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Electrocatalysis and Chlorine Evolution Reaction at Ruthenium Dioxide Deposited on Conductive Diamond

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The instability of the commonly adopted support (e.g., Ti, Ti−Pd alloys, Ta) for the preparation and characterization of different electrode materials has been overcome by depositing the electrode material of interest (RuO_2) on conductive, boron-doped diamond (BDD). The present paper reports results on the model chlorine evolution reaction, investigated at BDD surfaces modified by RuO_2 loadings of 1.2×10^{13}, 6.0×10^{14}, and 2.65×10^{16} molecules cm^{-2}. A radical spillover mechanism is proposed for the reaction occurring at the electrode having the lowest noble-metal oxide loading.

Introduction

Metal-oxide film electrodes (e.g., IrO_2, RuO_2, Co_3O_4, ...) have been widely investigated for their electrocatalytic activity[1−6] and good perspective of application as electrochemical supercapacitors (ref 7 and literature therein), charge-storage mechanism being the main factor in both cases. The most common preparation method consists of an oxidative pyrolytic treatment of gel-like precursor salt deposits on the chosen metal support[1,8] (generally a valve-metal). Due to the complication of the precursor path, the composition of the resulting catalyst films is further enriched with byproducts of the incomplete thermal decomposition of reactants. Another essential point is that the metal support is also involved in the oxidative process, particularly in the initial stage of the supported-film preparation. Consequently, also metal-support ions enter the supported film composition and affect their electrochemical properties, playing a role so far underestimated, both in its pure and applied implications.[9]

The control of the preparation may reduce or eliminate the encapsulation of impurities from precursor solutions, but cannot avoid the attack to the metal-support, intrinsic to its nature and to the deposition temperature. This limitation hinders the possibility of investigating the electrochemical behavior of small amounts of noble-metal oxide loadings, from the submonolayer to a few monolayers, because of the heavy involvement of the support species in their composition. This important element in the understanding of the charging mechanism of the mentioned oxide films is consequently conditioned by the improvement in the conductive support preparation.

In recent years, important results have been achieved in the preparation of conductive diamond (e.g., highly boron-doped diamond (BDD) films) exhibiting an exceptional stability, both toward chemical and electrochemical oxidation.[10−14] Among the different applications of these new materials, their use as support for noble-metal oxide films is certainly to be considered. The reasonable stability of the carbon−oxygen bond, the volatility of the final oxidation products[15] (CO, CO_2), the very high stability of the sp^3 bond network in the diamond structure, may represent the ideal compromise of properties that a support for RuO_2 and IrO_2 should exhibit. In fact, while the very stable sp^3

bond network makes the oxidation of conductive diamond quite slow and possibly limited to its surface, the presence of oxygenated functions at the diamond surface may favor a more stable bonding of metal-oxide clusters during the oxide deposit formation. Locally occurring oxidation, leading to CO and CO_2 cannot be excluded, also in consideration of the presence of sp^2 carbon impurities in the diamond matrix. However, these volatile products should not affect the composition of growing metal-oxide phases. Moving from the above considerations, a research study has been recently carried out on the electrochemical properties of nanoparticles of RuO_2 synthesized on highly conductive boron-doped diamond (BDD) thin films. Amounts of oxide electrocatalyst were[16] between 1.2×10^{13} and 2.65×10^{16} molecules cm^{-2}, corresponding to a nominal surface coverage between 0.01 and 10 (assuming that 10^{15} oxide molecules cm^{-2} correspond to a monolayer surface coverage).

In the present work the research has been further developed to describe the catalytic activity of BDD-supported RuO_2 nanoparticles, in the chlorine evolution reaction.

Experimental Section

Highly boron-doped diamond electrodes were deposited on low-resistivity (1 mΩ cm) silicon wafers, as described elsewhere;[17] the diamond layer had a thickness of about 1 μm (±10%) and a resistivity of 15 mΩ cm (±30%). After a thermal treatment of the BDD supports at 400 °C for 30 min (in order to obtain more hydrophilic BDD surfaces), ruthenium dioxide modifications were deposited on BDD by a traditional sol−gel method,[18] applying a solution of $RuCl_3$ dissolved in 2-propanol and pyrolyzing the precursor salt at 400 °C for 30 min under oxygen. The properties of the thermal treated BDD support and of the modified surfaces were investigated in situ by cyclic voltammetry (CV) in 1 N sulfuric acid.

