1. Introduction

The structure and energetics of two types of oxygen-terminated diamond surfaces, the keto and ether configurations, were investigated by density functional theory. To explore OH generation, we studied the approach of a hydroxyl radical to these surfaces. The OH radical strongly interacted with the ether-type surface, whereas the radical was repelled in the keto configuration. The kinetics of OH generation in alkaline solutions (OH = \textit{e}^{-} + \textit{HOH}) on oxygen-terminated diamond electrodes was investigated in light of the theory of catalyzed electron transfer. Our results suggested that the electron transfer occurs in the outer-sphere mode with an activation energy of 0.5 eV.

Methods

First-Principles Calculations

Periodic density functional theory (DFT) calculations were performed with the DACAPO code,[12] which utilizes an iterative scheme to solve the Kohn–Sham equations of DFT self-consistently. A plane-wave basis set was used to expand the electronic wavefunctions, and the inner electrons were represented by ultrasoft pseudopotentials,[13] which allow the use of a low-energy cutoff for the plane-wave basis set. Electron–electron exchange and correlation interactions were treated with the generalized gradient approximation (GGA) in the version of Perdew and Wang (PW91).[14] The parameterization of the energy cut-off and the \textit{k}-points sampling of the Brillouin zone on the basis of the Monkhorst–Pack grid[15] was considered. Both parameters were increased systematically until the change in the absolute energy was less than 0.02 eVÅ\(^{-1}\).

Reference cited therein.

1. Introduction

The electrochemical properties of BDD electrodes are determined by their surface composition. Usually, a diamond structure exhibits hydrogen[1–5] or oxygen[3,6,7] terminations. The latter can be obtained by several methods such as electrochemical oxidation and \textit{O}_{2}-plasma treatment.[5] The surface groups generated may depend on the crystal face; for instance, hydroxyl groups could be found on (111) materials, whereas two chemical bonds are found for a single carbon atom in the first layer of an ideal (100) diamond surface; hence, carbonyl (top) and ether (bridge) groups are expected. An advantage of surface oxidation treatment is that it changes the electrochemical nature of the diamond electrodes and facilitates their functionalization for several applications. Water treatment[4,9] and fuel cells are of paramount importance, and they are two of the most investigated applications of diamond electrodes. The former exploits two features, the high potential for oxygen evolution and the possibility to anodically produce hydroxyl radicals in a very effective manner.[10] In the case of energy-conversion systems, the search for a promising electrocatalyst with the requirements of high electrocatalytic activity, stability, and low price has focused on metal oxides, which are mainly stable in alkaline media. In this respect, doped diamond surfaces could be used as inert and stable substrates for the deposition of nanoparticles or films.[11]

In this context and taking into account that diamond structures could be electrochemically oxidized in the oxygen evolution potential region, the present work is centered on the behavior of oxygen-terminated diamond electrodes in the presence of hydroxyl radicals to gain deeper understanding of the fundamental principles governing the involved processes. In particular, we explore the kinetics of the production of the OH radical in alkaline solutions.
Diamond Modeling

Under vacuum, the (100) oxygen-terminated surface exhibited a (2 x 1) reconstruction. The behavior of OH was investigated by first-principles calculations and in light of the theory of electrocatalysis proposed and developed by Santos and Schmickler. A (2 x 1) reconstructed (100) diamond surface was modeled with a slab consisting of 10 carbon layers and a vacuum region equivalent to 12 layers. Two different oxygen-terminated configurations were studied: the keto and ether configurations. In the former, each surface C atom is linked to another two C atoms by a single bond and to an O atom by a double bond (Figure 1, right). For ether-type adsorption, the surface carbon atom is connected to O and C atoms by single bonds (Figure 1, left); oxygen atoms adsorbed at the bridge sites within two-carbon dimer row were considered.

To avoid dangling bonds at the truncated C-C bulk, hydrogen atoms were used to maintain sp$^3$ hybridization of the bottom carbon layer. The presence of hydrogen introduces changes in the electron density of the bottom layer, but according to ref. [22], H termination does not have a significant effect on the energetics of the top layer, at which the adsorption is studied.

The terminal oxygen atoms, the first carbon layer, and the H in OH were allowed to relax fully. The oxygen atom in the radical was kept fixed in all coordinates at different z distances perpendicular to the corresponding surface.

Diamond electrodes are usually highly doped to make them conductive, and boron is the most commonly used dopant. However, at practical doping levels the concentration of the dopant is much smaller than that of the carbon atoms, and thus, its presence at the surface can be safely ignored. Therefore, we only considered the structure of pure diamond surfaces.

