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New Boron Doped Diamond Materials for Electrochemical Applications

by

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Thesis

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For Grandad

"The world is full of obvious things which nobody by any chance ever observes." - Mark Haddon, The Curious Incident of the Dog in the Night-Time

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Abbreviations

2D	Two dimensional
3D	Three dimensional
ADF	Annular dark field
BDD	Boron doped diamond
BF	Bright field
BSD	Backscatter detector
BSE	Backscattered electrons
CE	Counter electrode
CNT	Carbon nanotube
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
DF	Dark field
DLS	Dynamic light scattering
DSC	Diamond stabilised non-diamond carbon
EAOP	Electrochemical advanced oxidation processes
EBSD	Electron backscatter diffraction
EC	Electrochemical
EDM	Electrical discharge machining
EDX	Energy-dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EM	Electron microscopy
EOP	Electrochemical ozone production
FCC	Face centred cubic
FCVA	Filtered cathodic vacuum synthesis
FE	Field emission
FIB	Focused ion beam
GC	Glassy carbon
GDMS	Glow discharge mass spectrometry
HAADF	High angle annular dark field
HER	Hydrogen evolution reaction
HFCVD	Hot filament chemical vapour deposition
HOPG	Highly oriented pyrolytic graphite
HPHT	High pressure high temperature
ICP	Inductively coupled plasma

IL	Identical location
MLLS	Multiple linear least squares
MP	Microparticle
MS	Mass spectrometry
MWCNT	Multi-walled carbon nanotube
MWCVD	Microwave plasma chemical vapour deposition
NP	Nanoparticle
NTA	Nanoparticle tracking analysis
OER	Oxygen evolution reaction
OES	Optical emission spectroscopy
ORR	Oxygen reduction reaction
PEMFC	Proton exchange membrane fuel cell
PIPS	Precision ion polishing system
PMMA	Polymethylmethacrylate
QRCE	Quasi-reference-counter electrode
QSC	Quinone surface coverage
RCF	Relative centrifugal force
RE	Reference electrode
RIE	Reactive ion etching
RMS	Root mean square
SAD	Selected area diffraction
SCCM	Standard cubic centimetres per minute
SCE	Saturated calomel electrode
SE	Secondary electrons
SECCM	Scanning electrochemical cell microscopy
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SI	Spectrum image
SIMS	Secondary ion mass spectrometry
SPE	Single particle electrode
STEM	Scanning transmission electron microscopy
SWCNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
UME	Ultramicroelectrode
WE	Working electrode
WLI	White light interferometry

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Declarations

I declare that the work presented in this thesis is entirely my own, except when carried out in collaboration, as outlined below. I confirm that this thesis has not been submitted for a degree at another university.

In chapter 3, SECCM experiments and analysis were carried out by Dr Viacheslav Shkirskiy. ICP-OES and ICP-MS measurements were recorded by Dr Lijiang Song.

In chapter 4, the EOP sections were truly a team effort; cell production and electrode fabrication were led by Joshua Tully, experimental data was collected by myself and Irina Terrero Rodríguez, and experimental design and interpretation of data were carried out together. The TEM images were predominantly collected by Fraser Laidlaw, alongside me, who also carried out the EELS analysis. Dr Sam Cobb prepared the laser micromachined samples and conceptualised the study.

In chapter 5, SEM, TEM, and STEM images were collected by me, Dr Haytham Hussein, Prof. Richard Beanland, Daniel Houghton, and Yisong Han. AFM images were collected by Dr Haytham Hussein. WLI measurements and the electrochemical etch were carried out by Joshua Tully. XPS data was collected by Dr. Marc Walker. EELS analysis was carried out by Daniel Houghton.

Parts of this thesis have been published, submitted, or are in preparation to be submitted, as detailed below:

Work from chapter 3 was published as:

High pressure high temperature synthesis of highly boron doped diamond microparticles and porous electrodes for electrochemical applications, Georgia F. Wood, Carmen E. Zvoriste-Walters, Mark G. Munday, Mark E. Newton, Viacheslav Shkirskiy, Patrick R. Unwin, and Julie V. Macpherson, *Carbon*, 2021, **171**, 845-856.

Work from chapter 4 was published as:

Assessment of acid and thermal oxidation treatments for removing sp^2 bonded carbon from the surface of boron doped diamond, Samuel J. Cobb,

Fraser H. J. Laidlaw, Geoff West, Georgia F. Wood, Mark E. Newton, Richard Beanland, and Julie V. Macpherson, *Carbon*, 2020, **167**, 1-10.

Work from chapter 4 has been submitted as:

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The importance of stable sp² bonded carbon in electrochemical generation of ozone using boron doped diamond dlectrodes, Joshua J. Tully, Georgia F. Wood, Irina M. Terrero Rodríguez, Timothy P. Mollart, Hossein Zarrin, and Julie V. Macpherson, *in preparation*.

Work from chapter 5 is in preparation as:

Electron beam transparent boron doped diamond electrodes for combined electrochemistry – transmission electron microscopy, Haytham E. M. Hussein, Georgia F. Wood, Daniel Houghton, Yisong Han, Richard Beanland, Marc Walker, and Julie V. Macpherson, *in preparation*.

Abstract

In this thesis, novel fabrication methods of conductive sp³ bonded boron doped diamond (BDD) materials are established. The intentional integration of sp² bonded carbon is also examined, where the contrasting physical and chemical properties when compared to sp³ bonded carbon can be exploited. BDD electrodes are desirable for many applications due to their superior material properties including wide anodic window in water and excellent chemical and electrochemical stability. High pressure high temperature (HPHT) synthesis of crystallographically well-defined BDD microparticles (MPs), suitable for electrochemical applications and using the lowest P and T (5.5 GPa and 1200 °C) growth conditions to date, is reported. A HPHT compaction process is used to create freestanding sub microscopic porous electrodes from the BDD MPs, which boast the electrochemical and mechanical robustness properties of BDD but with the additional benefits of a large, electrochemically accessible, surface area. These HPHT BDD electrodes also offer an alternative to traditional chemical vapour deposition (CVD) grown BDD, with potential for low cost scalability. Moving to the nanoparticle (NP) size regime is also investigated, by mechanically grinding CVD BDD using a planetary ball mill. BDD NPs are desirable for applications such as proton exchange membrane fuel cells (PEMFCs), where traditional sp² bonded carbon catalyst supports suffer from short lifetimes due to corrosion.

The MP compacted electrodes can be laser micromachined into perforated (slotted) geometries and in this thesis, are then utilised for electrochemical ozone production (EOP) from water, an attractive, green technology for disinfection. The HPHT BDD electrodes are shown to exhibit high EOP, producing 2.23 ± 0.07 mg L⁻¹ of ozone per ampere of current, at consistent levels for a continuous 20 hr period with no drop off in performance. BDD EOP electrodes are fabricated with varying percentages of sp² bonded carbon (from 5% to 80%), revealing the importance of sp² carbon presence for EOP. The sp² carbon is introduced during laser micromachining, where the BDD is converted during oxidative acidic treatment to a ~5 nm thick layer of robust sp² bonded carbon, termed diamond stabilised non-diamond carbon (DSC). The improved EOP is thought to be due to stronger hydroxyl (·OH) and oxygen (·O) radical absorption which ultimately equals increased ozone output and

current efficiency. The DSC is shown to be stable over numerous oxidative acid treatments and believed to be stable over 20 hr continuous EOP, as no reduction in performance is observed. Finally, two novel fabrication routes are developed to produce electron beam transparent BDD substrates for combined electrochemical (EC)-transmission electron microscopy (TEM). The first involves ion milling whilst the second involves electrochemically induced lift off of a thin BDD membrane.

1 Introduction

1.1 Electrochemistry

1.1.1 The electrochemical cell

Electrochemistry has been widely exploited for countless applications in an exhaustive collection of industries and research themes due to its low cost, ease of use, and flexibility. Exploring the relationship between electricity and chemical changes within a system, the basic electrochemical cell is an electrical circuit, driven by the movement of charged particles (namely electrons) at an interface, typically between a solid (electrode) and a liquid (electrolyte solution containing redox species). Electrochemical techniques are commonly classed as potentiometric (where a voltage is measured at equilibrium) or voltammetric (a dynamic measurement where a potential is applied and a resultant current measured). In this work, voltammetric methods are the focus, with the most significant parameters being the potential (E, volts) versus a constant value (the reference) and current (I, amps).

The voltage is applied to a working electrode (WE), versus the reference, at the surface of which electron transfer will occur as the redox reaction of interest takes place. A good WE must conduct electricity well whilst being as chemically inert as possible, so typically gold, platinum, or carbon materials are used. These can also be produced to very high purity standards. To complete the circuit, the reference electrode (RE) is used to establish an electrical potential which the potential of the WE is measured against. A RE must have a stable, well-known potential, typically achieved by using a redox system with a constant concentration of the potential determining ions. Commonly used REs include: the saturated calomel electrode (SCE), and the silver/silver chloride (Ag|AgCl) electrode.¹

Most electrochemical methods use a 3-electrode cell (Figure 1.1) due to the addition of a counter, or auxiliary, electrode (CE). The potential of the CE is not measured, it simply provides a pathway for current to flow to avoid passing current through the RE, which ensures that its potential stays constant. An inert conductor, commonly platinum, is used as a CE. It is important that the surface area is higher than that of the WE, so that the reaction kinetics at the



Figure 1.1: Diagram of a three electrode cell setup.²

CE do not limit the reaction occurring at the WE. A coil or mesh CE is often employed.