Si/BDD and Si/BDD/RuO_2 electrodes were placed at the bottom of the electrochemical cell and the exposed area had a nominal value of 0.785 cm^2 (a disk with a diameter of 1 cm); a cylindrical platinum grid and a double-walled saturated calomel electrode (SCE), with an intermediate saturated $NaNO_3$ solution, were the counter and the reference electrode, respectively. NaCl solutions were prepared at different concentration with milliQ water, maintaining a constant ionic strength by
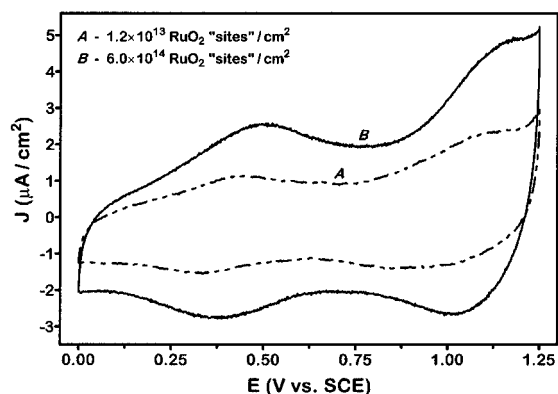
Figure 1. Cyclic voltammetry curves of two RuO_2-modified BDD electrodes, recorded in 1 N sulfuric acid at a scan rate of 300 mV s^{-1}.

addition of monohydrate $NaClO_4$; all chemicals were of analytical grade.

The electrochemical study was carried out by an Autolab PGSTAT20. Cyclic voltammetric measurements were performed at room temperature and at a scan rate of 100 mV s^{-1} (unless otherwise stated); the chosen potential range was cycled using a step potential of 2 mV with repetition at least 5 times or until reproducible signals were generated; in each case, the last cycle was recorded. Quasi steady-state polarization curves were carried out at a scan rate of 0.5 mV s^{-1} and with a step potential of 0.45 mV, in solutions stirred by bubbling nitrogen or recycled by a peristaltic pump (solution withdrawal was performed in very close proximity to the electrode surface). Concerning the role of the proton concentration, pH was varied by addition of small quantities of 15 M NaOH, thus maintaining constancy of ionic strength. In each case, curves were recorded starting from the higher value and conditioning the electrode at the initial potential for 15 s. The stability of electrode materials was tested recording a CV curve (as previously discussed) before and after each polarization.

Results and Discussion

Background cyclic voltammetries were recorded in 1 N sulfuric acid, to examine the effect of variation of the oxide deposits. Although not explicitly reported here, the above-discussed thermal treatments do not modify the electrochemical response of Si/BDD electrodes; on the contrary, Figure 1 shows that minimal amounts of RuO_2 significantly change the CV response of the electrode. The main features of the voltammogram are already present for the smallest oxide deposit (curve "A": nominally, 1.2×10^{13} RuO_2 molecules cm^{-2}) and they remain unchanged by increasing the oxide loading. The voltammetric currents increase with increasing the ruthenium dioxide loading at the BDD surface. On the other hand, the efficiency of charge-storage (which is related to the voltammetric— anodic or cathodic—area) is not directly proportional to the oxide loading and it seems dependent on the external surface area exposed by the three-dimensional oxide phase. This topic will be discussed in detail in a following paper, but further interpretations in this paper will take into account the "effective" number of noble-metal sites that undergo electron-transfer processes.

The measurements carried out in the presence of sodium chloride (for the investigation of the chlorine evolution reaction) gave different results, depending on the amount of noble-metal oxide deposited on the BDD surface.