2. Structure and Energetics

To investigate the energetics and stability of the O-terminated structures under consideration, binding energies ($E_b$) were calculated relative to $O_2(g)$ and a reference state slab according to Equations (1) and (2):

$$E_{b,keto-D} = -\frac{1}{N_0} (E_{keto-D} - E_D) + \frac{1}{2} E_{O_2}$$

$$E_{b,ether-D} = -\frac{1}{N_0} (E_{ether-D} - E_D) + \frac{1}{2} E_{O_2}$$

in which $E_{keto-D}$ and $E_{ether-D}$ are the total energies of the O-terminated diamond surface in the keto and ether configurations, respectively; $E_D$ represents the total energy of the pure (2 x 1) reconstructed (100) diamond surface; $N_0$ is the number of oxygen atoms, and $E_{O_2}$ is the total energy of the oxygen molecule in the gas phase. Because of the well-known difficulties of DFT with the oxygen molecule, we used the experimental value. Zero-point energy corrections were not included, and the energies are given at $T = 0$ K. For all the possible oxygen-terminated scenarios, only the ether and keto configurations indicated in Figure 1 were investigated for our purpose.

Our results show that the oxygen in the ether configuration is energetically favorable, with a binding energy of about $-5.36$ eV for an oxygen-surface coverage up to 50%, with the reconstructed diamond surface preserved. Our binding energy is in good agreement with the literature ($-5.68$[23] and $-5.35$ eV[24]). The ether species are bonded covalently to the carbon dimers (C-C distance = 1.53 Å) in a (2 x 1) reconstructed (100) diamond surface with an O-C bond distance of about 1.44 Å, again in accord with the literature data[23-25].

Investigation of an adsorbed oxygen monolayer on the reconstructed diamond surface indicated that the lowest energy appeared if the oxygen atoms were in the ketone form during cleavage of the dimer bond. Each oxygen atom is double bonded to the surface with an O-C bond distance of about 1.21 Å and a binding energy around $-5.86$ eV for 100%
oxygen-surface coverage. Unlike ether adsorption (50% oxygen coverage), in which the reconstructed diamond structure remained unchanged, in the keto adsorption (100% oxygen coverage) the diamond surface is highly perturbed, the reconstruction is lost, and the diamond surface becomes almost undistorted and forms a zigzag surface pattern with O–C–C angles deviating from the ideal structure by ±20° (Figure 2). Similar results were found by Petrini et al.\textsuperscript{23} A comparison with the binding energy for a full monolayer of ether termination (−6.22 eV\textsuperscript{23,27}) confirmed that the latter is thermodynamically more favorable than keto terminations (−5.86 eV) in accordance to refs. [23,26–28]. Interpretation of these results suggests that in the most energetically stable structure for oxygen-terminated surfaces, the (2\times1) reconstruction is lifted; comparable results were reported in ref. [27].

As mentioned in the Introduction, we were particularly interested in the generation of the OH radical in alkaline solution. To investigate the fate of the OH radical at the surface, we investigated its approach to an oxygen-covered surface. The corresponding energy–distance curves were also required to calculate the free-energy surface for OH generation, which will be discussed below.

Figures 3 and 4 show the behavior of OH as it approaches the oxidized diamond surface. The radical was fixed at several distances to the electrode, as described previously (see the section on Diamond Modeling). To calculate the perpendicular distance of OH to the electrode, the $z$ coordinate of the oxygen atoms in the keto/ether-type termination was used as a reference.

Figure 3 exhibits the approach of OH to the keto-type terminated surface. Repulsive interactions and steric effects were detected due to high coverage and a high electronic charge concentration on the surface. Therefore, the favored situation was found at larger distances of OH from the oxidized diamond, and as expected, the energy smoothly increased with decreasing separation of OH from the electrode. For larger distances ($>0.5$ Å with reference to the O termination) the O–H bond remained unmodified at about 0.99 Å, whereas the O–C bond in the keto-terminated diamond slightly moved up with an O–C–C angle oscillating around 90° (Figure 3); this in turn corresponds to an almost-undistorted diamond structure.

At shorter distances ($<0.5$ Å) from the electrode, the formation of an unstable adsorbed H–O–O species was observed with the following geometrical parameters (Figure 3): O–O distance of 1.48 Å (in agreement with the reported data for the hydroperoxide species\textsuperscript{29}), H–O distance of 0.99 Å, and O–C distance of 1.30 Å. Elongation of the O–C bond suggests that the double bond no longer exists and that a single bond was formed, although our value (1.30 Å) is rather small in comparison to an O–C single bond ($\approx 1.43$ Å\textsuperscript{29}).