A potentiostat is used as an external power source to control the potential applied to the WE (with respect to the RE).³ The three electrodes are connected to the potentiostat and experiments are set up and output data is collected by connection to a computer and using the potentiostat software. A supporting, or background, electrolyte (commonly KNO₃ or KCl) that is inert i.e., not electroactive within the experimental conditions used, is added to the solution in high concentration to increase the solution conductivity and ionic strength. This minimises both ohmic drop from uncompensated solution resistance between electrodes and transport of the redox active species by ion migration.⁴

1.1.2 Cyclic voltammetry

Cyclic voltammetry (CV) is a popular electrochemical method used to investigate a wide variety of redox processes and electron transfer initiated chemical reactions. An indispensable application of CV is also the characterisation of properties of electrodes and electrochemical systems, including reaction kinetics.^{5–7} A specified potential is applied to the WE versus RE and the potential is linearly swept at a fixed speed (scan rate) in one direction to a maximum value. The scan direction is then reversed, and the potential is then swept back in the opposite direction, thus cycling the WE within a defined potential range (Figure 1.2 a). The potential is applied, and the resulting current measured by the potentiostat, and a CV trace of potential vs current is produced. As the redox reaction proceeds, driven by sweeping the potential, the ratio between the concentrations of the reduced and oxidised

species changes at the electrode surface with respect to the bulk solution. This establishes a diffusion layer between the electrode surface and bulk solution. The magnitude of this concentration change for a given potential is reflective of the mass transport and electron transfer kinetics of the system.

For a reversible, mass transport (diffusion) limited process at a macroelectrode (\approx > 25 µm)⁸ a transient, peak shaped, CV is obtained (Figure 1.2 b), with a characteristic peak to peak separation. This is the case where the heterogenous rate constant, k_0 (describes the rate of electron transfer at E^0 , where E^0 is the electrode potential under standard conditions) is significantly larger than the rate of mass transport, k_t , i.e., $k_0 >> k_t$. Here, a peak shaped is observed because the diffusion layer thickness, and thus concentration gradient, changes throughout the scan. As the electrode is large in comparison to the diffusion layer, diffusion to the electrode surfaces is predominately linear, resulting in depletion of the redox species within the diffusion layer. For a reversible, diffusion limited system, where sufficient supporting electrolyte is present to negate possible migration effects, $i_{p,a} \approx i_{p,c}$, where $i_{p,a}$ and $i_{p,c}$ are the anodic and cathodic peak current maxima, respectively.

At equilibrium, where there are equal concentrations of the reduced species and the oxidised species, the reaction potential of a reversible reaction can be described by the Nernst equation (1.1):

$$E = E^{0'} - \frac{2.303RT}{nF} \log \frac{[R]}{[O]}$$
(1.1)

where *E* is the measured/applied electrode potential in volts, $E^{0'}$ is the formal electrode potential in volts, *R* is the gas constant (8.135 J K⁻¹ mol⁻¹), *T* is the absolute temperature in K, *n* is the number of electrons transferred in the redox reaction, *F* is Faraday's constant (9.684 x 10⁴ C mol⁻¹), *[R]* is the concentration of the reduced species, and *[O]* is the concentration of the oxidised species. For a single electron transfer process at room temperature (298 K) the difference in potential between the anodic and cathodic peaks (termed peak to peak separation, ΔE_p) should be 57 mV (=2.22*RT/F*).⁹ This value arises from classical CV theory formulated by Nicholson and Shain, and is a numerical solution of the equations derived.^{7,10} The effect of scan rate, *v*, in volts per second, can also be related to the peak current maximum, *i_p*, in amps, by the Randles-Sevcik equation (1.2) assuming a temperature of 298 K:

$$i_n = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$
(1.2)

where *A* is the electrode area in cm^2 , *D* is the diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$, and *C* is the concentration of the redox species in mol cm^{-3} .

For microelectrodes (\approx < 25 µm), also known as ultramicroelectrodes (UMEs), two cases may occur due to differences in mass transport within the diffusion layer. At high scan rates the diffusion layer is thin and so the UME is comparatively larger and a transient response (comparable to the CV shape observed at a macroelectrode) is obtained (Figure 1.2). However, as the scan rate is reduced, the diffusion layer becomes thicker and thus large in relation to the UME diameter. In this regime, radial diffusion dominates and increased flux to the UME means the diffusion layer is no longer depleted. Now, a sigmoidal shaped steady state CV is observed with a maximum diffusion limited current, *i*_{lim}, reached, as the diffusion layer thickness, and thus concentration gradient, is has reached a constant value.

The measured current can be related to the UME radius, *a* (assuming an inlaid disk geometry), by equation (1.3):

$$i_{lim} = 4naFDc^* \tag{1.3}$$

where c^* is the bulk concentration of the redox species, and the other variables are defined above.¹¹ The Tomeš criterion of reversibility states that for a reversible process, the difference in quartile potentials, $|E_{1/4}-E_{3/4}|$, for a one electron process at 298 K should equal 56.4 mV.¹²



Figure 1.2: Plots to show a) CV waveform, b) CV shape obtained at a macroelectrode, and c) CV shape obtained at a microelectrode.

CV can also be utilised in the absence of any redox active species, that is with supporting electrolyte alone, to collect characteristic properties of the WE with no interference from additional processes. This method is commonly employed to determine the solvent window of an electrode, the stable potential range for use between the potential limits at which the solvent is reduced and oxidised. A wide solvent window is often desired in e.g., electroanalysis, as this allows a wider operating window of potential. Similarly, by reducing the potential range the double-layer capacitance can be measured within defined potential limits.^{6,13} Low capacitance materials are desirable for low concentration species detection, as there is minimal interference from background processes.

1.1.3 Electrodeposition

Electrochemical deposition of metals involves the reduction of metal ions $(M_{solution}^{z+})$ at an electrode surface from an electrolyte solution to a solid metal lattice $(M_{lattice})$ by providing an external supply of electrons as described by equation (1.4):^{14,15}

$$M_{solution}^{z+} + ze \to M_{lattice} \tag{1.4}$$

Deposition processes can be classed as either (1) electroless, where a reducing agent in solution provides electrons (hence no external power supply is required) or (2) electrodeposition, where electrons are delivered by applying a potential at the electrode/electrolyte interface.^{14,15} In this thesis, only the latter method will be employed. Electrodeposition is most commonly used for electroplating, i.e., deposition of thin uniform metal coatings, but is also widely used as a technique for fabrication of nanostructures, including nanowires and NPs, from a variety of different metals.^{16–19}

Equation (1.4) encompasses four fundamental issues which define the electrodeposition process: (1) the electrode/electrolyte interface as the location where deposition occurs, (2) the mechanism and associated kinetics of the metal deposition process, (3) the mechanisms of nucleation and growth, and (4) the resulting structure and properties of the deposits.¹⁴ Though electrodeposition methods are simple to apply, the mechanisms governing phase formations are complex, and often not fully understood.^{20–23} The electrodeposition process is incredibly sensitive to a large collection of deposition parameters including, but not limited to: temperature, nature of the electrode material and surface, concentration of metal ions in electrolyte solution, deposition potential and the length of time for which this is applied, the presence or absence of solution stirring, solution pH and conductivity, and

the evolution of hydrogen bubbles which may also occur at the electrode surface in parallel to metal deposition.¹⁵ Increased understanding of nucleation and growth mechanisms, combined with tight control and knowledge of the influence of deposition parameters, allows better control over nanostructure morphology, which can be tailored to the needs of the application.²³

1.2 Production of carbon materials for electrochemistry

The diverse allotropes and associated properties of carbon materials make carbon an attractive material for use in electrochemistry. Particularly desirable properties of carbon based materials include: (i) temperature and chemical stability; (ii) fast heterogenous electron transfer; (iii) good mechanical properties; (iv) low cost; (v) relatively inert electrochemistry; (vi) biocompatibility. Carbon electrodes have been extensively studied and are utilised in a myriad of applications including fuel cells,²⁴ electroanalysis,^{25,26} electrocatalysis,27,28 energy storage.29-31 conversion and and biotechnologies.³² Nearly all types of sp² bonded carbon (Figure 1.3 a) have been investigated for such uses, including carbon black, glassy carbon (GC), randomly oriented graphite, highly oriented pyrolytic graphite (HOPG), amorphous carbons, and low dimensionality carbon materials with unique properties such as carbon nanotubes (CNTs) and graphene.³³



Figure 1.3: Schematic to show a) sp² hybridised carbon bonding for a single carbon atom and incorporated into the extended graphite structure, and b) sp³ hybridised carbon bonding for a single carbon atom and incorporated into the extended diamond structure.

sp³ bonded carbon, also known as diamond (Figure 1.3 b), has recently gained significant use an electrode material, which will be a primary focus of this thesis.

1.2.1 sp² bonded carbon materials

As highlighted in section 1.2, there are many different sp² bonded carbons which have found use in electrochemical applications. Although the hybridisation of carbon is the same in these materials, synthesis routes and resulting material properties vary significantly.