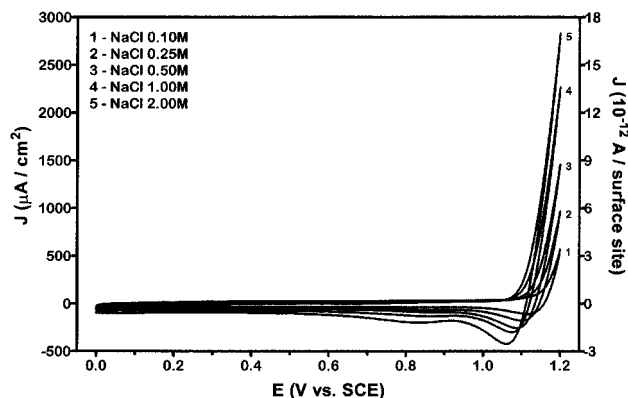**Highly Modified Diamond (HMD) Electrode.** Figure 2 shows a set of cyclic voltammetric curves recorded in 0.01 M

Figure 2. Cyclic voltammetry for the BDD/RuO_2 electrode with 2.65×10^{16} RuO_2 molecules cm^{-2}, in 0.01 M perchloric acid + xM sodium chloride and $(4 - x)$M sodium perchlorate ($x = 0.1$, 0.25, 0.5, 1.0, and 2.0). Scan rate: 100 mV s^{-1}.
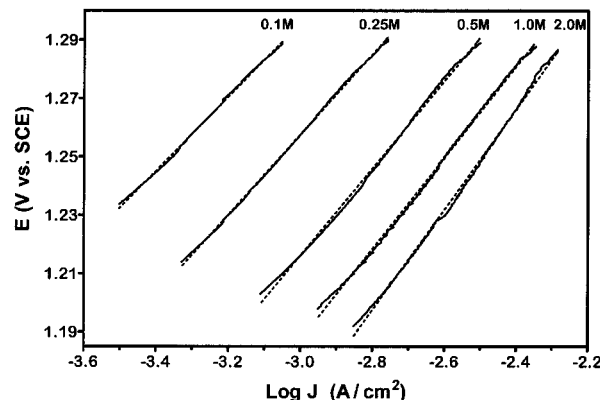

Figure 3. Current−potential curves for chlorine evolution in xM NaCl/$(4 - x)$M NaClO$_4$/0.01 M HClO$_4$. Effect of the chloride concentration. BDD/RuO_2 electrode with 2.65×10^{16} RuO_2 molecules cm^{-2}.

perchloric acid + xM sodium chloride and $(4 - x)$M sodium perchlorate (in order to maintain a constant ionic strength of four) for the sample with the highest oxide loading (nominally, 2.65×10^{16} RuO_2 molecules cm^{-2}). The pH of the test solutions was quite constant at a value of 1.0. As expected, the CV current increases while the onset of chlorine evolution shifts to less positive potentials as the chloride concentration increases. In the cathodic sweep, the catalytic activity of RuO_2 toward the chlorine evolution reaction is manifested by the good reversibility of the reaction, as the reduction of chlorine, produced during the anodic sweep, takes place at a potential close to that at which the chloride ion is oxidized. As observed in the case of DSA-type (titanium-supported) RuO_2 film electrodes[19] and also in the case of diamond,[17] two cathodic peaks are present in the cyclic voltammogram, probably related to different species of dissolved and electroactive chlorine,[17] i.e., chlorine itself and hypochlorous acid formed by hydrolysis of anodically formed Cl_2 or by direct electro-oxidation of Cl^- (the potential threshold for this reaction decreases with increasing the solution pH and/or the chloride concentration).

To investigate the mechanism of the chlorine evolution reaction, a set of quasi-steady polarization curves has been obtained in the same solutions used for CV analysis and the results, in terms of Tafel plots, are shown in Figure 3. The linearity is quite good (some noise is caused, in the instrument, by the automatic scale change for the measured current) and the slope (b) is 0.149 ± 0.017 V. From Figure 4, showing the log j/log c_{NaCl} plots at four different potentials in the region of linearity of the E/log j plots, a reaction order (R) of about 0.7
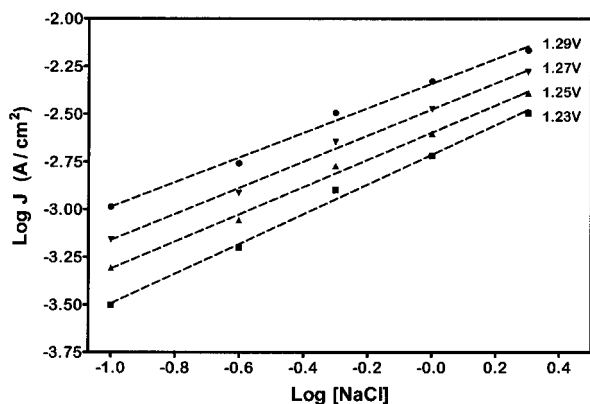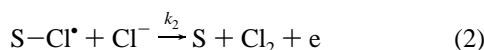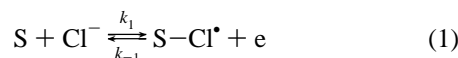
Figure 4. Dependence of the reaction rate for chlorine evolution on the Cl$^-$ concentration in xM NaCl/(4 − x)M NaClO$_4$/0.01M HClO$_4$. BDD/RuO$_2$ electrode with 2.65 × 10^{16} RuO$_2$ molecules cm^{-2}.