Different behavior was found if the OH approached an ether-terminated (100)-(2\times1) reconstructed diamond (see Figure 4). As mentioned previously, an oxygen-surface coverage up to 50% was considered. For larger distances of the hydroxyl radical to the surface, the energy increased, and a typical reconstructed diamond was found: C–C dimer distance of 1.54 Å and C–O bond of 1.43 Å. Unlike the keto case, the most favorable scenario occurred if the OH was surrounded by ether groups at 0.4 Å (with reference to the O termination, Figure 5).
The most prominent feature was the tendency to restore the diamond undistorted structure, with C–C bond lengths around 2.70 and 2.83 Å (see Figure 5) compared with 2.52 Å for an ideal C–C bond.26

The overall picture can be summarized as follows: several individual or combined parameters can affect the behavior of the diamond. Its structure and reactivity can be mainly modified by the surface coverage, the type of termination bond, and the environment. The diamond structure will vary between an ideal or reconstructed structure depending on which one is energetically more favorable for the system under consideration.

For the sake of completeness, we additionally examined the effect of OH radicals on the H-terminated (100)-(2×1) diamond surface (hydrogen surface coverage up to 100%). The combination of a hydroxyl radical with a terminal hydrogen leads to the formation of a water molecule plus the creation of a dangling bond in the diamond surface with a reaction energy ($E_r$) of about −1.8 eV. This value, which in this particular case accounts for the formation of water plus its interaction with the diamond surface, was evaluated according to Equation (3):

$$E_r = E_{\text{tot}} - E_{\text{H$_2$O}} - E_{\text{OH}}$$

in which $E_{\text{tot}}$ is the total energy of the hydrogen-terminated diamond surface that has lost one hydrogen due to the interaction with OH plus a water molecule, $E_{\text{H$_2$O}}$ accounts for the total energy of the H-terminated diamond surface, and $E_{\text{OH}}$ is the total energy of the hydroxyl radical in the gas phase. Zero-point energy corrections were not included and the energies are given at $T = 0$ K.

In these circumstances, the water molecule interacts with the diamond surface at a H$_{\text{diamond}}$–diamond distance of 1.85 Å; one hydrogen points down with respect to the surface and the other one points up to preserve the H–O–H angle. The water structure remains geometrically unchanged with values of about 0.97 and 1.02 Å for the H$_{\text{up}}$–O and H$_{\text{down}}$–O distances, respectively, and 104.9° for the H–O–H angle. As expected, a subtle elongation of the bond length due to water–surface interactions was detected for the H$_{\text{down}}$–O bond.

Taking into account the result of our optimization procedure, two highly favorable products were obtained: a water molecule and a 75% H coverage reconstructed diamond with an isolated dangling bond. The removal of a hydrogen atom on the water molecule reduced the electrostatic repulsion between the neighboring CH polar groups and favored the formation of an isolated dangling bond, which led to higher stability, and this is in agreement with the data reported by Zilillotti et al.27

3. Electrochemical Generation of the OH Radical

Because of its chemical inertness, OH radicals can be generated at BDD,28 which in turn may serve as a useful reagent for a variety of reactions. The mechanism of OH generation depends on the pH. In acid solution, it follows Equation (4):

$$\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ + e^-$$

According to Kapalka et al.,32 the standard equilibrium potential at pH 0 is about 2.38 V versus the normal hydrogen electrode in alkaline solutions the mechanism follows Equation (5):

$$\text{OH}^- \rightarrow \text{OH} + e^-$$

The standard equilibrium potential of 1.55 V for pH 14 given by Bard, Parsons, and Jordan44 is cited out of order. In alkaline solutions the mechanism agrees well with the value quoted above for acid solutions.

According to our investigations above, an OH radical can follow one of several courses: On a hydrogen-covered surface, it combines with hydrogen to form water and is lost as a re-

1 The initial structure used for the optimization was a OH radical at several angstroms from a H-terminated reconstructed diamond surface. Hydrogen surface coverage: 100%. For the relaxations, the terminal hydrogen atoms, the first carbon layer, as well as the OH were allowed to be fully optimized.
agent. On an oxygen covered surface in the ether configuration, it is strongly adsorbed. On an oxygen covered surface in the keto configuration, it is repelled at short distances. Therefore, continuous OH generation can only take place at a keto surface or at a surface coverage of 50% oxygen in the ether configuration and 50% OH coverage. In either case, further OH adsorption is no longer possible. To be specific, we investigated OH generation in alkaline solutions according to Equation (5) in the keto configuration, but the results should be very similar to those obtained in the other case.

