Understanding anodic wear at boron doped diamond film electrodes

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ABSTRACT

This research investigated the mechanisms associated with anodic wear of boron-doped diamond (BDD) film electrodes. Cyclic voltammetry (CV), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS) were used to measure changes in electrode response and surface chemistry as a function of the charge passed and applied current density. Density functional theory (DFT) modeling was used to evaluate possible reaction mechanisms. The initial hydrogen-terminated surface was electrochemically oxidized at lower potentials than water oxidation (≤ 1.83 V/SHE), and was not catalyzed by the hydrogen-terminated surface. In the region where water oxidation produces hydroxyl radicals (OH•), the hydrogen-terminated surface may also be oxidized by chemical reaction with OH•. Oxygen atoms became incorporated into the surface via reaction of carbon atoms with OH•, forming both C=O and C-OH functional groups, that were also detected by XPS measurements. Experimental and DFT modeling results indicate that the oxygenated diamond surface lowers the potential for activationless water oxidation from 2.74 V/SHE for the hydrogen terminated surface to 2.29 V/SHE for the oxygenated surface. Electrode wear was accelerated at high current densities (i.e., 500 mA cm−2), where SEM results indicated oxidation of the BDD film resulted in significant surface roughening. These results are supported by EIS measurements that document an increase in the double-layer capacitance as a function of the charge passed. DFT simulations provide a possible mechanism that explains the observed diamond oxidation. DFT simulation results indicate that BDD edge sites (−CH3) can be converted to COOH functional groups, which are further oxidized via reactions with OH• to form H2CO3(aq) with an activation energy of 58.9 kJ mol−1.

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1. Introduction

Boron-doped diamond (BDD) film electrodes have been extensively studied for their ability to oxidize a wide range of water contaminants. Contaminants can be oxidized by a combination of direct electron transfer and reaction with hydroxyl radicals (OH•) produced from water oxidation [1–5]. BDD electrodes have also been reported to possess high stability under anodic polarization [6–9], which has motivated the use of these electrodes in various emerging water treatment and sensor applications [10–12].

The traditional metric used to test electrode stability is the accelerated lifetime test (ALT). The ALT employs very high anodic current densities (e.g., >1 A cm−2), and monitors the time until electrode failure. Results from the ALT have shown that film delamination is the primary failure mode of BDD electrodes, and thus extensive research has focused on increasing the adhesion of BDD films to various substrates [8,13–16]. As a result of this work, reported lifetimes for BDD electrodes as high as 804 Ah cm−2 have been achieved, as measured by the ALT [15]. Although the ALT is useful for comparing the relative stability of various electrodes under high anodic current densities, the conditions of the ALT are not representative of water treatment applications that employ much lower current densities (e.g., <20 mA cm−2). Therefore, the ALT could force failure modes that do not occur under conditions used in water treatment applications.

Although BDD electrodes are generally considered to have a high anodic stability, several studies indicate that measurable wear of the BDD film can occur upon high, applied anodic charges (e.g., >100 Ah cm−2) and current densities (e.g., 1–2 A cm−2) [16–19]. Experimental evidence suggests that BDD resistance to wear is enhanced with increasing boron-doping levels [17], and wear is accelerated in the presence of organic electrolytes (e.g., acetic acid [18] and alkaline conditions [20,21]). However, the specific mechanisms associated with anodic wear on BDD electrodes have not been thoroughly explored.

Various studies have shown that anodic polarization under low current densities (e.g., <20 mA cm−2) results in oxygen incorporation into the BDD surface, which may represent a starting point for BDD oxidation. X-ray photoelectron spectroscopy (XPS) measurements indicate that freshly prepared BDD electrodes are
hydrogen terminated [22–25], and these hydrogen terminations are easily converted to oxygen-containing functional groups (e.g., carboxyl, carbonyl, and hydroxyl groups) upon anodic polarization [23–28]. The functional groups on the BDD surface have a strong effect on charge transfer in both anodic and cathodic reactions [25,29–32]. The formation of oxygenated groups has been shown to both inhibit some reactions while facilitating other types of reactions [25,26,29–32]. The electrochemical response of solution phase redox couples has also been reported to depend on whether the electrode surface was anodically or cathodically polarized prior to the measurement [16,19,33,34], suggesting that the surface functional groups continuously evolve on the BDD surface. This changing surface chemistry can affect the reproducibility of electrode performance in water treatment and sensor applications.

Despite evidence from ALTs indicating that BDD film delamination is the primary failure mode at high anodic current densities and charges, at low anodic current densities studies have shown that the BDD surface becomes oxidized, suggesting BDD wear is possible under conditions encountered in water treatment applications. Since BDD oxidation can affect the performance of water treatment and sensor applications, a fundamental understanding of the mechanisms of BDD wear is needed. Thus, the aim of this work was to characterize the wear mechanisms of BDD electrodes during long-term anodic polarization. Specifically, changes in the electrochemical response of BDD electrodes were assessed as a function of the cumulative charge passed using a combination of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Changes in surface termination were assessed by XPS, and surface morphology changes were assessed by scanning electron microscopy (SEM). Density functional theory (DFT) calculations were used to interpret the experimental results, and to gain insight into important mechanisms related to the formation of oxygenated-functional groups and the wear of BDD electrodes during anodic polarization.