(0.71 ± 0.05) is obtained with respect to the chloride concentration. Both the values of b and R agree well with a Volmer-Heyrovsky mechanism,[20] with a rate-determining electrochemical desorption, provided a value of about 0.7 is assumed for the coverage by the intermediate chlorine radicals:[21]

$$S + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S-Cl^\bullet + e \qquad (1)$$

$$S-Cl^\bullet + Cl^- \overset{k_2}{\longrightarrow} S + Cl_2 + e \qquad (2)$$

The rate of the chlorine evolution reaction was found to be independent of the solution acidity, in support of the above mechanistic hypothesis (the Volmer-Heyrovsky sequence of steps does not involve protons); this result will be discussed in a following section of this paper.

Test of the Mechanism. The suggested Volmer-Heyrovsky mechanism implies the second step to be rate-determining; accordingly, the current density of the reaction can be written as

$$i_2 = Fk_2 C_{Cl^-} \theta_{Cl^\bullet} \exp[(1 - \beta)F\eta/RT]$$

where F is the Faraday constant (96484.6 C/mol), C_{Cl^-} is the chloride molar concentration, $\theta_{Cl^\bullet}$ represents the chlorine radical coverage at the electrode surface, while β, η, R, and T are the symmetry factor, the applied overpotential, the molar gas constant and the absolute temperature, respectively.

Following the quasi-equilibrium hypothesis, the Cl$^\bullet$ coverage can be expressed by the Langmuir electrochemical adsorption isotherm, at least as a first approximation:

$$\theta_{Cl^\bullet} = \frac{K_1 C_{Cl^-} \exp(F\eta/RT)}{1 + K_1 C_{Cl^-} \exp(F\eta/RT)}$$

where $K_1 = k_1/k_{-1}$ is the quasi-equilibrium constant for step (I). Substituting the expression for the coverage into the expression for the current, one obtains

$$i_2 = Fk_2 C_{Cl^-} \frac{K_1 C_{Cl^-} \exp(F\eta/RT)}{1 + K_1 C_{Cl^-} \exp(F\eta/RT)} \exp[(1 - \beta)F\eta/RT]$$

which can be rearranged to give:

$$\frac{\exp[(1 - \beta)F\eta/RT]}{i_2} = \frac{1}{FK_1 k_2 C_{Cl^-}^2 \exp(F\eta/RT)} + \frac{1}{Fk_2 C_{Cl^-}}$$

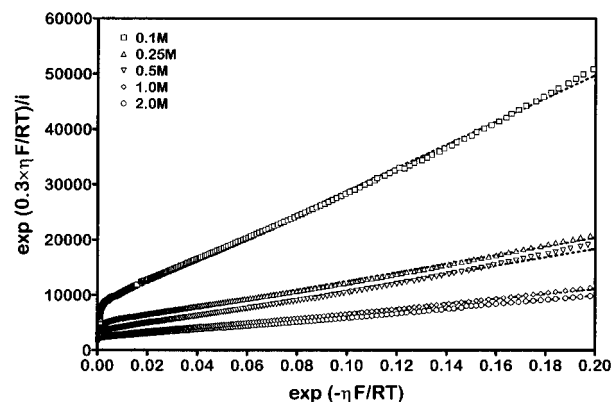Therefore,[22,23] a plot of $\exp[(1 - \beta)F\eta/RT]/i$ against $\exp(-F\eta/$