1.2.1.1 Structure

Figure 1.4 shows TEM images of different sp² bonded carbon materials. Full imaging conditions can be found in the corresponding references.^{34–39} Graphene (Figure 1.4 a) is monoatomic layer of carbon atoms, tightly bound in a two dimensional (2D) hexagonal honeycomb lattice, with a surface area of > 2000 m² g⁻¹.³³ Graphene sheets are sold commercially in sheets up to tens of cms, however, the larger the sheet the higher the incidence of defects. Graphene is the basic building block of many higher order carbon allotropes, including CNTs and graphite.⁴⁰ CNTs (Figure 1.4 b) are cylindrical molecules, with lengths up to several microns, that can be thought of as rolled up graphene sheets. Two main classes exist, single-walled (SWCNTs) with a diameter of approximately 1 nm, or multi-walled (MWCNTs) which consist of concentric interlinked tubes and can have diameters of > 100 nm.⁴¹ CNTs have a typical surface area of 1315 m² g⁻¹.⁴²

Randomly oriented graphite (Figure 1.4 c) consists of graphitised carbon with randomly oriented microcrystallites. HOPG (Figure 1.4 d) is a high purity form of synthetic graphite with stacked parallel sheets where the graphite crystallites are well aligned with each other. GC (Figure 1.4 e) is an isotropic material with a turbostratic structure, i.e., the basal planes of the crystal structure have slipped out of alignment, of defective graphitic planes arranged in tangled ribbons. Carbon black (Figure 1.4 f) is a high surface-area-to-volume ratio sp² bonded carbon powder, comprised of amorphous carbon NPs which form three dimensional (3D) porous aggregates. Typically, particle sizes range from 8 to 100 nm in diameter. The carbon NPs that make up carbon black are typically porous, with average pores 10-20 Å in size.⁴³

Amorphous carbons have also been utilised for electrochemistry, typically produced and used in thin film format.^{44–49} Amorphous carbons (Figure 1.4 g) have no crystalline structure and typically contain a mixture of both sp² and sp³ hybridised carbon atoms. This also includes diamond-like carbons (DLCs,

Figure 1.4 h), which display some diamond-like properties as they contain significant amounts of sp³ bonded carbon.⁵⁰ Amorphous carbon can also be generated by ion implantation to pattern insulating substrates e.g., intrinsic undoped diamond, for device fabrication.⁵¹



Figure 1.4: TEM images of a) graphene,³⁴ b) a MWCNT,³⁵ c) randomly oriented graphite,³⁶ d) HOPG,³⁷ e) GC,³⁸ f) carbon black,³⁹ g) amorphous carbon,⁵² and h) DLC.⁵³

1.2.1.2 Synthesis

CVD has been used as a production method for both CNTs and graphene. For CNTs, metal catalyst NPs (most commonly nickel, cobalt, iron, or a combination of these) supported on a high surface area support material such as MgO or Al₂O₃.⁵⁴ CNTs are also produced via arc discharge (where an arc is generated in between two graphitic rods) or laser ablation (vaporising a graphite target in a high-temperature reactor), though CVD is typically favoured for product purity and largescale production.^{55,56} For graphene, thin sheets or foils of catalytic metals (e.g., Ni, Fe, Pt, Pd, or Co,), which can also be C doped, are used as the substrate for CVD synthesis.⁵⁷ Exfoliation methods

(microcleaving of HOPG) are also commonly employed to make graphene, with the preferred growth technique determined by the intended application: graphene with the lowest number of defects and highest electron mobility has been produced by exfoliation⁵⁸ but CVD growth offers the advantage of large substrate area coverage for large scale applications.⁵⁷

Randomly orientated graphite is produced via heat-treatment of carbon-rich precursors made from petroleum pitch.⁵⁹ HOPG is typically produced by thermally cracking hydrocarbons at very high temperatures (>2000 °C), followed by annealing under compressive stress high pressure and temperature.⁶⁰ Carbon black is produced in large quantities at low cost in furnace-based plants through incomplete combustion (also referred to as thermal oxidative decomposition) of heavy petroleum products (fluid catalytic cracking tar, coal tar, ethylene cracking tar).⁶¹ GC is synthesised by controlled pyrolysis of highly cross-linked polymers (e.g., phenolic resins) which convert into GC without passing through a plastic phase. A final heat treatment at 1500-2500 °C is applied to produce chemically pure GC. To make amorphous carbons, growth can be carried out by various methods including sputtering,^{45,46} CVD synthesis,⁴⁷ and filtered cathodic vacuum arc (FCVA) synthesis.^{48,49} The exact structure, including sp²/sp³ bonded carbon ratio and crystallinity, of an amorphous carbon varies dependant on how the material has been produced. Unlike other sp² bonded carbon materials, amorphous carbons have no long-range crystalline structure; some short-range order can be observed.

1.2.1.3 Properties and applications

MWCNTs are always metallic conductors, and SWCNTs can be either metallic or semiconducting depending on their structural parameters.⁶² CNT modified electrodes have found use in electrochemical detection and biosensing, offering advantages such as enhanced detection sensitivity and reduced surface fouling.^{42,63} Because fabrication of CNTs usually employs metal catalysts, CNTs usually contain metallic impurities, along with carbon based impurities; completely pure and defect free CNTs are virtually impossible to produce. There has been much debate in the literature as to whether the electrochemical signal comes from the CNTs themselves, or from such impurities. Another point of contention is whether the electrochemical activity should be attributed solely to the defected edges, or if the CNT sidewalls play a role. It is clear that further research must be carried out to truly understand the origins and mechanisms of electrochemical response obtained for CNT modified electrodes.^{42,63}

Graphene has been exploited for its large surface area (>2000 $m^2 g^{-1}$), resulting in improved adsorptive capacity, low charge-transfer resistance, wide electrochemical potential window, and electrical conductivity of ca. 64 ms cm⁻¹.³³ Graphene's high surface area, and thus high capacitance capability, has also led to use in supercapacitor and energy storage applications.^{64,65} Again the biocompatibility of carbon finds use as proteins easily adsorb to graphene, facilitating electron transfer between the electrode and protein molecule.66 Like with CNTs, the edges and the planes exhibit different electrochemical behaviour, with the edges (containing a higher density of defect sites) typically observed to be more electroactive. Again, the presence of defects introduced during production also influence electrochemical response, with different oxygen containing functional groups present on the surface, dependent on preparation protocol.⁶⁷ Often, the electrochemical performance of graphene is enhanced by heteroatom and/or transition metals doping, and such materials have been used for many applications including the catalysis of the oxygen reduction reaction (ORR).67

Much less research exists employing randomly oriented graphite electrodes, chiefly as their relatively large (in comparison with those of GC and HOPG) background currents render them not useful for electroanalysis, but not large enough for charge storage/supercapacitor applications.⁵⁹ As such, these electrodes have only found limited use in electro-organic synthesis.⁶⁸

Once again, HOPG has both basal planes and edge planes that typically exhibit differing electrochemical properties, with the edge planes widely considered much more active.³³ However, like CNTs and graphene, there seems to be no definite solution with considerable activity reported on the basal planes of HOPG in some cases.⁶⁹ Electron transfer kinetics depend significantly on the exact nature of plane/edge sites, including the presence of defects, which, as we have seen, can vary considerably with exact fabrication techniques and parameters.³³

GC combines the properties of graphite with glassy and ceramic properties including high temperature resistance, resistance to chemical attack, low

electrical and thermal resistance, and hardness, hence its use in electrochemistry.⁷⁰ However, electrochemical oxidation at high anodic potentials has been shown to degrade GC electrodes, demonstrating that though GC electrodes are often desired for their stability, this is not applicable for all environments.⁷¹ The physical and electrical properties are generally consistent despite variation in the polymer precursors and exact synthetic details employed.^{70,72,73}

With its very high surface-area-to-volume ratio and high mesoporous distribution, carbon black is perhaps the most commonly used sp² bonded carbon material in a commercial electrochemical application, for PEMFCs. It should be noted that carbon black is an umbrella term used to describe the general case of these amorphous carbon NP agglomerate powders. Specific product names describe actual particle size (usually 8-100 nm diameter) and exact properties. PEMFCs, which are a key development in the pursuit for clean energy for transport,⁷⁴ contain a metal NP catalyst network, typically platinum, on a high surface area carbon support, carbon black.⁷⁵ Carbon black is attractive due to its low cost at bulk scale and the fact it can form a 3D network. However, microstructural degradation and corrosion significantly limits stability, which prevents PEMFCs from achieving the durability needed to find widespread application in electrochemical energy conversion. The sp² carbon is electrochemically oxidised by the high potentials reached during fuel cell start-up and shut-down, and local hydrogen starvation at the anode.⁷⁶ Carbon black is also typically employed as the anode material of choice, through a combination of electrochemical, economic and environmental reasons, in most commercial lithium ion batteries, where Li⁺ ions intercalate into the graphite structure on charging to form graphite intercalation compounds.⁷⁷ However, there are disadvantages too, including a low specific capacity and low rate capacity when compared to other metal based anode materials.78

Another application area in which carbon black has found use is in the fabrication of screen printed electrodes. These planar devices build up layers of conducting printed inks on an insulating substrate. Layers of hydrophobic polymer or wax constrain the analyte flow, generated through capillary forces alone due to the small size of the device.^{79–81} Screen printed electrodes offer many advantages, such as fast analysis time, low cost, flexibility (both

physically and to create complex designs), disposability, low sample consumption, reliability, and the capability for mass production.^{82–85} Though carbon black is a cheap and easily accessible conductive material for producing such inks, devices exhibit high background currents and are prone to surface fouling which results in poor detection limits and ultimately a reduced device lifetime.⁸²

Due to the differences in structure that can be achieved when depositing amorphous carbon films, different electrochemical properties have been observed. This class of carbons boasts a wide potential window, low background current, and easy to functionalise surfaces, but suffer from low conductivity and some chemical reactivity.⁸⁶ DLC is typically used for coatings rather than electrochemical applications, due to its mechanical properties such as hardness and toughness.⁸⁷ Thin film type electrodes also suffer commonly from pinhole formation and delamination.^{88–90}

1.2.2 Boron doped diamond

Intrinsic diamond is a wide band gap semiconductor, and thus electrically insulating (Figure 1.5 a). However, incorporating boron during diamond growth introduces sufficient charge carriers (p-type acceptors, or holes) into the lattice structure to allow charge to flow (Figure 1.5 b).⁶ At dopant densities greater than 10²⁰ B atoms cm⁻³, (i.e., 1 B atom for every 1000 C atoms) semi-metallic behaviour is observed (Figure 1.5 c).⁶



Figure 1.5: Electronic band structure of boron doped diamond.