We calculated the free-energy surface for the reaction within the framework of the theory of catalyzed electron transfer.[17,18,33] For this purpose, we needed the electronic interaction of the reactant with the electrode surface. As is evident from Figure 4, the energy of the OH radical increases strongly as it approaches the oxygen-covered surface. Therefore, the electron transfer takes place in the outer-sphere mode, with an optimal distance of about 3 Å from the surface, so we needed the interaction at distances of this order. For reactions in the outer-sphere mode, the interaction is characterized by a single interaction energy $\Delta_e$, which is the broadening of the reactant’s valence level due to its interaction with the electrode.

Values of $\Delta > 10^{-2}$–$10^{-1}$ eV are sufficient to make the reaction adiabatic.

At short distances, the interaction energy $\Delta$ can directly be obtained from the density of states of the p orbital of the oxygen atom of OH. Thus, for a distance of 1.5 Å we obtained $\Delta = 0.2$ eV, and for a distance of 2.0 Å we obtained $\Delta = 0.15$ eV. At larger distances, $\Delta$ can no longer be obtained from the energy broadening, as it becomes too small. In this range, interaction energies fall off exponentially, with decay lengths of the order of 0.5 to 1 Å, so we may safely conclude that at 3 Å, the interaction is in the adiabatic range.

Solvation reorganization plays an important role in electron transfer; therefore, we investigated the solvation of HO$^-$ near the interface. In the bulk, the solvation energy of this ion is about 4.8 eV.[35,36] Its variation near the interface is given by the potential of mean force (pmf), which gives the work required to move the particle from the bulk towards a given position near the electrode surface. The latter was determined by molecular dynamics simulations with umbrella sampling as described in ref. [38]. The effect is comparatively small, as HO$^-$ fits well into the water structure. Thus, at a distance of 3 Å, the distance at which the reaction takes place, the pmf is only 0.13 eV and it rises slowly towards the surface to reach a value of 0.26 eV at 2 Å. Given that this change in the solvation energy plays only a very minor role in the reaction, we do not describe the details of the simulations here but leave this to a future paper on the adsorption of OH$^-$ (see below) for which its effect is more important.

The solvation energy $\Delta_{sol}$ can be split into two parts: the energy of reorganization $\lambda$ and the fast solvation energy $\delta_{sol}$.[34]

The division is given by the Pekar factor [Eq. (6)]:[41,42]

$$\lambda = (\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}) \Delta_{sol}$$

where $\varepsilon_\infty$ and $\varepsilon_0$ are the optical and the static dielectric constant, and the term in brackets is the Pekar factor, which for water is about 0.5.[43] The OH radical has a solvation energy of about 0.42 eV,[40] which must be subtracted from the solvation energy of the anion to obtain the change in the solvation energy. We note that the energy of reorganization is much larger than the energy broadening $\Delta$, so that the latter has no effect on the energy of activation.[34]

The interfacial capacity of BDD in contact with an aqueous solution depends on the preparation and the doping, but it is always small of the order of 4 μF cm$^{-2}$ or less,[3] as may be expected for a semiconductor. Therefore, any potential drop between the bulk of the solution and the bulk of the electrode will primarily take place within the semiconductor itself, and the electric field in the surface region of the electrolyte will be weak; therefore, it can be safely neglected in our calculations.

With this information, we performed calculations for alkaline solutions and for the case in which the reaction was in equilibrium. The resulting free-energy surface is shown in Figure 6. It was plotted as a function of the distance of the reactant from the surface and of the solvent coordinate $q$. The latter is familiar from the early works of Marcus[38] and Hush[36] and characterizes the state of the solvent. During the reaction, the configuration of the solvent passes from that appropriate for the HO$^-$ anion to that for OH$^-$; in our normalization, a value $q$ of the solvent coordinate indicates that the solvent configuration would be in equilibrium with a charge of $-q$ on the reactant. Thus, during the oxidation $q$ passes from $-1$ to 0.

As was expected, the free-energy surface shows features of a typical outer-sphere electron transfer: two minima of equal depth separated by a barrier. At closer distances the reaction is less favorable, as the energies of the reactants rise. The energy of activation is about 0.5 eV, which is the value of $\Delta/4$ predicted by Marcus theory. However, our model differs significantly...
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Keywords: carbon · density functional calculations · electron transfer · radicals · oxygen-terminated diamond

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Oxygen-Terminated Diamond Electrodes in Alkaline Media: Structure and OH Generation

Not only a girl’s best friend: Boron-doped diamond is important as an electrode material. Oxygen-terminated diamonds and the kinetics of OH generation in alkaline solutions on this type of surface are studied theoretically; this allows detailed structure and energetics characterization of the systems, as well as an understanding of the reaction dynamics that proceed in an outer-sphere mode.