Figure 5. Testing of the electrochemical-desorption-controlled mechanism for the chlorine evolution reaction at different chloride concentration.
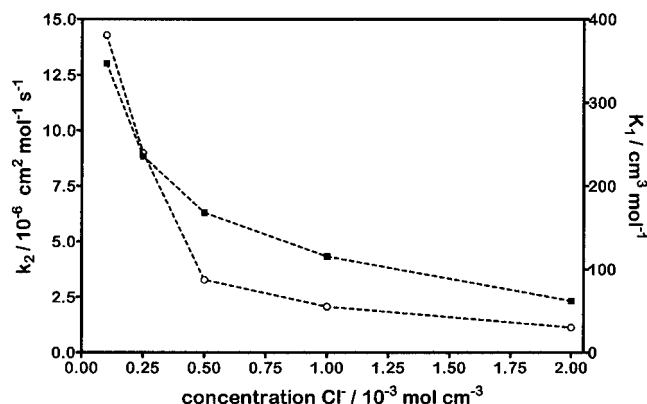

Figure 6. Values of the kinetic constants K_1 (○) and k_2 (■) for the Volmer-Heyrovsky chlorine evolution reaction mechanism (electrochemical desorption being considered rate-determining), as a function of chloride concentration in solution.

RT) should give a straight line of slope $1/FK_1 k_2 C_{Cl}^{-2}$ and intercept $1/Fk_2 C_{Cl^-}$, as shown in Figure 5 (the plot has been restricted to high overpotential values, considering that the model mathematical expression is based on the high-field approximation). For the selection of β, the shape of the polarization curves suggests a value larger than one-half. In the plots, a value of 0.7 has been chosen, also in consideration of the fact that for this value a better linearity is observed. From the slope and the intercept of the plots, both k_2 and K_1 can be easily evaluated, for each chloride concentration. Related values are reported in Figure 6. Interestingly, the values of k_2 are significantly[22] high, in good agreement with the quasi-reversibility of the cyclic voltammetric curves shown in Figure 2. Although very different in their meaning, both constants change in a quasi-exponential way with respect to [Cl$^-$]. This trend can be possibly related with an exponential contribution still present in the mathematical formulation of the constants. Actually, a Frumkin isotherm, which contains an exponential term, taking into account the lateral interactions between adsorbed radicals, would be a better hypothesis, although not easily verifiable. The quasi-exponential decay of k_2 suggests that the lateral interactions should have a repulsive character.

Considering the role of pH, an analogous elaboration has been performed and results have shown that both constants K_1 and k_2 do not change significantly as a function of the proton concentration.

Slightly Modified Diamond (SMD) Electrode. The parameters of the chlorine evolution reaction at the sample having the lowest catalyst loading are less easily interpretable. The slope
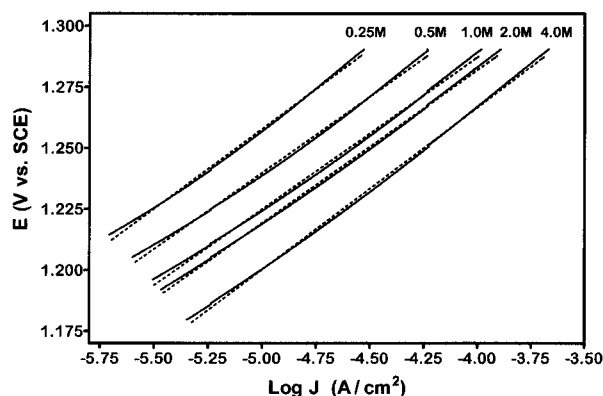
Figure 7. Current−potential curves for chlorine evolution in xM NaCl/$(4 - x)$M NaClO$_4$/0.01 M HClO$_4$. Effect of the chloride concentration. BDD/RuO$_2$ electrode with 1.2×10^{13} RuO$_2$ molecules cm^{-2}.
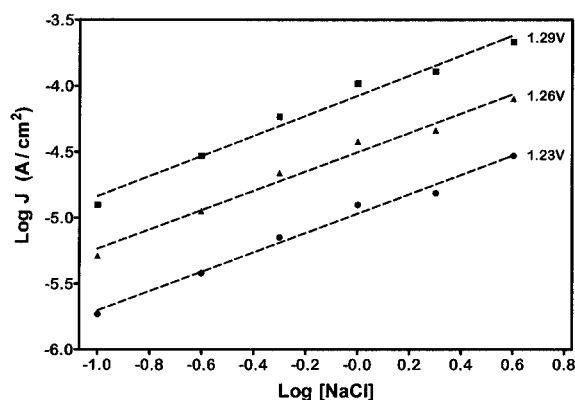