The boron impurities insert into the face centred cubic (FCC) diamond lattice as substitutional defects (Figure 1.6). BDD offers extraordinary electrochemical and material properties, including a wide solvent window, low background currents, reduced fouling, extreme hardness, and a resistance to both chemical corrosion and degradation under extreme operating conditions.^{6,91} It should be noted particularly that these properties tend to be superior to those exhibited by sp² bonded carbon electrodes, as discussed in section 1.2.1.3, where high background currents, narrower solvent windows. and susception to corrosion can limit use. Many of these remarkable properties stem from diamond's sp³ FCC crystal lattice structure (Figure 1.3 b and Figure 1.6). BDD electrodes have found use in a wide variety of electrochemical applications^{92,93} including, but not limited to, wastewater treatment,94-96 electroanalytical identification, quantification and/or production of both inorganic and organic molecules,97-100 and biological sensing.101-103



Figure 1.6: Schematic of the sp³ BDD lattice structure where black atoms are carbon and blue is boron. The red square indicates one FCC face.

Generally, BDD electrodes are fabricated in a thin film format over large areas on a support material by chemical vapour deposition (CVD).^{104–108} Diamond can be grown on a variety of substrate materials including diamond, silicon, copper, tungsten, steel, and molybdenum.¹⁰⁹ Though diamond substrates offer the best lattice parameter match, high quality large area diamond is expensive and thus use is uncommon, unless single crystal diamond is required. Nondiamond substrates require a pre-treatment step to enhance nucleation densities and encourage homogenous film growth, for example by abrasion,
electrical biasing, or through artificial nucleation with diamond nanoparticle (NP) seeds.¹¹⁰

During CVD growth, a high concentration of hydrogen gas is flowed into the reaction chamber with low concentrations of gaseous carbon and boron sources (usually methane and trimethylborane, respectively). A hot filament (HFCVD) or microwaves (MWCVD) are used to create a predominantly hydrogen plasma containing a small proportion of carbon and boron, which activates the gaseous reactants. Carbon atoms dissociate in the plasma producing radicals, which deposit onto a solid substrate, growing the diamond lattice. Hydrogen molecules also dissociate, and the high concentration of atomic hydrogen stabilises diamond growth. Furthermore, atomic hydrogen terminates dangling surface bonds, preventing surface reconstruction and preferentially etching sp and sp² hybridised carbon atoms from the growing diamond surface.^{111,112}

Typically CVD synthesis is achieved at substrate temperatures of 500 to 1200 °C, plasma temperatures of approximately 2200 °C, and at ambient pressure (Figure 1.7).¹⁰⁹ HF-CVD is typically favoured commercially as this allows larger growth areas, however, MW-CVD produces higher phase purity BDD and faster growth rates can be achieved as higher plasma temperatures can be reached.¹¹³ Thicker films (\geq 100 microns) can be removed from the growth substrate and polished to give a nm roughness free-standing BDD wafer.⁹³ The hydrogen growth atmosphere results in a hydrophobic, hydrogen-terminated surface. After prolonged exposure to air, the BDD surface slowly undergoes oxidation to give a hydrophilic oxygen terminated surface.⁶ Surfaces can also be deliberately converted from H-termination to O-termination, for example by boiling in acid,¹¹⁴ alumina polishing,¹¹⁵ photochemical oxidation,¹¹⁶ and exposure to oxygen plasma,^{117,118} and vice versa by exposure to hydrogen plasma.¹¹⁹

Growth conditions such as gas concentrations, plasma temperature and pressure can be varied, all of which significantly affect the resulting material properties. These parameters are tremendously important and can be controlled to vary film thickness and texture, grain size, dopant concentration, and sp² to sp³ carbon ratios.¹⁰⁹ Under the right conditions CVD growth produces high quality, metal-like doped BDD material with negligible sp² incorporation, but this can be a slow and relatively expensive process. Unless

single crystal substrates are deliberately used, the films produced are polycrystalline, containing diamond crystals with different crystallographic facets, or grains.⁹¹ The grain size and roughness of the resultant polycrystalline film is governed by the growth time, with longer growth times producing larger grains and rougher growth surfaces.⁶ Grains grow in a columnar fashion, away from the growth substrate, or nucleation face, towards the growth face. This results in the crystal orientation with the fastest vertical growth rate 'outgrowing' slower growing crystal faces.¹²⁰ Hence at longer growth times the (101) facet predominates as the (100) and (111) facets grow at a slower rate due to differences in their growth mechanisms.¹²¹ As the BDD grows, the different grain orientations incorporate boron at different rates, with (111) > (110) > (100), producing grains with differing boron dopant concentrations and therefore a heterogeneously doped surface.¹²²



Figure 1.7: Carbon phase diagram.

Diamond can also be produced by high pressure high temperature (HPHT) synthesis.¹²³ Conditions for both CVD and HPHT diamond growth are compared in Figure 1.7. This technique mimics the conditions under which diamonds grow naturally in the Earth's mantle. Large presses that weigh hundreds of tonnes are used to generate pressures of 5.5 to 10 GPa and

temperatures of 1800 to 2400 °C.¹²³ A small amount of diamond seed crystals are mixed with graphite (the carbon source) and a metal catalyst (e.g., nickel, iron, manganese) powders.^{124,125} When the synthesis temperature and pressure are reached, the molten metals facilitate dissolution of carbon atoms from the graphite, which recrystallise on the surface of the diamond seeds, extending the diamond seed lattice.¹²³ HPHT synthesis typically produces large volumes of micron to millimetre sized diamond particles,¹²⁴ or 'grit' (Figure 1.8), quickly and at a relatively lower cost when compared to CVD synthesis.



Figure 1.8: Photographs of a) CVD grown freestanding BDD wafers (© Jon Newland) and c) HPHT grown BDD grit (both a and b are black in colour due to high levels of boron doping).

Again, growth parameters such as temperature and pressure profiles, the type of press used, and ratio of starting materials can be varied to tune the properties of the diamond particles produced. HPHT diamond particles are commonly used to fabricate grinding and abrasive tools, and are typically doped with a few hundred ppm of nitrogen, from residual atmospheric nitrogen in the growth capsule and chamber.¹²⁶ By also adding a boron containing source (in solid form) to the growth mixture, BDD microparticles (MPs) can be produced by HPHT synthesis.^{124,125,127,128}

However, producing HPHT diamond with the boron levels high enough to achieve the metallic-like conductivity required for electrochemical applications is challenging, and there has been little research on BDD synthesis by this route.^{124,125,127–132} High levels of boron in HPHT diamond can also cause crystallographic defects,¹²⁷ which can also result in impairment of the materials' chemical and physical properties. Though production of BDD through a HPHT route is complex, it would offer a cheaper alternative to CVD,

at large scale. Using different compression strategies, the particles could be packed into porous 3D structures or used as freestanding compacted electrode. Currently no published research describes the use of BDD HPHT electrodes.

Given the presence of nitrogen, which is difficult to exclude, it is possible to form electrically neutral nitrogen-boron (N-B) aggregates as nitrogen atoms can also substitute into the diamond lattice where they act as an n-type dopant. Thus, even if the concentration of boron is thought to be sufficient, if nitrogen dopants are present, N-B charge compensation will act to reduce the number of charge carriers that are freely available for electron transfer.¹³³ Hence, measuring the boron concentration alone, especially with HPHT material, is not sufficient to ascertain viability for electrochemical applications. To reduce nitrogen incorporation into the lattice for diamond growth, growers have added nitride forming elements (typically Al, Ti, or Zr) to the growth mixture, which complex the free nitrogen.¹³⁴

To date, there has been little research on the HPHT synthesis of BDD particles. Furthermore, of the few studies which have been undertaken, the use of BDD produced as an appropriately doped electrochemical material is yet to be demonstrated. In some cases, the boron content is not quantified,^{127,131} incomplete experimental conditions are reported,^{128,129} or the boron content is found to be insufficient for use in electrochemical applications.^{125,130} The highest boron doping levels achieved, $(1.4-2.7) \times 10^{21}$ cm⁻³, were obtained from a Mg-Zn (catalyst)-B-C system at over 1750 °C (full experimental conditions were not reported).¹²⁸ Mg and Zn are not carbide forming metals and thus higher temperature and pressure conditions are required. Moving to a solvent system containing carbide forming catalyst metals such as Fe, Ni, Mn, and Co permits a reduction in growth temperature and pressure, decreasing the cost and energy consumption of production.¹²⁴ It has been postulated that this is due to a lower eutectic temperature of carbide containing boron-graphite-liquid systems.¹³⁵

In contrast, a Co (catalyst) B-C system required growth conditions of 8 GPa and 1400-1600 °C and resulted in HPHT BDD with an estimated boron content of around 10²⁰ cm⁻³. The material was, however, in the form of polycrystalline aggregates in which inhomogeneous boron doping was reported.¹³² BDD has also been obtained from a Ni-Mn (catalyst) B-C system,

at 5 GPa and 1500-1600 °C, with a boron content of $(2\pm1) \times 10^{20}$ cm⁻³.¹²⁴ The particles produced at this doping level were found to have very rough surfaces with a layer-like structure, lacking well-defined crystal faces. For all these studies no information was provided on the nitrogen levels and no nitrogen getters were employed during synthesis.

1.3 Applications of boron doped diamond

Due to the many advantages BDD electrodes offer over competing electrode materials, they have impacted a wide variety of electrochemical applications. These advantages include but are not limited to: (i) a very wide electrochemical solvent window; (ii) low background and capacitive currents; (iii) low fouling; (iv) biocompatibility; (v) high temperature, pressure, electrochemical, and chemical stability.