2. Materials and Methods

2.1. Electrodes

All electrodes consisted of ultranocrystalline BDD films on 1.0 cm² p-silicon substrates (Advanced Diamond Technologies, Romeoville, IL). The BDD films were deposited on the substrates by chemical vapor deposition (CVD). The BDD films were grown to a thickness of approximately 2 μm under conditions of 750–12000 parts-per-million of trimethyl borane in flowing CH₄ at temperatures between 700–800 °C. Prior to use, the BDD films had measured resistivities between 0.05–0.1 ohm-cm.

2.2. Reagents

All chemicals were used as received (Sigma-Aldrich) without any additional purification and were of reagent grade purity. Background electrolyte solutions of 1 M NaClO₄ were used for all experiments, as this electrolyte has been shown to be nonreactive at BDD anodes and cathodes [30,35].

2.3. Electrode Ageing Experiments

Electrodes were aged under anodic polarization in 200 mL Pyrex® beakers. Circular 1 cm² BDD disk electrodes were mounted into custom PEEK® electrode holders. Electrical contact was made with the backside of each electrode using a 316 stainless steel current collector contained within the electrode holder, and a water-tight seal was accomplished by sealing the face of the electrode with a Viton® gasket. The cell holder provided a 0.35 cm² area exposed to the solution. The BDD electrode was used as the anode and was held stationary in the center of the beaker. A 10 cm by 18 cm 316 stainless steel 18 mesh screen (TWP inc., Berkeley, CA) was used as the cathode and was wrapped around the inner circumference of the beaker. The background electrolyte was 1 M NaClO₄ and the solution was continuously stirred using a magnetic Teflon-coated stir bar. The electrodes were connected to a MASTECH® (Hong Kong) model HY1803D galvanostatic power supply operated without a reference electrode, and polarized at constant anodic current densities of 0, 5, 50 and 500 mA cm⁻², termed from here on as BDD-0, BDD-5, BDD-50, and BDD-500, respectively.

2.4. Electrochemical Characterization Methods

BDD films were characterized electrochemically using CV and EIS. The temperature was controlled at 22 °C using a circulating water bath. Currents and electrode potentials were controlled and monitored using a Gamry Series G 750 potentiostat/galvanostat. The BDD electrodes were mounted in the electrode holders described previously. A Princeton Applied Research (PAR) model 316 rotating disk electrode (RDE) assembly was used to rotate the electrodes at 3000 rpm during EIS measurements, and the electrode was held stationary during CV scans. The counter electrode was a 12 cm long by 0.3 mm diameter Pt wire and the reference electrode was a PAR Hg/Hg₂SO₄ electrode saturated with K₂SO₄. Potentials are reported versus the standard hydrogen electrode (SHE). To prevent contamination of the electrode surface from adsorbed organic compounds from the atmosphere, the BDD electrode was cleaned via anodic polarization in the electrolyte solution at a current density of 20 mA cm⁻² for 10 minutes before each set of measurements. CV experiments were conducted in a 1 M NaClO₄ background electrolyte in the absence and presence of 5 mM K₃Fe(CN)₆ and 5 mM K₄Fe(CN)₆, and the potential was swept at a scan rate of 100 mV s⁻¹.

EIS experiments were conducted in a 1 M NaClO₄ background electrolyte containing 5 mM K₃Fe(CN)₆ and 5 mM K₄Fe(CN)₆. EIS measurements were made at the open circuit potential (~0.465 V/SHE) with an amplitude of ±10 mV and over a frequency range of 0.1 to 3 × 10⁵ Hz. EIS data was fit by equivalent circuit models using Echem Analyst™V 5.6.1a software (Gamry Instruments). Average values for double-layer capacitances (C_dir (F cm⁻²)) were extracted from values determined for constant phase elements according to methods by Brug et al. [36]. The total impedance (Z) for the equivalent circuit model can be expressed as:

\[ Z = R_\text{r} + \frac{1}{j\omega \eta} \]  

(1)

where \( R_\text{r} \) is the solution resistance (ohm cm²); \( j \) is the notation for the imaginary unit; \( \phi \) is the radial frequency (radians s⁻¹); \( \eta \) is related to the angle of rotation of a purely capacitive line on the complex plane plots (dimensionless), and is equal to 0 for a pure resistor and 1 for a pure capacitor; and \( T \) (F cm⁻² s⁻¹) can be expressed according to equation (2) [36].

\[ T = C_{\text{dir}} \left( R_\text{s}^{-1} + R_\text{r}^{-1} \right)^{1-\phi} \]

(2)

\( R_\text{r} \) represents the resistance to charge transfer (ohm cm²) for a Faradaic reaction.

2.5. Quantum Mechanical Simulations

Density functional theory (DFT) simulations were performed to gain insights into the reaction behavior of the functional groups on the BDD surface and to investigate the mechanisms associated with electrode oxidation. Two structures were used to model the BDD electrode surface: a previously-described 10-carbon atom cluster terminated by hydrogen atoms [30], and a previously-described
hydrogen terminated 34-carbon structure with a central boron atom [37]. All DFT calculations were performed with the DMol³ [37–39] package in the Accelrys Materials Studio [40] modeling suite on a personal computer. All simulations used double-numeric with polarization (DNP) basis sets [41] and the gradient-corrected Becke–Lee–Yang–Parr (BLYP) [42,43] functionals for exchange and correlation. The nuclei and core electrons were described by DFT optimized semilocal pseudopotentials [44]. Implicit solvation was incorporated into all simulations by use of the COSMO-ibs polarizable continuum model [45]. Thermal smearing of 0.005 Ha was used for numerical convergence.

