules (7E+14) exchanging two electrons per molecule. This low charging yield, at a relatively high loading, reflects both the previously mentioned effect, related with the diamond film surface, and the building up of the three-dimensional oxide phase through clusters of molecules. The latter can be clearly seen in

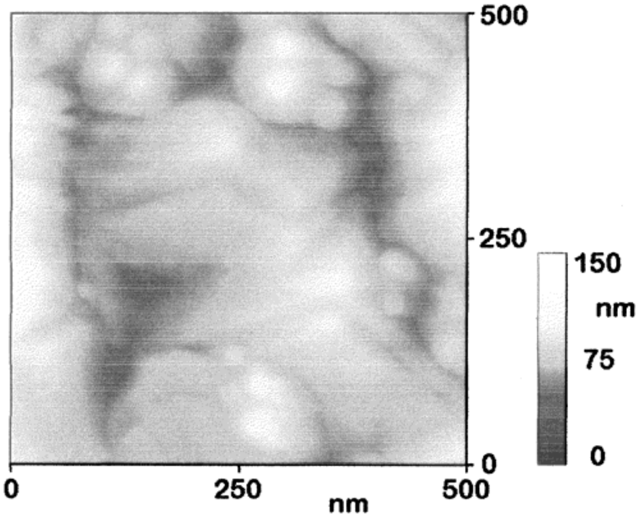

Figure 3. AFM image of a BDD/RuO_2 sample, with a nominal deposit of 2.65E+16 molecules/cm^2.

the AFM image in Figure 3. A simple calculation, based on the average number of the approximately spherical particles and their size, leads to an estimated charge of 24.90 μC, assuming that only the first layer of RuO_2 molecules can undergo oxidation state changes at the clusters surface. This number is about one-half the experimental one. In consideration of the presence of channels in the rutile structure, this disagreement may be due to the restriction of the charge storage to the surface sites only.

Within the same frame, the larger voltammetric area for the IrO_2 loading (Figure 1B) can be justified by the more acidic character of this oxide, compared with RuO_2, with higher proton mobility expected in this case.

To ascertain the stoichiometry of the deposited oxide, XPS measurements have been carried out for the ruthenium-based samples. The signals relative to $Ru3d_{5/2}$, $Ru3p_{3/2}$, and O1s have been used for this part of the investigation. The binding energy of the first signal (280.6 eV) and the ratio between the other two (2.0 ± 0.2) are evidence for the formation of a RuO_2 phase in all the investigated samples. Interestingly, the rate of increase of the Ru signals with the amount of oxide deposited is quite small and does not follow a linear law, supporting the hypothesis formulated on the basis of the charge-storage results.

As above-mentioned, the electrochemical oxidation of chloride ions to chlorine was used as a model anodic reaction, to trace the effect of RuO_2 modifications of BDD films. A set of polarization curves has been obtained in x M NaCl/$(4 - x)$ M $NaClO_4$/0.01 M $HClO_4$, with $0.1 \leq x \leq 4$.

The results, in terms of polarization curves and Tafel plots, for $x = 1$, are shown in Figures 4 and 5, respectively. As the extension of the working surface is different in the three cases taken into consideration, current values have been normalized to the number of surface atoms at which the reaction takes place. In the case of BDD film, the number of C atoms/cm^2 has been used, assuming in a first approximation a unitary roughness factor. The number of active sites for the two modified surfaces depends on the oxide dispersion. Basing on previously discussed CV data, for the smaller loading the nominal number of RuO_2 molecules/cm^2 of 1.2E+13 has been chosen. Making use of the latter and of the ratio between the voltammetric charges found for the two modified electrodes, the estimate for the higher loading was 1.77E+14. The slope of the Tafel plot for the BDD electrode is about 0.150 V, giving evidence for a rate-determining discharge of chloride ions.[14,15] At the sample with the highest oxide coating, the chlorine evolution reaction proceeds with a much higher rate, as expected for a RuO_2 electrode. The Tafel slope is about 0.150 V, with a reaction order of 0.7 with respect to Cl^-. A Volmer–Heyrovsky mechanism[14] with a rate-determining electrochemical desorption can account for the experimental evidence, provided a value of about 0.7 is assumed for the coverage by the intermediate chlorine radicals.[16] As a further support to this mechanistic hypothesis, the rate of the chlorine evolution reaction was independent from the solution acidity.

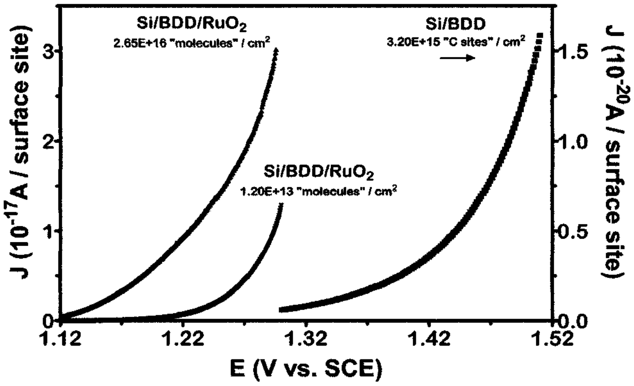

Figure 4. Current potential curves for chlorine evolution in 1 M NaCl/3 M $NaClO_4$/0.01 M $HClO_4$. Current values are normalized to the number of surface sites.