As examined in section 1.2.2, BDD offers these improved electrochemical properties due to its sp³ bonding, in comparison to alternative sp² bonded carbon electrode materials, considered in section 1.2.1.3. As BDD is typically grown in a polycrystalline format, sp² bonded carbon incorporation at the grain boundaries during growth (see section 1.2.2 for further discussion) is hard to avoid completely, though it can be minimised. Sp² bonded carbon is more reactive to many electrochemical processes, including oxygen reduction and the oxidation of surface bound redox species, than sp³ bonded carbon present in the BDD, the narrower the solvent window and the larger the capacitive current. For these reasons, minimal sp² bonded carbon content is desired for electrochemical applications and must be considered when interpreting data.

1.3.1 Electroanalysis

The extended cathodic window has been exploited in anodic stripping voltammetry techniques for heavy metal sensing to sub ppb-levels,¹³⁸ where traditional mercury-based electrodes have become obsolete due to toxicity and safe disposal concerns. Identification and detection of heavy metals is of particular importance in environmental, pharmaceutical, and food systems as many of these elements are toxic at high concentrations. A broad range of ions have been investigated using BDD including Pb²⁺, Cd²⁺, Ag⁺, Cu²⁺, and Hg²⁺.^{91,138,139} The low background currents exhibited by BDD electrodes allow

for such low-level species detection in electroanalysis.^{140–142}BDD electrodes have also been used to detect many organic species, often in conjunction with complimentary techniques such as flow injection analysis, liquid chromatography, or capillary electrophoresis.^{143–147} Due to the ease at which the BDD surface can be chemically functionalised, BDD electrodes have also found widespread use for biosensing applications. Modification with a broad range of molecules have been investigated, including linker molecules to enable attachment of DNA and peptides and reduce nonspecific bind events, halogens, amines, carboxyl groups, and more, depending on the desired application.^{148–151}

1.3.2 Advanced Oxidation and Electrosynthesis

Perhaps the most impactful industrial use of BDD electrodes has been their use in waste-water treatment,^{94,152} where commercial water treatment systems are currently available that employ BDD electrodes.⁹³ Use in these applications stem from the fact the electrocatalytic inefficient BDD surface promotes the electrochemical generation of hydroxyl radicals (·OH) in solution from water oxidation, in both acidic and neutral pH environments.¹⁵³ The hydroxyl radical is strongly oxidising with a very short lifetime and will react with organic pollutant molecules in solution, causing degradation to harmless products. This is known as electrochemical advanced oxidation processes (EAOPs).^{106,154} An important advantage of BDD in these applications is also the robustness of the material towards chemical attack itself, from the hydroxyl radical or any reactive species generated. BDD electrodes have also found commercial use in the electrochemical production of disinfectants e.g., in the generation of dissolved ozone, a powerful antimicrobial, in addition to free chlorine, a primary disinfectant used to treat contaminated water.^{155,156}

Electrochemical ozone production (EOP) on BDD is considered to occur via a surface adsorbed hydroxyl radical route. The generally accepted mechanism was proposed by Da Silva et al. in 2003 and is described by equations (1.5) to (1.10).¹⁵⁷ First, weakly surface bound ·OH radicals are electrochemically generated by water discharge (1.5), which decay to adsorbed oxygen radicals, ·O (1.6). These adsorbed ·O are then able to chemically react with each other to form adsorbed oxygen molecules (1.7), which can either leave the surface as oxygen gas (1.8) or they are available on the surface to generate ozone by combining with an unreacted adsorbed ·O (1.9). The overall electrochemical

equation is given by (1.11). It is thought that the surface coverage of adsorbed ·O vs adsorbed oxygen molecules controls the efficiency of EOP over the oxygen evolution reaction (OER). Electrodes with high overpotentials for OER have been previously investigated including SnO2,¹⁵⁸ PbO2,^{159,160} Pt,¹⁶¹ and GC,¹⁶² and found to produce ozone, but these materials lack durability over time in such oxidative environments. They also, in the case of SnO2, PbO2 and Pt present concerns with dangerous environmental heavy metal contamination.¹⁶³ BDD electrodes are thus extremely attractive commercially as BDD poses no safety concerns (being mostly carbon), has a very wide anodic window in water due to the OER being strongly disfavoured on BDD, and exhibits excellent electrochemical stability.^{163,164} For these reasons, commercial EOP devices typically employ BDD electrodes.

Electrochemical steps:

$$H_2 0 \to (H0 \cdot)_{ads} + H^+ + e^-$$
 (1.5)

$$(H0 \cdot)_{ads} \to (0 \cdot)_{ads} + H^+ + e^- \tag{1.6}$$

Chemical step:

$$2(0 \cdot)_{ads} \to 0_{2_{ads}} \tag{1.7}$$

Oxygen evolution:

$$0_{2_{ads}} \to 0_2 \uparrow \tag{1.8}$$

Oxygen formation:

$$(0 \cdot)_{ads} + \mathcal{O}_{2_{ads}} \to \mathcal{O}_{3_{ads}} \tag{1.9}$$

$$O_{3_{ads}} \to O_3 \uparrow \tag{1.10}$$

Overall reaction:

$$3H_2 0 \to 0_3 + 6H^+ + 6e^- \quad E^\circ = 1.51 V$$
 (1.11)

Although BDD exhibits a high overpotential for OER, it is known that the •OH radicals are very weakly adsorbed to the BDD surface.⁹⁴ It is this property that makes BDD electrodes desirable for EAOP in wastewater treatment, as the •OH radicals will easily desorb from the electrode surface allowing attack of unwanted species in the bulk solution. Though beneficial for EAOP, weak •OH adsorption could pose a disadvantage for EOP due to fact the proposed mechanism relies on surface mediated radical pathways.

Commercial EOP electrolytic cells commonly consist of distinct and separate anode and cathode compartments, separated by a PEM such as Nafion®. This allows the use of water without added electrolyte as the PEM acts as a solid electrolyte, and permits proton transfer between the two compartments.^{164,165} Perforated electrodes are employed, to both provide a solution pathway to the Nafion[®] membrane and maximise the contact area between the Nafion[®] membrane, anode, and the solution (known as the "triple-point"). In the literature it is believed that this boundary is the active electrode area (i.e., where the ozone is electrochemically generated).^{163–165} To achieve perforated electrodes, two main routes have been adopted: (1) laser micromachining slots or holes all the way through freestanding BDD electrodes,¹⁶³ and (2) growing thin film BDD over pre-perforated substrates.^{164,166} Though thin film coatings are usually cheaper to produce, freestanding BDD electrodes provide an unrivalled robustness and durability in harsh environments, and do not carry risk of failure through pinhole formation and/or film delamination, as is common for thin films.^{88–90} A key factor not considered in previous literature, is that whilst both methods can produce electrodes with identical geometries, the material characteristics are not the same. This is due to laser micromachining of freestanding BDD surfaces introducing non-diamond, sp² bonded carbon¹⁶⁷ into the laser cut surfaces. Therefore, a perforated freestanding BDD electrode will consist of two pristine diamond faces, plus the sp² carbon surfaces of the laser cut slots.

Prior work focused on optimising freestanding BDD electrode geometry for maximum ozone output.¹⁶³ An investigation into the effect of slot geometry and material thickness of freestanding BDD electrodes concluded that the slot geometry, in particular slot edge length, had a significant effect on ozone output and current efficiency.¹⁶³ However, the impact of sp² bonded carbon introduction during electrode processing was not considered. Secondly, as the total hole area machined from a fixed size electrode is increased, more BDD is removed, resulting in a decrease in electrode area. Thus, for a given current, the current density for each different electrode geometry will vary; again, this was not considered.¹⁶³

There are only two research papers which have considered the impact of sp² bonded carbon on EOP, and both introduce the sp² bonded carbon via the CVD growth process.^{168,169} Thin film BDD on perforated Si growth substrates were

used for these studies with both a varying boron and sp² bonded carbon content. In one study, an increase in ozone output from ca. 4 (for 1% B/C ratio) to 6 mg L⁻¹ (for 5% B/C ratio) was observed at a current of 2.5 A. The current efficiency obtained was 42% for 5% B/C ratio, almost double the 25% measured for 1% B/C ratio. The switch on potential at which ozone production could be detected decreased from 2.8 V for 1%, to 2.2 V for 5%.169 However, as both boron concentration, and therefore conductivity, and sp² carbon content were varied simultaneously, it is impossible to attribute this finding to sp^2 carbon content alone. The increase in material conductivity as a result of increased boron content is likely to account for the lower switch-on potential observed for higher boron content electrodes. In the second study, BDD with a B content of 7.1×10^{19} atoms cm⁻³ produced an ozone output of 2.10 ppm at 2.65 A, compared to BDD with a B content of 5.5×10^{21} atoms cm⁻³ produced an ozone output of 8.43 ppm at 3.97 A. Again, a significant improvement in current efficiency was measured from 17.2% (7.1×10^{19} B atoms cm⁻³) to 46.1% (5.5×10^{21} B atoms cm⁻³). This work also emphasised the importance of keeping the fraction of sp² bonded carbon impurities very low in order to retain the durability of the electrode and maintain the structural stability of the BDD film.

Thin-film BDD was grown on slotted silicon wafers at a variety of boron to carbon (B/C) ratios to vary sp² content. It was concluded that the electrodes with the highest sp² content produced the highest ozone concentration. However, as both boron concentration, and therefore conductivity, and sp² carbon content were varied simultaneously, it is impossible to attribute this finding to sp² carbon content alone. The increase in material conductivity as a result of increased boron content is likely to account for the lower switch-on potential observed for higher boron content electrodes. Even the highest B/C ratio trialled is likely to have only achieved a low surface coverage of sp² carbon (<1%) and even if higher ratios could be achieved there may be issues with long term surface stability as these electrodes become less diamond-like.