Figure 8. Dependence of the reaction rate for chlorine evolution on the Cl$^-$ concentration in xM NaCl/$(4 - x)$M NaClO$_4$/0.01 M HClO$_4$. BDD/RuO$_2$ electrode with 1.2×10^{13} RuO$_2$ molecules cm^{-2}.
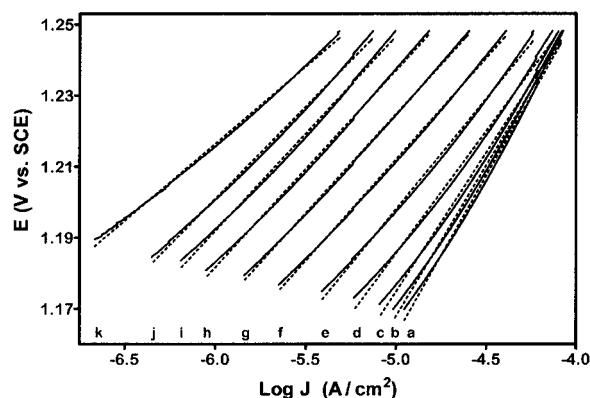

Figure 9. Current-potential curves for chlorine evolution in 1 M NaCl/$(4 - x)$M NaClO$_4$/xM HClO$_4$. Effect of the measured solution pH. BDD/RuO$_2$ electrode with 1.2×10^{13} RuO$_2$ molecules cm^{-2}.

of Tafel plots (Figure 7) is again slightly influenced by the chloride concentration and the value of b is 0.065 ± 0.004 V. The elaboration of the data, in terms of log j vs log c_{NaCl} (at different potentials, in the region of linearity of Tafel plots), is shown in Figure 8. The linear regression analysis, applied to experimental points, gives a reaction order of 0.74 ± 0.02 with respect to Cl$^-$. At variance with the previously investigated HMD electrode, the acidity affects the chlorine evolution reaction (Figure 9), the reaction order with respect to H$^+$ being about -0.6. As shown in Figure 10, the dependence changes significantly for pH values greater than 2; a possible explanation to this behavior is part of the next paragraph.
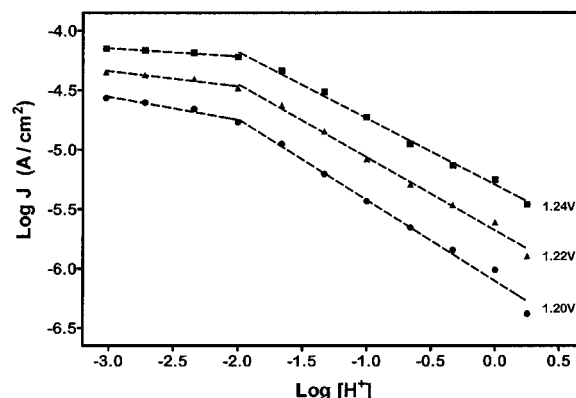

Figure 10. Dependence of the reaction rate of chlorine evolution at constant Cl$^-$ concentration on the pH of the solution. BDD/RuO$_2$ electrode with 1.2×10^{13} RuO$_2$ molecules cm^{-2}. (a) Solution "as prepared", (b) pH 0.00, (c) pH 0.33, (d) pH 0.66, (e) pH 1.00, (f) pH 1.33, (g) pH 1.66, (h) pH 2.00, (i) pH 2.34, (j) pH 2.72, (k) pH 3.02.

The Role of pH. While the chlorine evolution has been deeply investigated at different electrode materials and conditions, the pH dependence of the reaction has received little or no consideration and is still debated. In the present paper, we report data obtained at RuO$_2$-modified BDD thin films, i.e., at electrodes having practically no porosity and a very smooth surface. Moreover, particular attention has been paid to the hydrodynamics of the system under measurement, to overcome possible problems related to local modifications of pH.