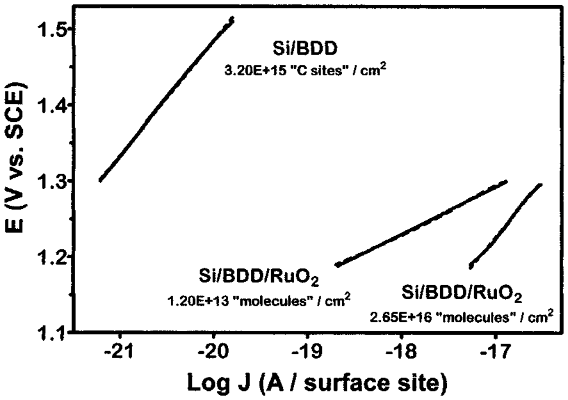

Figure 5. Tafel plots for chlorine evolution in 1 M NaCl/3 M $NaClO_4$/0.01 M $HClO_4$. Current values are normalized to the number of surface sites.

The parameters of the chlorine evolution reaction at the sample with the lowest catalyst loading are less easily interpretable. The catalytic activity of the modified electrode is quite higher, compared with the unmodified one, which is in agreement with the measurable presence of ruthenium oxide at the electrode surface. However the Tafel slope is now 0.060 V, and the acidity affects the chlorine evolution reaction, the reaction order with respect to H^+ being −0.6.

In this case, AFM does not show any particle, indicating that oxide clusters should have a diameter not larger than ca. 9−10 nm. The very small size of the catalyst patches, at which the chloride discharge takes place, may possibly favor the subsequent surface diffusion of the chlorine radical from the formation site on the catalyst surface to a neighboring C(diamond) site. The electrochemical desorption step can easily take place at the latter, due to the poor interaction with the radical. As the C(diamond) sites can be largely hydroxylated under the given thermal and polarization conditions, the influence of the solution acidity on the chlorine evolution rate could also be accounted for along the above lines.

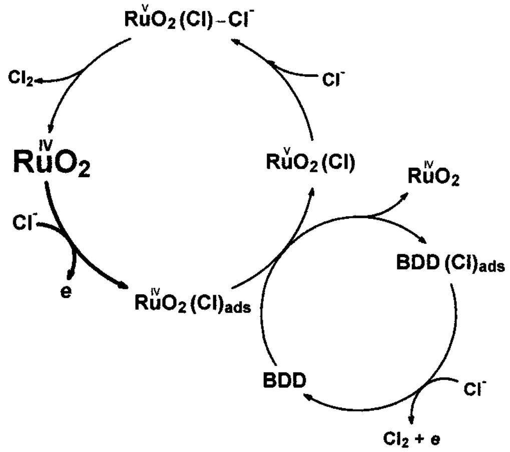

Figure 6. Schematic representation of the reaction pattern for the chlorine evolution reaction at BDD/RuO_2 electrodes. At low RuO_2 coverage, radical spillover can take place.

The above reaction scheme could be seen as an example of radical spillover, well-known in heterogeneous catalysis of gas-phase reactions[17] and also hypothesized in very specific cases of electrochemical oxidation reactions.[18,19] The pronounced chemical and electrochemical stability of BDD films allows the deposition of submonolayers of donor phases (e.g., RuO_2, IrO_2, Pt) and obtainment of well-defined bifunctional surfaces where the C(diamond) phase acts as an acceptor of adsorbed radicals formed at the oxide surface.

Contrary to the expectations, the normalized values of current at the two RuO_2 coatings do not coincide. The decrease of activity, with decreasing the oxide loading, can be understood only assuming a strong diamond−ruthenium oxide interaction, more important for thinner deposits. Apparently, the catalytic activity at the oxide surface, requiring a rearrangement of oxidation state of the metal ions in the oxide lattice, is enhanced by the existence of underlying oxide layers, where such rearrangements can take place as well. On the basis of this interpretation, the chlorine evolution reaction at the electrode with the lowest oxide loading can be tentatively described by Figure 6, which takes into consideration the two possible routes of the chlorine radical consumption. The assumption of interaction of adsorbed radicals with higher oxidation states of the metal ion at the surface would necessarily imply the participation of the whole near-surface region of the oxide film. Similar effects and interpretations have been described[20] in heterogeneous catalysis at supported RuO_2.

The above-emphasized interest of conductive diamond supports in the fundamental investigation of oxide electrocatalysts cannot overshadow the importance of stable supports in film electrodes for industrial oxidative processes.

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