1.3.3 Electrocatalysis

BDD alone, whether O- or H-terminated, is typically not active for electrocatalysis due to its incredibly low background current and featureless solvent window that is exploited for use in electroanalysis. BDD electrodes also display electrocatalytically retarded processes and so push out the kinetics to more extreme potentials. That being said, it is possible to deliberately impart electrocatalytic activity on the BDD electrode, most commonly achieved by covering the surface with metal NPs (including gold, silver, copper, platinum, cobalt, lead, nickel, cadmium, and many others⁹⁷). The BDD acts as an excellent electrochemically inactive support, with resistance to extreme conditions, e.g., highly acidic/alkaline media, high operating potentials, and chemical corrosion.⁹⁷ Metal NP coverage results in a much higher surface area, enhanced diffusion, and a significantly larger number of active (surface) sites when compared to a bulk metal.^{170,171} This simple surface modification enhances the selectivity and sensitivity by combining the catalytic ability of the metal with the low background currents of BDD, thus reducing signal to noise and lowering detection limits. Modification methods frequently employed include metal ion implantation,^{172–174} electrochemical deposition from metal salts,^{175–177} and physical deposition techniques including sputtering^{178,179} and drop-casting presynthesised NPs.^{180,181}

1.3.4 BDD Particles

As discussed in section 1.2.2, production of BDD MPs through a HPHT route is also an interesting alternative to CVD growth, at a lower cost and on a much larger scale. Packing these particles into a porous 3D structure or freestanding compacted electrode, as opposed to a solid wafer, provides the advantage of increased flexibility with regards to electrode size and geometry. This opens up a wide range of new application areas not previously accessible. Using BDD MPs as building blocks to create 3D composite electrodes is of interest for many electrochemical applications including gas diffusion electrodes, where high surface area composite electrodes are desired. BDD MPs are also a suitable precursor for processing down to the NP size, which again reveals new application possibilities.

BDD NPs could find use, for example as the corrosion free carbon support in gas porous electrodes for PEMFC applications¹⁸² and as the conducting ink, in screen printed devices, as discussed in section 1.2.1.3. In the former, one of the big problems with long term use is corrosion of the carbon black support and loss/detachment of the catalyst NPs which sit on this support, with time.^{183–185} BDD, if it can be made at high enough dopant densities and in small enough particle sizes, is an ideal corrosion free support. Traditionally carbon blacks are used in screen printed devices,^{186–190} but the high

background currents and surface fouling cause poor detection limits and reduced device lifetimes.⁸² BDD offers both increased sensitivity due to its low background current and wide solvent window, and an increased lifetime due to its chemical inertness and resistance to fouling. Therefore, utilising BDD enables the fabrication of sensing devices with enhanced performance compared to their carbon-based counterparts. Conducting ink containing BDD powder can be screen printed onto any substrate to make a quick and disposable electrode. Like with carbon powder electrodes,^{191–193} functional molecules could also be easily introduced to produce analyte-specific sensors, and so BDD screen printed electrodes could be designed for an endless number of potential applications across many fields within science and technology. It is important to note that due to the sp² nature of the carbon atoms in carbon powder electrodes, compared to the sp³ carbon in BDD, different functionalisation strategies may be needed.

The use of BDD powder in fabricating screen printed devices is now beginning to emerge,^{82,85,194} and the same is true for PEMFC applications.^{195,196} However, for both applications the BDD powders are made using CVD which is unfeasible for high volume production. Screen printed BDD electrodes have been used to detect both biological species (norepinephrine and serotonin) and heavy metals (Pb and Cd).82 Though these studies show successful use of BDD NPs for electrochemistry, high background currents and some resistivity were observed and only quasi-reversible behaviour was seen for the reversible inner-sphere redox couple Fe(CN)₆^{3-/4-}.^{15,30} This may be due to insufficient cleaning of the particles and/or poor connectivity, and shows that the method is still not perfect and needs optimising. A flexible electrolysis unit based on a BDD powder polymer composite has also been produced with work progressing for application in dental treatments.⁸⁵ The BDD components of these devices exhibited the high sensitivities and lower fouling compared to carbon alternatives that is typical of BDD electrodes.82,85,194 Wider solvent windows and smaller backgrounds were observed compared to carbon, however these were still not comparable to freestanding BDD electrodes and thus there may be room for improvement.

Example geometries of such devices can be seen in Figure 1.9. In these cases, the conductive BDD NP powder which is added to the ink was produced by MWCVD growth of BDD on the surface intrinsic diamond NPs, completely

coating each particle with a BDD layer.^{15,194} Studies such as these are now beginning to show the viability of screen printed BDD powder based devices as disposable electrochemical sensors in a huge number of application fields.



Figure 1.9: a) i) Schematic diagram and ii) photograph of a BDD powder printed electrode.¹⁹⁴ b) i) Photograph and ii) schematic of the device design of a BDD powder printed electrode used for biological species detection, and iii) schematic design of a BDD powder printed electrode used for heavy metal detection.⁸²

Pure BDD NPs can be produced through mechanical milling of CVD grown BDD films.¹⁹⁷ Highly doped BDD NPs have been produced from CVD grown BDD using a vibration mill.⁸³ A multistep milling process was employed to yield a stable blue colloidal solution of 30-70 nm BDD NPs. The approximate boron concentration of the NPs was reported as 2.3×10^{21} cm⁻³, which is sufficient for use in electrochemical applications, however the use of the BDD NPs for such applications was not explored in this study.

It follows, therefore, that HPHT BDD MPs could be used as an alternative feedstock for the mechanical milling of BDD to produced NPs. As discussed in section 1.2.1, HPHT offers the advantages of scalability and lower cost when compared to CVD diamond growth.

1.4 Electron microscopy techniques for carbon materials

Electron microscopy (EM) is a versatile field encompassing a range of techniques that use a beam of accelerated electrons for obtaining high resolution images of a diverse scope of materials, allowing investigation of fine structural details not achievable by light microscopy.

1.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is an imaging technique that involves raster scanning a focused high energy electron beam across the surface of a sample. Interactions between the electron beam and atoms within the sample produce signals collected by a detector, and the detected signal intensities and beam position are combined to generate an image. The signals produced include secondary electrons (SE), backscattered electrons (BSE), and characteristic X-rays; each type of signal is collected by a specialised detector and provides different information about the sample. SEM can provide both topographical and compositional information of a sample.^{198,199} The maximum spatial resolution of modern SEMs is 1-20 nm.²⁰⁰

The electron beam is generated by thermionic emission from an electron gun containing a thin tungsten wire filament which is heated to around 2800 K.²⁰¹ The high energy electrons (0.2 keV to 40 keV) are accelerated down the column where they pass through electromagnetic lenses. First, the condenser lens controls the beam size spot size, and can be adjusted to change the electron beam diameter and current. The objective aperture is placed below the condenser lens to eliminate high angle electrons before the beam finally passes through the objective lens, which focuses the electron beam onto the sample surface (typically 0.4 nm to 5 nm in diameter). As the beam hits the sample, the high energy electrons penetrate the top few microns of the surface. The space over which the electrons spread is known as the interaction volume (Figure 1.10). The interaction volume size increases with increasing accelerating voltage of the electron beam and decreases with increasing sample atomic number (i.e., density).²⁰² The electron beam position is controlled by scanning coils that reside above the objective lens and deflect the beam in X and Y to allow raster scanning of the beam over the sample surface. The sample is mounted onto a stage (generally using adhesive carbon tabs) which can be moved in X, Y, and Z, and be tilted and rotated, in the main chamber and both the column and chamber are kept under vacuum during operation.199,201



Figure 1.10: Schematic to show a cross section of the SEM interaction volume, and the varying depths into the sample at which different signals arise.

Small or large (and thin or thick) samples can easily be imaged with SEM, and generally for conducting materials no particular sample preparation is necessary. Non-conducting materials, however, must be coated in an ultrathin coating of electrically conducting material (for example carbon, gold, or platinum which is typically sputter coated or evaporated) to prevent samples from collecting charge when scanning. Sample charging is a common problem if there is an insufficient conducting path for the incident electrons hitting the sample surface to travel to ground. Charging creates problems with drift, blur, and low contrast, producing blurry or false images.²⁰³ Other techniques that may be employed to minimise charging include connecting parts of the sample to the stage with copper tape or silver paint and reducing the accelerating voltage.