The activation energies (ΔEa) for direct electron transfer as a function of the electrode potential were calculated by the method of Anderson and Kang [46]. Reactant energies were calculated as a function of the reaction coordinate, defined as the bond length of the bond that was formed or broken by the reaction. Product energies were calculated using the atomic positions determined from the optimized reactant structures, followed by self-consistent field optimization of the electronic configurations. The energy of the free electron on the vacuum scale was adjusted to the SHE scale by subtracting 4.6 eV [46]. Product energies were adjusted to reflect the electrode potential by shifting the energy profile of the product species downwards by 96.5 kJ mol⁻¹ (i.e., 1.0 eV) to increase the electrode potential by 1.0 V and upwards by 96.5 kJ mol⁻¹ to decrease the electrode potential by 1.0 V. Intersection of the product and reactant energy profiles yields the bond length of transition state and the ΔEa for the reaction. Simulations involving solvated protons included 2 explicit water molecules to more accurately mimic physical reality [47].

2.6. Analytical Methods

XPS measurements were performed at the University of Arizona Laboratory for Electron Spectroscopy and Surface Analysis. XPS measurements were not conducted as a function of time that the BDD electrode was exposed to air after anodic ageing, so any surficial chemistry changes that may have occurred during this time were not documented. SEM images were performed at Advanced Diamond Technologies (Romeoville, IL).

3. Results and Discussion

3.1. Oxidation of C-H Surface Sites

Initial CV scans in 1 M NaClO₄ are shown in Fig. 1 for the BDD-0 electrode that was subjected to the anodic surface cleaning treatment only (20 mA cm⁻² for 10 minutes). The first anodic scan shows a distinct, broad oxidation peak at 2.38 V (Fig. 1a), which indicates that a significant number of reduced sites (e.g., =C-H) were still present on the BDD surface after the anodic surface cleaning treatment. However, the peak at 2.38 V disappeared after four consecutive anodic scans, indicating that the reduced sites were oxidized (Fig. 1b). This peak reappeared when the CV scans were initially swept in the cathodic direction (Fig. 1c). After three consecutive scans (-2 V to 3 V), the size of the peak at 2.38 V showed no further change (Fig. 1d), and an additional smaller peak at 1.44 V appeared (Fig. 1e). The cathodic scans also showed the appearance of a reduction peak at -1.4 V. DFT modeling was used to interpret the CV scans shown in Fig. 1. Two clusters based on the structure of diamond were used in order to investigate mechanisms of BDD surface oxidation, as shown in Fig. 2. The structure in Fig. 2a includes a B atom and the structure in Fig. 2b does not. These structures include three distinct CHₓ sites: B=CH-H and =C-H sites present on the BDD facets, and =CH₂ sites which would likely be present at diamond grain boundaries. These sites exist on freshly-prepared BDD electrodes, and are expected to be electroactive [48]. DFT simulations were used to investigate the following reactions that may occur on a freshly-prepared BDD electrode:

\[ \equiv\text{C-H} \rightarrow \equiv\text{C}^+ + \text{H}^+ + e^- \]  
\[ \equiv\text{CH}_2 \rightarrow \equiv\text{C}^+ + \text{H}^+ + e^- \]  
\[ \equiv\text{B=CH-H} \rightarrow \equiv\text{B=CH}^+ + \text{H}^+ + e^- \]  

The activation barriers for reactions (3)-(5) as a function of electrode potential are shown in Fig. 3. The activation barriers for reactions (3), (4), and (5) become comparable to the thermal energy (RT = 2.45 kJ mol⁻¹) at potentials of 1.83, 1.79, and 0.74 V, respectively, indicating that these reactions could readily occur at and above these potentials. Near these potentials, mA level current began to flow, as shown in Fig. 1a. The disappearance of the broad peak in Fig. 1b can likely be attributed to depletion of the oxidizable H atoms on the electrode surface. The absence of a measurable peak corresponding to reaction (5) may be attributed to the low concentration of these sites on the electrode surface.

The DFT modeling also indicates that loss of H atoms from the electrode surface resulted in the formation of double bonds between adjacent C atoms (discussed in detail in Section 3.5). The data in Fig. 1c and d indicate that surface oxidation resulting in H atom loss was at least partially reversible upon cathodic polarization. The production of atomic hydrogen by the Volmer discharge reaction (H⁺ + e⁻ → H) produces atomic hydrogen that can react with the surface C atoms. The large separation between the anodic and cathodic peaks in Fig. 1d indicates that the oxidation and reduction reactions involved a multi-step mechanism where bond breakage and formation occurred. The exact mechanism of this process has not been previously determined, and is beyond the scope.
of the current study. However, previous studies have attributed this behavior to the oxidation/reduction of sp² C basal and edge planes [49], an increase in carrier concentration due to subsurface hydrogen incorporation during cathodic treatment [29], and surface roughening due to electrochemical oxidation [29]. Additional studies using XPS measurements indicate that a portion of oxygenated functional groups (i.e., C=–OH) can be removed upon cathodic polarization resulting in a corresponding increase in CH₃ functional groups [25]. The above processes are not mutually exclusive, and all may contribute to the behavior shown in Fig. 1.