The picture can be summarized as follows:

(i) at unmodified BDD electrodes.[17] The reaction is pH dependent and its order, with respect to [H$^+$], is ≈ 0.5.

(ii) Chlorine evolution reaction at highly RuO$_2$-modified BDD electrodes. The reaction is pH independent and insensible to hydrodynamic conditions (solution stirred by bubbling nitrogen or recycled by a peristaltic pump, creating an approximately laminar solution flux at the electrode surface).

(iii) Chlorine evolution reaction at slightly RuO$_2$-modified BDD electrodes. In this case, the reaction is again pH dependent but the reaction order, with respect to [H$^+$], is about -0.6.

(iv) As far as the literature is concerned,[24] the available data show that polycrystalline RuO$_2$ (relatively thick deposits on titanium substrates) presents a variable, nonzero order of reaction with respect to [H$^+$], while no effect of pH is observed at single-crystal faces of RuO$_2$.

From the comparison of the various results, it seems quite reasonable that the pH dependence, when present, is correlated with the state of the electrode surfaces, i.e., the surface charge. The rate of the chlorine evolution reaction at polycrystalline RuO$_2$ electrodes, BDD electrodes, and also at the SMD electrode shows a pH dependence as a possible consequence of an electrode surface with different active sites; on the contrary, for single-crystal RuO$_2$ electrodes and the HMD electrode, no pH effect is observed and, in fact, the electrode surfaces should be considered as "more defined", in terms of homogeneity of sites.

The effect of the solution acidity on the kinetics of the chlorine evolution reaction has been studied by various authors and extensively reviewed by Trasatti[24] and, more recently, thoroughly discussed by Conway and Ping.[25] In refs 24 and 25, particular importance was assigned to the role of electric potential (ϕ^*) at the reaction plane, related, in turn, to the acid−base properties of active sites. Along these lines, the data presented in the present paper can be satisfactorily accounted for.

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At unmodified BDD electrodes, the rate of the chlorine evolution reaction is controlled by the discharge step, in which case, as discussed in ref 17, the increase in the solution acidity causes an increase in the chlorine evolution rate. As shown in Figures 9 and 10, at the SMD electrode the opposite effect is observed, because the rate control is not due to the discharge but rather to the desorption, although through a complex mechanism. In this case, the increase in the stabilization of the chlorine radical, related with an increase in the solution acidity, results in a decrease of the chlorine evolution rate.

Details on the Chlorine Evolution Reaction at the Slightly RuO$_2$-Modified BDD Electrode. Considering that the oxide loading of the SMD electrode is as low as 1.2×10^{13} molecules cm^{-2}, which represents an average coverage between about 0.1 and 0.01 (depending on the effective roughness factor attributed to the original BDD surface), it may be of interest to give some microscopic (AFM) evidence of the modified surface. As reported elsewhere,[16] at the sample with the highest oxide loading (2.65×10^{16} molecules cm^{-2}), different semispherical particles can be seen, with diameters from 30 to 70 nm; on the contrary, at samples with lower oxide loading, no particle could be observed, despite the measurable presence of ruthenium dioxide at the electrode surfaces (as detected by CV and XPS). The absence of visible RuO$_2$ particles at the BDD surface suggests that oxide clusters have a diameter not larger than, e.g., 10 nm.

In view of the very small size of the catalyst patches, at which the chloride oxidation takes place, and of the presence of a conductive surface (the diamond itself) all around the RuO$_2$ sites, it seems reasonable to imagine a spillover[26−28] of chlorine radicals from the donor phase (RuO$_2$) to the acceptor one (diamond). Accordingly, the electrochemical desorption could easily take place at the latter, due to the lack of stabilizing interaction with the C(diamond) surface. Alternatively, chemical desorption can occur at the boundaries between the two materials.