An SEM can operate in different modes with multiple detectors that each collect different signals from the sample. The in-lens detector sits above the pole piece, which directs the EM field, of the objective lens and so collects mainly SE1 secondary electrons. SE1 electrons are generated in the uppermost range of the interaction volume and therefore contain detailed information

about the sample surface. This produces high contrast images of surface features and topography.²⁰⁴

The traditional SE detector (Everhart-Thornley) is positioned outside the lens system and positively biased to draw SEs towards it. The detector position favours collection of SE1, SE2 and BSEs. BSEs are elastically scattered electrons that originate from deeper in the interaction volume and so carry depth information along with the surface morphology information from the SEs. As larger interaction volumes are produced for lower atomic number elements, SE2 generation increases, and signal is collected by the SE detector from a wider range of escape depths. This causes a blurring effect and thus a reduction in contrast and resolution. For this reason, in-lens imaging is commonly favoured over SE imaging when imaging small features such as metal NPs on a low atomic number support such as carbon or alumina.²⁰⁴ Such objects can typically be imaged by SEM with a resolution of 5-6 nm at best.²⁰⁵

A traditional BSE detector (BSD) sits above the sample surface but below the lens system. BSD imaging is sensitive to the sample material atomic number (larger atoms scatter electrons more strongly and so the higher the atomic number, the brighter the image appears), and so can provide topography and compositional information. As BSEs emerge from deeper in the interaction volume, BSE images typically have lower resolution than SE images.²⁰⁶

Even deeper in the interaction volume, X-rays are emitted when the beam displaces an inner shell electron, causing a higher energy outer shell electron to fill the inner shell and release the difference in energy in the form of an X-ray. As the energy difference between inner and outer shells is unique to each element, detection of these X-rays and measurement of their energies allows elemental identification.²⁰⁰ This technique is commonly referred to as energy-dispersive X-ray spectroscopy (EDX, also sometimes referred to as EDS or XEDS). EDX measurements can be recorded in single spots, across a line scan, or in a 2D scan. Combining this with an SEM image allows mapping the abundance of elements and their distribution across the sample. Removable silicon-drift detectors are used to collect these characteristics X-rays, which are placed very close underneath the sample to record measurements.²⁰⁷

SEM has been used routinely in the study of carbon materials. Both sp^2 and sp^3 carbon surfaces can be imaged directly as carbon is sufficiently conducting

to produce good SEM images and avoid charging effects. The crystal facets of polycrystalline BDD can clearly be visualised using SEM (Figure 1.11), enabling quantification of grain size and observation of grain boundary locations. The contrast differences between the different crystal facets grains are reflective of heterogeneity in local boron dopant density. Higher doped grains appear darker and lower doped grains appear lighter, as conductivity increases with boron doping level. The higher conductivity grains are able to remove charge from the surface more efficiently.^{6,122,208}



Figure 1.11: FE-SEM image of a polycrystalline BDD surface. This is a freestanding BDD material, and it is the polished growth face. The image was recorded with an accelerating voltage of 3 kV using the in-lens detector of a Zeiss Gemini.

1.4.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is a powerful technique that uses a beam of high energy electrons to visualise specimens at incredibly high magnification and resolution, with a resolution limit of around 0.2 nm.²⁰⁹ A significantly higher resolution can be achieved than by light microscopy due to the much smaller de Broglie wavelength of electrons compared to visible light.²¹⁰ TEM imaging can reveal the finest details of materials, including crystal structure, features such as dislocations and grain boundaries, chemical composition, and in some cases even down to imaging of single atoms.^{23,211}

The electron gun generates the electron beam. It contains an electron source (typically a tungsten filament or a LaB₆ single crystal) and is connected to a high voltage source (100-300 kV). The resultant current causes the gun to emit electrons (by thermionic or field emission, FE) into the TEM column. Within the column there are a set of electromagnetic converging lenses. Electromagnetic lenses contain the yoke, where the magnetic coil is housed, and the pole piece. This is a symmetrical magnetic pole that further constricts the electron path through a narrow gap in the pole piece. The electron beam is first accelerated by a series of electrostatic plates until the desired operating voltage is reached. Next, the condenser lens system focuses the emitted electrons into a narrow coherent beam onto the specimen. A condenser aperture is used to exclude high angle electrons and reduce spherical aberration. The beam then hits the specimen, with electrons interacting with the sample as the beam is transmitted through it. Electrons either hit the specimen and scatter or travel straight though with no interaction, depending on the thickness and electron beam transparency of the material. The objective lens sits below the specimen and forms an initial image, focused and magnified onto a fluorescent phosphor screen.

This screen can be viewed directly within the TEM through a viewing chamber or on a computer though a charge-coupled device (CCD) camera. Apertures can also be inserted into the beam path which allows modulation of the beam to different degrees of precision by restricting which transmitted electrons contribute to the final image. Objective apertures can enhance contrast by blocking out peripheral, high-angle electrons. Selected area apertures can be used to block a large fraction of the electron beam to select small areas of the specimen for selected area diffraction (SAD) experiments to determine crystal structure.^{210,212,213}

The TEM column must be operated under high vacuum (10^{-4} to 10^{-9} Pa) for 3 key reasons, (1) to exclude any particulates i.e., dust that could deposit onto the specimen causing contamination, (2) to remove gas molecules that electrons could interact with, thus increasing the mean free path of electrons travelling down the column, and (3) to prevent voltage arcing arising from the voltage difference between the cathode and the ground.²¹⁰

It is also a key requirement that the specimen must be ultra-thin, nominally < 100 nm thick, to ensure sufficient electron beam transparency with minimum

energy loss. Specimens are typically a thin section of a bulk material, or a suspension of the sample deposited onto a thin support grid. The most commonly used commercial TEM grids consist of a metal frame (Cu, Ni, Au) with a thin (5-20 nm) amorphous carbon (section 1.2.1) support layer produced by thermal evaporation from carbon rods under vacuum, onto a support sheet (typically mica) floated in water from the support onto the metal frame (Figure 1.12).²¹⁴ These amorphous carbon films can be utilised for two purposes to act as an electron beam transparent support to image the deposited structures^{215–217} or in more advanced applications to act as electrode surface onto which materials can be electrodeposited and subsequently imaged. As these TEM grids are widely commercially available and are used as a support for other materials of interest, there is a lack of discussion in the literature regarding the exact nature of the amorphous carbon films used. As discussed in section 1.2.1, the precise structural arrangement of sp² carbon materials can have a significant impact on the observed properties. This is of particular importance when moving to such advanced applications (examples are given in section 1.4.3) where the carbon film is acting not only as support but as an active electrode surface, for example.



Figure 1.12: Commercial TEM grid structure.

The material to be imaged thus sits on the support film. These films can be continuous, or they can intentionally contain holes (holey carbon or lacey carbon),²¹⁸ which prevent the specimen from falling through the holes of the

metal grid but provide areas of increased image contrast in the regions of the holes as there is no scattering from the support film, which contributes to background noise.²¹⁹

Focused ion beam (FIB) and combined focused ion beam – scanning electron microscope (FIB-SEM) techniques are routinely used to prepare thin specimens for TEM analysis from a vast array of materials. A thin cross-sectional lamella is removed from a bulk sample typically 10-15 μ m wide, 8-10 μ m deep, and approximately 100 nm thick. The lamella can be cut to encompass a feature of interest, and so specific defects or interfaces can be imaged with this method. In brief, the procedure involves depositing a thin metal layer (typically Pt) to prevent damage to the surface, before an ion beam (Ga) is used to cut trenches around this area, producing a thin lamella which can be lifted out from the bulk sample. This thin specimen is then attached to a carrier grid, commonly a Cu half disc with labelled prongs for lamella attachment (known as a 'lift-out grid'), which is then used to image the lamella in the TEM.²²⁰

TEM is a versatile technique with a large number of operating modes that can be utilised, depending on the specimen information desired. Conventional bright field (BF) imaging is the most frequently adopted method. When electrons pass through the specimen, some parts of the material will stop or deflect the electrons more than other areas. Where electrons are unscattered and pass straight through, the image collected is bright. Consequently, where electrons are scattered and do not pass through, the image is dark. Within these extremes, a range of greys are observed, where again the lighter the image, the less the electron beam has been scattered in that region of the specimen. This contrast arises from several image contrast mechanisms. These include: (i) differences in thickness or density across the specimen (massthickness contrast); (ii) differences in atomic number where atoms with a higher atomic number will cause more electron beam scattering and thus produce a darker image (Z contrast); (iii) differences in crystal orientation (crystallographic contrast); (iv) quantum-mechanical phase shifts induced in electrons as they pass through atoms in the specimen (phase contrast.)^{210,212,213,221}

In the inverse case, scattered electrons are selected, with unscattered electrons excluded by the aperture; this is known as dark field (DF) imaging. In DF

images, the sample appears bright, and the background appears dark. DF imaging is typically used to enhance image contrast, particularly if crystalline features are too small to see in BF imaging. As the scattered electrons are selected by the aperture, small crystalline features such as the crystal lattice, crystal defects, stacking faults, dislocations and particle/grain size can be imaged in this mode.²²²

In addition to conventional TEM imaging, as described above, many modern microscopes also offer imaging in a scanning TEM (STEM) mode. STEM combines principles of both TEM and SEM techniques; images are formed by electrons passing through the specimen, but the electron beam is focused to a fine spot at the specimen, 0.05-0.2 nm in diameter, which is raster scanned over the sample.²²³ In STEM mode, a wider variety of signals (e.g., elastic, inelastic, scattered, and non-scattered electrons) emitted from the sample can be collected by detectors located below the sample.²²⁴ Depending on the position and angle of the detector, both BF and DF images can be obtained with STEM. Imaging in the STEM mode allows for nanodiffraction, EDX analysis on the nanoscale, high-resolution Z-contrast chemical imaging (also referred to as high-angle annular dark-field imaging, HAADF), and EELS analysis.²²⁴ In general, TEM imaging is used for routine phase contrast imaging, and STEM is used for HAADF imaging in combination with spectroscopy to enable atomic scale analysis that is not achievable with TEM alone.

Despite advances in technologies in recent years, it's impossible to fabricate perfect lenses for use in electron microscopes. This means that practically, the theoretical resolution determined by the wavelength of the electron is not achievable. The best resolution attainable is therefore limited by both the wavelength, λ , and by the quality of the objective lens. This point resolution limit, L_{PR} , is given by equation (1.12):

$$L_{PR} \sim C_s^{1/4} \lambda^{3/4} \tag{1.12}$$

where C_s is the coefficient of spherical aberration (the main factor that determines lens quality).²²⁵ Spherical aberration focuses the rays passing through the lens at higher angles to the optic axis closer to the lens that those passing through at lower angles. The result of this a smearing to the image

produced.²⁰⁹ The L_{PR} can be improved by reducing or eliminating C_s , improving microscope performance.