Hydroxyl radical attack of CH₃ sites was also investigated using DFT simulations. Hydroxyl radicals are produced via water oxidation according to:

\[ \text{H}_2\text{O} \rightarrow \text{OH}^* + \text{H}^+ + e^- \]  

(6)

The activation barrier for this reaction as a function of electrode potential is shown in Fig. 4. At potentials > 2.74 V, the activation barrier became comparable to RT, and thus the reaction can readily proceed at room temperature. The modeling results are confirmed by the data in Fig. 1 where the currents for O₂ evolution become greater than 1 mA at potentials > 2.7 V. The fact that significant water oxidation did not take place at potentials < 2.7 V indicates that oxygenation of surface functional groups by OH* occurs only after electrochemical oxidation of CH₃ sites via reactions (3)-(5). Once OH* are produced, the DFT modeling indicates that the removal of an H atom from the BDD surface via reactions (7)-(9):

\[ \equiv\text{C} - \text{H} + \text{OH}^* \rightarrow \equiv\text{C}^* + \text{H}_2\text{O} \]  

(7)

\[ \equiv\text{C}_2 + \text{OH}^* \rightarrow \equiv\text{C}^* + \text{H}_2\text{O} \]  

(8)

\[ \equiv\text{C} - \text{H} + \text{OH}^* \rightarrow \equiv\text{C}^* + \text{H}_2\text{O} \]  

(9)

proceeds without an activation barrier. Energy is released in each reaction, with \( \Delta E = -112.1 \) kJ mol⁻¹ for reaction (7), \( \Delta E = -103.2 \) kJ mol⁻¹ for reaction (8), and \( \Delta E = -265.7 \) kJ mol⁻¹ for reaction (9).

3.2. Formation of Oxygenated Functional Groups

The surface carbon radicals formed in reactions (3)-(5) and (7)-(9) are not stable, and thus may react with water or OH* to form oxygenated functional groups. Experimental evidence indicates the electrochemical response of the BDD electrodes changed dramatically as a result of extended anodic polarization. CV scans for the BDD-5 electrode are shown in Fig. 5 after passing a charge of 1 Ah cm⁻². Three distinct oxidation peaks at 1.44, 1.88, and 2.49 V were observed prior to oxygen evolution. After a charge of 10 Ah cm⁻² was passed, only the peak at 1.88 V remained.

In order to obtain a measure of the functional groups present on the surface of the BDD electrode as a result of anodic oxidation, XPS analysis was performed on electrodes BDD-5 (10 Ah cm⁻²), BDD-50...
These reactions release energy, with $\Delta E = -276.4 \text{ kJ mol}^{-1}$ for reaction (10), $\Delta E = -294.9 \text{ kJ mol}^{-1}$ for reaction (11), and $\Delta E = -118.1 \text{ kJ mol}^{-1}$ for reaction (12).

The formation of $=\text{C}=\text{O}$ groups on the BDD surface was investigated at $=\text{CH}=\text{OH}$ sites on the BDD cluster which was formed via reaction (11). Formation of $=\text{C}=\text{O}$ groups requires the removal of two $\text{H}$ atoms, which is simulated electrochemically in the following direct electron transfer reactions, in which the hydrogen bonded to the carbon is removed in the first step:

$$=\text{CH}=\text{OH} \rightarrow =\text{C}^*=\text{OH} + \text{H}^+ + e^-$$ (13)

$$=\text{C}^*=\text{OH} \rightarrow =\text{C}=\text{O} + \text{H}^+ + e^-$$ (14)

The order of hydrogen removal may be reversed so that the hydrogen bonded to the oxygen is removed in the first step:

$$=\text{CH}=\text{OH} \rightarrow =\text{CH}=\text{O}* + \text{H}^+ + e^-$$ (15)

$$=\text{CH}=\text{O}* \rightarrow =\text{C}=\text{O} + \text{H}^+ + e^-$$ (16)

Simulations found that reaction (13) becomes activationless at $\geq 1.72 \text{ V}$ and reaction (15) becomes activationless at $\geq 1.73 \text{ V}$. The final steps to form $=\text{C}=\text{O}$ surface groups are activationless at lower potentials than the initial steps, and should thus readily occur after reactions (13) or (15). Reaction (14) becomes activationless at $\geq -0.60 \text{ V}$ and reaction (16) becomes activationless at $\geq 1.55 \text{ V}$.

Because reactions (13) and (15) become activationless at potentials similar to reactions (3) and (4), the individual reactions would not be distinguishable in the CV scans. However, Figs. 1 and 5 show an oxidation peak at 1.44 V, which may be due to the formation of $=\text{C}=\text{O}$ sites according to reaction (16). The peak current density for the freshly prepared electrode was 0.3 mA cm$^{-2}$ (Fig. 1e), and was 5 mA cm$^{-2}$ for the BDD-5 electrode after passing a 1.0 Ah cm$^{-2}$ charge (Fig. 5a). The growth of the peak with anodic ageing supports the proposed mechanism for $=\text{C}=\text{O}$ formation. The peak at 1.44 V was not present after an applied charge of 10 Ah cm$^{-2}$ (Fig. 5b), indicating that much of the available $=\text{CH}_2$ sites had already been converted to $=\text{C}=\text{O}$ at this electrode age. The peak does not reappear with cathodic polarization, indicating the conversion to $=\text{C}=\text{O}$ is not reversible at the cathodic polarizations used. Results also indicate that the formation of $=\text{C}=\text{O}$ sites begins to stabilize the surface with respect to further electrochemical reactions. The stability of the $=\text{C}=\text{O}$ site to oxidation reactions is investigated in more detail in Section 3.6.