As far as the involvement of the surface is concerned, changes in its working fraction, for the three cases taken into consideration (the two modified BDD films and the BDD itself, as a comparison) can be introduced by normalizing the measured current (for the chlorine evolution reaction) to the number of "active sites" at which the reaction takes place. For the unmodified diamond film, the evaluation was based on the number of C atoms required for a monolayer, assuming a unitary roughness coefficient (this approximation does not modify significantly the result, as the surface is polycrystalline but not porous). Concerning the BDD/RuO$_2$ electrodes, the number of active sites was based on the nominal value, for the lowest oxide loading, and on the "effective value", as obtained from the ratio of the voltammetric areas (Figure 1), for the highest oxide loading. The dependence of the normalized currents on the applied potential, in terms of a Tafel plot, is shown in Figure 11; it is evident that there is a role of the catalytic oxide at the electrode surface as well as a different chlorine evolution reaction mechanism, at least for the two modified electrodes, although not reflected by the Tafel slope values.

Conclusions

The high chemical/electrochemical and mechanical stability of diamond has allowed the preparation of thin films of ruthenium dioxide, without any interference coming from the support. As a limiting condition, the high conductivity and the lack of catalytic activity of BDD allows studies to be made at
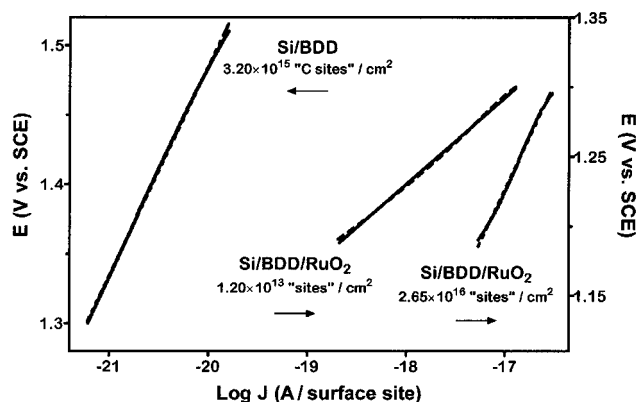
Figure 11. Current−potential curves for chlorine evolution in 1 M NaCl/3 M NaClO$_4$/0.01 M HClO$_4$. Current values are normalized to the number of surface sites.
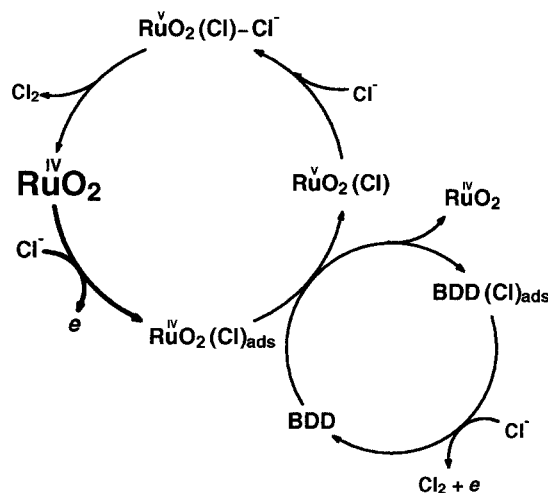
Figure 12. Schematic representation of the reaction pattern for the chlorine evolution reaction at BDD/RuO$_2$ electrodes. At low RuO$_2$ coverage, radical spillover can take place.

electrode materials deposited at the level of submonolayers. In any case, diamond acts as an inert support if the number of active sites is sufficiently high to sustain the required passage of current (which is a function of the applied potential). However, if this requirement is not satisfied, diamond can itself play the role of electrode material, but the difference in terms of catalytic activity becomes important in defining the mechanism of the reaction.

On the basis of the results presented, it is suggested that the chlorine evolution reaction at the electrode with the lowest oxide loading occurs through a spillover mechanism involving the RuO$_2$ particles as the material at which chloride ions are discharged (this process is simpler since RuO$_2$ acts as a catalyst). After this first step, the adsorbed radical may spill over to the diamond surface as a consequence of thermal agitation, or may interact with a metal site, reacting again at the oxide surface, until gaseous chlorine molecules are formed and can then leave the surface. As represented in Figure 12, the involvement of the diamond surface can be also an escape route for the case where the ruthenium site is unable to change its oxidation state. Essentially, the interaction of the metal ion with the adsorbed radical requires the participation of the whole near-surface region of the oxide film; such reorganization may be impossible or not effective enough, if the oxide particles are too small. Similar effects are well-known[29] in heterogeneous catalysis at supported metal oxides.

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