Once the BDD surface becomes oxidized additional direct electron transfer reactions can occur that produce radical sites on the BDD surface. Reactions at $=\text{C}=\text{OH}$ and $=\text{C}=\text{C}=\text{OH}$ sites are shown below:

$$=\text{C}=\text{OH} \rightarrow =\text{C}=\text{O}* + \text{H}^+ + e^-$$ (17)

$$=\text{C}=\text{C}=\text{OH} \rightarrow =\text{C}=\text{C}=\text{O}* + \text{H}^+ + e^-$$ (18)

Simulations found that reaction (17) becomes activationless at potentials $\geq 1.74 \text{ V}$ and reaction (18) becomes activationless at $\geq 0.80 \text{ V}$. These reactions may also contribute to the oxidation peaks shown in Figs. 1 and 5. The oxygen radical sites have also been suggested to be important active sites for compound oxidation on BDD electrodes [31].

The peaks at 1.44 V and 1.88–2.49 V shown in Figs. 1 and 2 have been observed in previous studies of BDD electrodes, and were attributed to oxidation of non-diamond C impurities present at the grain boundaries of the electrode, originating from the CVD process [16,19,49–51]. The $=\text{CH}_2$ sites used for DFT modeling are representative sites that are present in non-diamond C, and thus the oxidation of $=\text{CH}_2$ to form $=\text{C}=\text{O}$ (as shown in reactions (4), (11), and (13-16)) are consistent with the oxidation of non-diamond C as well as diamond edge sites. Other oxidation reactions, such as the oxidation of hydroquinone-like structures on the surface, have also
been proposed [19,51]. DFT simulations indicate hydroquinone oxidation becomes activationless at potentials ≥ 0.72 V, which is close to the potential at which µA levels of current started flowing in the CV scans in Figs. 1 and 5, indicating that these sites are not abundant on the BDD surface. Oxidation of hydroquinone-like sites and other oxygenated sites, but not fully oxidized, sites (e.g., =CH=O (reaction 16)) could also explain the peak at 1.44 V, because this peak only appears on the aged electrodes. Therefore, the oxidation peaks observed in Figs. 1 and 5a may be attributed to oxidation of both diamond and non-diamond C impurities. The reactions above also provide a feasible pathway that explains the formation of ≡C–O and ≡C=O sites on BDD electrodes during anodic polarization.

3.3. Effect of Surface Termination on Water Oxidation

Results shown in the inset of Fig. 5 clearly show that increasing the applied charge from 1.0 to 10 Ah cm⁻² for the BDD-5 electrode resulted in a significant reduction in the overpotential for oxygen evolution. This suggests that oxygen atoms incorporated into the BDD surface may catalyze the water oxidation reaction.

DFT simulations were used to investigate the mechanisms of water oxidation on the BDD surface, according to reaction (6). The reaction is initially examined independent of the BDD surface, simulating a hydrophilic surface (e.g., ≡C–H, B≡C–H, and ≡CH₂) that does not interact with the water molecules. Fig. 4 shows the E₂ for the uncatalyzed reaction as a function of electrode potential. The reaction is activationless at potentials ≥ 2.74 V, close to the potential at which current rapidly increased for a fresh electrode (see Fig. 1). This result suggests that for a fresh electrode, the surface does not catalyze water oxidation.

To investigate how a more oxygenated surface may catalyze water oxidation, H₂C≡O and H₂CO⁺ molecules were added to the system to simulate surface ≡C–O, B≡C–O⁺, and ≡C=O sites. The E₂ for the H₂C≡O catalyzed water oxidation reaction is shown in Fig. 4 as a function of electrode potential, and becomes activationless at potentials ≥ 2.29 V. The lower activation barrier for H₂C≡O catalyzed water oxidation indicates that oxygenated functional groups may catalyze the water oxidation reaction. A similar catalytic effect was found for H₂CO⁺. Surface site catalysis is consistent with the shift of water oxidation to lower potentials that can be seen in Fig. 5 (inset) after electrode aging.

3.4. Electrode Wear Under High Current Density

Prior work has shown that very high anodic polarization can lead to observable wear of BDD electrodes [16–19]. To investigate the mechanisms of electrode oxidation, BDD electrodes were subjected to current densities of 50 and 500 mA cm⁻² for different applied charges. CV scans for the BDD-50 electrode performed in 1 M NaClO₄ show that the peak originally present at ~ 2.38 V was greatly attenuated after an applied charge of 1 Ah cm⁻² was passed (Fig. 7a). After an applied charge of 10 Ah cm⁻² was passed, an increased separation of the forward and reverse scans was observed. This separation corresponds to increased capacitance/pseudo-capacitance of the electrode (Fig. 7b and inset.). After a charge of 50 Ah cm⁻² was passed, an oxidation/reduction peak couple appeared at ~ 1.9 V, and a significant increase in capacitance/pseudo-capacitance was once again observed (Fig. 7c). The overpotential for oxygen evolution also decreased with increased applied charge, which is consistent with the experimental and DFT modeling results discussed in Section 3.3.

CV scans for BDD-500 in 1 M NaClO₄ are shown in Fig. 8. After an applied charge of 1 Ah cm⁻², a current response was observed at ~ 1.5 V that extended until the end of the anodic scan at 3.0 V. This electrochemical response is different than that observed for previous electrodes tested (i.e., BDD-5 and BDD-50). The very broad current response may be attributed to a severe distortion of the diamond lattice, which likely occurred due to the high, applied current density of 500 mA cm⁻². The oxidation of C=C bonds in the diamond lattice may have caused bond breakage and the creation of defect sites, which would both increase the surface area of the electrode and create electroactive sites with varying redox potentials. However, at higher applied charges (i.e., 50 and 100 Ah cm⁻²) the peak at potentials >2.0 V was no longer observed (Fig. 8b–c). Instead, at an applied charge of 50 Ah cm⁻² a peak was observed at ~ 1.9 V in the CV scan, and at applied charge of 100 Ah cm⁻² the CV scan showed an increased separation between the forward and reverse scans, indicative of an electrode with high capacitance/pseudo-capacitance [52]. The lack of distinct peaks in the CV scan after passing an applied charge of 100 Ah cm⁻² suggests that the electroactive sites on the BDD surface were fully oxidized. That is, the sp² carbon was oxidized to CO₂, and the diamond sites were converted to oxygen functionalities (e.g., ≡C=O and ≡C=O).

SEM analysis was conducted to determine if physical changes occurred to the BDD electrodes as a result of anodic polarization. Significant changes in surface morphologies were observed for BDD-500. The SEM micrographs shown in Fig. 9 compare the surface morphologies of BDD-500 at locations exposed to 0 and 100 Ah cm⁻² applied charges. It is apparent from the results that the electrode subjected to anodic polarization (100 Ah cm⁻²) underwent physical changes as a result of the electrochemical treatment. The black areas in the SEM micrograph represent areas on the BDD electrode where the diamond has been etched away, and the white areas represent areas of raised topography. These results have been observed in prior studies with BDD electrodes subjected to current
densities of 1.0 A cm$^{-2}$ [16–19]. The SEM results help to explain XPS results for the BDD-500 electrode in Fig. 6. The BDD-500 electrode did not show a significant decrease in C-C content after anodic ageing, which may be attributed to an increase in surface area related to the morphology changes observed in the SEM micrograph in Fig. 9. The diamond crystal size of the freshly prepared BDD films was on the order of approximately 2.5 nm, and etching of the BDD grain boundaries and edge sites (=CH$_2$) during anodic ageing may have decreased the grain size and exposed more underlying C-C sites. Since the depth of penetration of XPS is on the nanometer scale [53], the BDD-500 electrode may contain smaller crystal size and therefore XPS data may reflect more of the bulk composition of the BDD film relative to the freshly prepared electrode. Other work has shown that low anodic current densities (100 μA cm$^{-2}$) resulted in more oxygenated functional groups than higher anodic current densities (100 mA cm$^{-2}$) [25], which is similar to our results shown in Fig. 6.

3.5. Mechanism for sp$^2$ Carbon Formation

DFT modeling results indicate that sp$^2$ C is formed on the BDD surface when two adjacent carbon atoms lose their attached hydrogen atoms and reconstruct to minimize the dangling bonds. For the structures shown in Fig. 2, this can occur at the =CH$_2$ and B=CH-H sites (each with a neighboring =C-H site). It was found that the initial step in sp$^2$ C formation is the removal of a hydrogen atom, which may be accomplished electrochemically, as in reactions (3)-(5), or chemically, as in reactions (7)-(9). In both cases, the B=CH-H site is most reactive, followed by the =C-H site. The energy for removal of a second hydrogen atom may be affected by removal of the first. Adjacent to a B=CH-H site, the possible reactions for the removal of the second hydrogen atom are shown in reactions (19) and (20).

\[
\text{C-H} \rightarrow \text{C}^* + H^+ + e^- \quad (19)
\]

\[
\text{C-H} + \text{OH}^* \rightarrow \text{C}^* + H_2O \quad (20)
\]

Reaction (19) becomes activationless at potentials $\geq 0.43$ V, and reaction (20) is activationless with $\Delta E = -236$ kJ mol$^{-1}$. Adjacent to a =C* site, the removal reaction for the second hydrogen is:

\[
\text{CH}_2 + \text{OH}^* \rightarrow \text{C}^* + H_2O \quad (21)
\]

Reaction (21) is activationless with $\Delta E = -53.6$ kJ mol$^{-1}$. In reactions (19) and (20), the second oxidation step occurs more easily adjacent to a =C* site than from a fully hydrogen-terminated surface (=C-H and =CH$_2$), since the surface reconstructs to form a stable double bond. This mechanism may be reversible and thus could help to explain the CV results shown in Fig. 1, but detailed DFT calculations regarding this mechanism are beyond the scope of this study.

3.6. Mechanism for BDD Electrode Wear

DFT simulations were also performed to understand mechanisms responsible for electrode wear, as observed in SEM images presented in Fig. 9. The =C=O site was chosen for further study, as it was detected on oxidized electrodes by XPS (Fig. 6), and previous work with graphite anodes suggests this site can be further oxidized to a =COOH site [54,55]. DFT simulations indicate that the oxidation of a =C=O site by OH* forms a =CO*OH adduct, by addition of OH* to the C atom, as shown in the following reaction.

\[
\text{=C}=\text{O} + \text{OH}^* \rightarrow \text{=C}^\text{=O}\text{OH} \quad (22)
\]

Reaction (22) has $E_a = 27.1$ kJ mol$^{-1}$ and $\Delta E = -69.5$ kJ mol$^{-1}$. The relatively low $E_a$ and the negative reaction energy indicate that this reaction is feasible at room temperature, and likely occurred during our experiments.

Further reactions were explored at the =CO*OH site, which provided a feasible mechanism for etching of the diamond surface (Fig. 10). As shown in Fig. 10, the =CO*OH site (labeled as C1) reconstructs to form a =COOH site, which is further oxidized to form aqueous H$_2$CO$_3$. The process of reconstruction to a =COOH site first requires the oxidative removal of a hydrogen atom from an adjacent carbon atom, creating a =C=O site (labeled as C2). Hydrogen removal can occur either electrochemically, as in reactions (3) and (5), or chemically, as in reactions (7) and (9). The energy for removal of the hydrogen atom is affected by the functional groups of the neighboring C atoms. DFT simulations indicate that hydrogen removal by the electrochemical pathway was activationless at potentials between 0.43 and 1.83 V (depending on neighboring C atom functionality), and the chemical pathway was activationless under all conditions tested. Once the hydrogen atom is removed from the C2 carbon, the surface reconstructs to minimize the dangling bonds. The two carbons atoms (labeled as C2 and C3) previously bonded to the =COOH, form a bond to each other and a C=COOH site is formed. The C2 and C3 carbon atoms remain in their original sp$^3$ hybridization. In the final step, an OH* attack at the =COOH...
site results in the formation of \( \text{H}_2\text{CO}_3 \), which dissociates from the diamond surface into solution, as shown in reaction (23).

\[
-\text{COOH} + \text{OH}^* \rightarrow \text{H}_2\text{CO}_3^{(aq)} \tag{23}
\]

Reaction (23) has \( \Delta E = 58.9 \text{kJ mol}^{-1} \) and a reaction energy, \( \Delta E = -64.3 \text{kJ mol}^{-1} \). The relatively high \( \Delta E \) of 58.9 \text{kJ mol}^{-1}, indicates that this process will proceed slowly at room temperature, and explains why electrode wear of BDD electrodes was not observed under ambient temperatures and low current densities (5–50 mA cm\(^{-2} \)) in this study. The above mechanism also explains the results from previous studies that document BDD oxidation or electrochemical polishing at high anodic potentials and elevated temperatures (40–60 °C) [17–19]. Based on the calculated \( \Delta E \) of 58.9 \text{kJ mol}^{-1}, increasing the temperature from 20 °C to 60 °C will increase the rate of reaction (23) by a factor of 18. Although the temperature of our experiments was controlled at 20 °C, ohmic heating during ageing of the BDD-500 electrode may have occurred, which caused an increase in the temperature of the electrode relative to the electrolyte solution and thus increased the rate of reaction (23). XPS results did not detect the formation of COOH functional groups, but results shown in Fig. 6 show a decrease in the content of =C=O functional groups with increasing current density, thus supporting the mechanism of conversion of =C=O to H\(_2\)CO\(_3^{(aq)}\).

Several studies have shown that electrolysis in the presence of organics [18] or alkaline conditions [20,21] greatly enhances BDD wear rates. Although the effects of solution conditions on electrode wear is beyond the scope of our study, the formation of H\(_2\)CO\(_3^{(aq)}\) as a product in reaction (23) suggests that alkaline conditions would enhance electrode wear. The H\(_2\)CO\(_3^{(aq)}\) formed would be converted to CO\(_2\) at elevated pH, and push reaction (23) towards products. However, a more detailed study is necessary to support this hypothesis and explore the mechanism of enhanced electrode wear in the presence of organics.

3.7. \textit{EIS Analysis}

EIS experiments were also conducted to more fully characterize the electrochemical response of the BDD electrodes as a function of anodic ageing by measuring values for \( R_t \) and \( C_{dl} \). EIS was conducted in a 1 M NaClO\(_4\) electrolyte containing 5 mM K\(_2\)Fe(CN)\(_6\) and 5 mM K\(_3\)Fe(CN)\(_6\). Results of the EIS model fits are shown in Table 1. Several trends are observed from the parameter values determined from the EIS model fits. The \( C_{dl} \) value for the fresh electrode (BDD-0) was 14.4 μF cm\(^{-2}\). For the electrodes polarized at 5, 50 and 500 mA cm\(^{-2}\), the \( C_{dl} \) values increased as a function of the applied charge passed. For applied charges of 10 and 50 Ah cm\(^{-2}\), the increases in \( C_{dl} \) were inversely proportional to the current density used to pass the charge. This indicates that the corrosion mechanism may be more related to the time of operation than to the applied current density.

The values for the \( C_{dl} \) began to plateau between applied charges of 50 and 100 Ah cm\(^{-2}\). A value for \( C_{dl} \) of 3.23 μF cm\(^{-2}\) was found for BDD-500 at 100 Ah cm\(^{-2}\). The large increase in the values of \( C_{dl} \) as a function of applied charge may be related to the electrochemical etching of the diamond grain boundaries and non-diamond C, which increased the surface area and the density of charged sites at the electrode surface [29]. Comparing the \( C_{dl} \) value for the BDD-500 at 100 Ah cm\(^{-2}\) (3.23 μF cm\(^{-2}\)) to the \( C_{dl} \) Value for the BDD-0 electrode (14.4 μF cm\(^{-2}\)), provides an estimate of the electroactive surface area for the BDD-500 electrode at 100 Ah cm\(^{-2}\) of 78.5 cm\(^{2}\), which is 224 times greater than the geometric surface area of 0.35 cm\(^{2}\). Other studies have found a 15–21 fold increase in the \( C_{dl} \) value upon roughening the microcrystalline BDD surface through a variety of methods (e.g., catalytic roughening, steam activation) [56,57]. The EIS data compliments the CV scans that showed high capacitance, and SEM images that showed a roughened surface upon anodic ageing. The \( C_{dl} \) value found for BDD-500 after an applied charge of 100 Ah cm\(^{-2}\) (3.23 μF cm\(^{-2}\), normalized by geometric surface area) was much higher than \( C_{dl} \) values for roughened microcrystalline BDD electrodes, where values as high as 165–234 μF cm\(^{-2}\) have been reported [56–58]. Nanocrystalline diamond films grown on micrometer porous silicon resulted in \( C_{dl} \) values between 230–990 μF cm\(^{-2}\) [59]. Therefore, the high \( C_{dl} \) values measured in our study may be a result of the nm crystal size and warrants further investigation.

The \( R_t \) values also show interesting trends. The fresh electrode (BDD-0) had an \( R_t \) value of 10.7 Ω cm\(^{2}\). Upon anodic ageing, the \( R_t \) value initially increased after an applied charge of 1 Ah

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Electrode & Applied Charge (Ah cm\(^{-2}\)) & \( R_t \) (ohm cm\(^{2}\)) & \( C_{dl} \) (μF cm\(^{-2}\)) & \( \Phi \) & \( \psi \) & \( \phi \) & \( \psi^{(1)} \) & \( \phi^{(1)} \) \\
\hline
BDD-0 & 0.01 & 9.1 & 10.7 & 2.19E–04 & 0.61 & 14.37 \\
BDD-5 & 1.0 & 11 & 44.2 & 2.16E–05 & 0.86 & 18.43 \\
BDD-5 & 10 & 12 & 44.4 & 1.03E–03 & 0.88 & 1763 \\
BDD-50 & 1.0 & 19 & 101 & 9.35E–05 & 0.92 & 168.0 \\
BDD-50 & 10 & 8.8 & 37.2 & 6.40E–04 & 0.89 & 1043 \\
BDD-500 & 50 & 50 & 23.8 & 1.59E–03 & 0.89 & 2974 \\
BDD-500 & 10 & 16 & 54.4 & 4.12E–04 & 0.60 & 7543 \\
BDD-500 & 50 & 10 & 22.9 & 1.76E–03 & 0.84 & 2594 \\
BDD-500 & 100 & 13 & 18.4 & 2.00E–03 & 0.85 & 3229 \\
\hline
\end{tabular}
\caption{Summary of equivalent circuit model fit to EIS data. Model is presented in Eqs. (1) and (2).}
\end{table}
cm$^{-2}$ was passed on all electrodes, followed by a slow decrease in the $R_C$ value with progressively higher applied anodic charges (10–100 Ah cm$^{-2}$). These trends are likely related to changes in the surface termination, sp$^2$ C content, and surface area of the BDD electrodes. Freshly prepared electrodes have a high content of hydrogen-terminated sites, which exhibit fast electron transfer kinetics for the FeCN$_4^{3+/2+}$ redox couple [29]. The increase in the $R_C$ value at an applied charge of 1 Ah cm$^{-2}$ is likely related to oxidation of the BDD surface, which slows the electron transfer kinetics of the FeCN$_4^{4+/3-}$ redox couple [29]. The increase in $R_C$ after an applied charge of 1 Ah cm$^{-2}$ was passed could also be related to electrochemical oxidation of a portion of the sp$^2$ C to CO$_2$. Previous work has shown that sp$^2$ C is active for the electron transfer of the FeCN$_4^{4+/3-}$ redox couple [49].

Upon further anodic ageing, the $R_C$ values steadily decreased, and reached a minimum value for the BDD-500 electrode after an applied charge of 100 Ah cm$^{-2}$ was passed (18.4 ohm cm$^2$). The decrease in the $R_C$ value is likely related to an increase in surface area and an increase in charged surface sites. An increase in surface area can be inferred from the high C$_6$H value measured by EIS and SEM images (Fig. 9), and an increase in charged surface sites is suggested by both CV scans (Fig. 8) and the high C$_{6}$H value measured by EIS.

The exponential $\phi$ in Eqs. (1) and (2) was found to be less than unity, which is attributed to a distribution in time constants caused by electrode surface roughness [60]. Values for $\phi$ ranged between 0.84 and 0.92, and in general decreased as a function of the applied charge passed. The decreasing trend of $\phi$ with the applied charge passed indicates that the electrodes became rougher during anodic ageing, which supports CV, SEM, and measured C$_{6}$H values.

4. Conclusions

The results of this study provide experimental and modeling evidence that explains the formation of oxygenated sites on BDD electrodes and anodic wear of BDD that has been documented in prior studies [16–19]. It is proposed that freshly prepared BDD electrodes that contain a high density of CH$_4$ surface sites can be oxidized by a sequence of direct electron transfer reactions and reactions with OH$^-$ to form $-$C=O and $-$OH functional groups. At high applied charges (e.g., 100 Ah cm$^{-2}$) SEM images indicate that the BDD electrode experienced significant wear. DFT modeling results identified possible mechanisms that occur at potentials at and below that of water oxidation that explain the oxidation of diamond edge sites ($-$CH$_2$) to H$_2$C=O$_{ad}$. These reactions provide quantitative information that helps to explain the observed wear of BDD electrodes.

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References


Materials Studio, v.4.2: Accelrys Corporation, San Diego, CA.


H.V. Patten, S.C.S. Lai, J.V. Macpherson, P.R. Unwin, Active sites for outer-sphere, inner-sphere, and complex multistage electrochemical reactions at polycrystalline boron-doped diamond electrodes (pBDD) revealed with scanning electrochemical cell microscopy (SECCM), Analytical Chemistry 84 (2012) 5427.