Small improvements in C_s were achieved first through use of better materials and pole piece design, but the real breakthrough was reached with the use of additional nonround, multipole lenses (a concept first discussed in 1947²²⁵), typically quadrupole, hexapole, or octupole lenses. These lenses generate a negative C_s value which essentially cancels out the positive C_s of the objective lens, eliminating C_s from equation (1.12). As a results, high angle rays are brought to the correct focus and the L_{PR} is extended.²⁰⁹ The advent of aberration correctors for the objective lens has dramatically improved attainable resolution limits, opening up new possibilities for material characterisation at the nano and atomic scales. Both TEM and STEM microscopes now routinely achieve resolution of 0.1 nm, or better.²²⁶

1.4.3 IL-TEM and *in-situ* electrochemical TEM

TEM imaging can reveal a wealth of high resolution information, with the caveat that only a very small area of the sample is being imaged and thus multiple images are often required to move towards a representative understanding of the whole sample. This is particularly key when TEM is used to monitor dynamic structural changes, which is typically performed by imaging prepared samples at different time intervals or stages throughout a process of interest. However, it does not enable the same structure or object to be followed. It is well known that minor changes in the morphology of nanostructures can result in significant effects on chemical and physical properties, for example electrocatalytic activity.²²⁷

Two methodologies have been developed to address this problem. The first is *in-situ* electrochemical TEM, first endeavoured in 1942²²⁸ but developed into a powerful technique in the 2000s,^{229,230} which has impacted greatly on the field on using TEM to study dynamic electrochemical processes. Use of *in-situ* liquid stages which allow investigation of dynamic electrochemical (EC) processes as they are occurring in real time.^{230,231} Known as *in-situ* liquid EC-TEM, this technique has been used to monitor structural evolution of varied electrode materials and interactions with electrolytes during operation. It is important to be able to distinguish electron beam effects from electrochemical processes at the electrolyte/electrode interface, as artifacts can be observed

due to interactions between the electron beam and the electrolyte fluid.²³² Due to the nature of imaging in *in-situ* liquid EC-TEM, whereby the electron beam passes through a liquid and thus scatters, the achievable resolution cannot compare to that possible when TEM imaging in a vacuum.

The liquid cells used for such experiments can be bought commercially^{232,233} or home built^{229,234} for the specific needs of the user; in many cases, commercial stages are adapted or customised by either the supplier or the user to tailor the cell setup to the desired experiment.^{235,236} Typically, the cell consists of two parallel electron beam transparent (ca. 50 nm thick) Si_xN_x windows with a small confined liquid chamber between them containing an anode, cathode, a counter electrode (CE) if required, and the electrolyte solution, sealed with O-rings or epoxy. The cell can either contain static electrolyte or operate as a microfluidic flow cell.^{229,232–236}

Many electrochemical processes have been investigated by *in-situ* liquid ec-TEM. Examples of this include the visualisation of nucleation and growth mechanisms of nanoscale Cu clusters during electrodeposition,²²⁹ and the observation of the electrodeposition and electropolishing of nanograined nickel from a NiCl₂ solution.²³⁴ Battery research has particularly benefited from the advent of *in-situ* liquid ec-TEM, as components can be studied under charge and discharge cycle conditions.²³³ Specifically, imaging lead deposition/stripping and quantification of local Pb²⁺ concentration has been achieved, with cell potential effect on nucleation, growth and dissolution mechanisms of lead dendrites also investigated.²³⁷ Studies have also been conducted focusing on the solid electrolyte interphase (SEI), visualising the lithiation/delithiation of silicon nanowires, gaining understanding of the fundamental mechanisms controlling SEI nucleation and growth, and monitoring the SEI microstructural and chemical evolution over time during operation.^{235,238}

The second, identical location (IL) TEM, is less well utilised but can provide significant insight without impairment in resolution. In IL-TEM the same sample is repeatedly imaged in the exact same location at ultra-high resolution, to provide snap shots of the dynamic process being investigated. For IL-TEM, the specimen is typically loaded onto a TEM grid with markers (e.g., grid coordinates) and the initial image captured. This grid is then be removed from the TEM for the specimen to undergo further treatment (e.g., electrochemical cycling, heating, exposure to air) whilst still on the grid. The grid is then put back into the TEM and the exact same region can be found and imaged again. This process can be repeated, as many times as necessary. IL-TEM can be incredibly useful to study morphological changes in many nanomaterials, particularly during electrochemical treatments.

One application where IL-TEM has found great use is in the study of electrocatalysts (typically Pt NPs on a C support) used in PEMFCs.²³⁹ Degradation of the Pt NPs and/or C support during use causes serious impairment of PEMFCs and can limit device lifetime. Understanding the causes and mechanisms of degradation and microstructural changes under operating conditions is vital to making improvements within the field. The reactivity of Pt-based catalysts can also be improved by changing size, morphology, and composition. The effect of the electrochemical activation (potential cycling) of Pt NPs on NP morphology has been studied by IL-TEM, with dramatic changes to morphology and NP migration to NP clusters revealed.^{240,241} IL-TEM has also been used to show Pt NP agglomeration at the high operating temperatures reached in PEMFCs.²⁴²

IL-TEM has also been used to provide atom-level insights into the early stages of gold nucleation and growth during electrodeposition. Electrochemically driven atom transport was observed, with cluster formation and finally progression to NPs through both gain and loss of neighbouring atoms.²³ Similarly, the electrochemical reduction of CO₂ into multicarbon alcohols on Cu dendrites was studied by IL-TEM to monitor the morphological changes of the Cu as Cu₂O and CuO phases were formed as the reaction progressed.²⁴³ Metal oxide anode degradation in lithium-ion batteries has also been investigated by IL-TEM.²⁴⁴

For IL-TEM experiments it is essential that the same region can easily be identified in subsequent imaging sessions. This is generally achieved by using 'finder'TM amorphous carbon coated TEM grids, which contain grid coordinates in the support frame that allow the user to locate a precise imaging area.^{240–242,244} The use of finder grids coated in a lacey or holey amorphous carbon support film, which contain irregularly shaped holes, can also be adopted to add more features that can be used to help find the same area on multiple occasions.²⁴⁵

1.5 Aims and objectives

This thesis aims to explore advances in both the growth and development of BDD based electrodes in two key application areas. In terms of growth, new HPHT methods are explored for the production of BDD particles suitable for electrochemical studies. In terms of application, the first area relates to EOP production using BDD electrodes and the second relates to the development of bi-functional electron beam transparent BDD electrodes for use as BDD EC-TEM supports.

Specifically, in chapter 3, the aim is to develop a novel HPHT synthesis route for the production of highly doped BDD MPs for use in electrochemical applications. By assessing both the inherent material properties, and also the electrochemical behaviour when moving to a compacted, porous electrode form, the potential for HPHT BDD electrodes to be used as an alternative to CVD grown BDD is demonstrated for the first time. Chapter 3 also highlights preliminary studies into reducing the size of BDD particles further by employing ball milling to produce BDD NPs. This work lays the groundwork for future investigations into unique electrode geometries and other applications, such as corrosion free fuel cell catalyst supports.

In Chapter 4, the role of sp² carbon in EOP production is elucidated. Moving away from incorporation of sp² carbon into the electrode by CVD, we instead focus on the use of laser micromachining as a method of sp² carbon incorporation into freestanding BDD. From this understanding the optimal EOP cell using fixed boron content CVD freestanding BDD electrodes is constructed. From the work in Chapter 3, the possibility of replacement of the CVD electrode with compacted HPHT electrodes is then explored, given the lower cost of such material when adopted at large scale. The implications for commercial use is also addressed.

In Chapter 5 procedures for the development of electron beam transparent freestanding BDD-TEM substrates are discussed. The advantages of such supports compared to amorphous carbon substrates are also highlighted and some of the possible application areas presented.

Finally, chapter 6 summarises and contextualises the work presented throughout this thesis and discusses areas for future study in this field.

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2 Experimental

2.1 Chemicals and solutions

All solutions used were prepared using Milli-Q ultrapure water with a resistivity of 18 M Ω cm at 25°C (Millipore Corporation). In chapter 4, EOP experiments were undertaken using a feedstock of deionised water with a resistivity of 15 M Ω cm (Veolia Water Technologies). All experiments were carried out at 25°C, unless otherwise stated. Chemicals were used as provided unless otherwise stated and weighed using a four figure analytical balance (Mettler Toledo). A list of the chemicals used throughout the thesis can be found in Table 2.1. Where multiple sources of the same chemical are listed, the experimental section of each results chapter details which source was used for specific experiments or procedures.

Chemical	Formula	Purity	Supplier
2-allylphenol	C ₉ H ₁₀ O	98%	Sigma Aldrich
2-n-butoxyethanol	C ₆ H ₁₄ O ₂	99%	Alfa Aesar
Ammonium hydroxide	NH₄OH	50%	Alfa Aesar
Hexaamineruthenium(III) chloride	Ru(NH ₃) ₆ Cl ₃	99%	Strem Chemicals
Hydrochloric acid	HCI	37%	Scientific and Chemical Supplies Ltd
Hydrochloric acid	HCI	37%	Sigma Aldrich
Hydrofluoric acid	HF	60%	Euro Lab Supplies Ltd
Manganese(II) chloride tetrahydrate	MnCl ₂	96%	Acros Organics
Methanol	MeOH	99%	Sigma Aldrich
Nitric acid	HNO ₃	70%	Scientific and Chemical Supplies Ltd
Phenol	C ₆ H₅OH	99%	Sigma Aldrich
Potassium chloride	KCI	99%	Sigma Aldrich
Potassium nitrate	KNO₃	99%	Scientific and Chemical Supplies Ltd
Potassium nitrate	KNO3	99%	Sigma Aldrich
Sulphuric acid	H ₂ SO ₄	97%	Scientific and Chemical Supplies Ltd
Sulphuric acid	H ₂ SO ₄	95%	Fischer Scientific

2.2 Boron doped diamond (BDD)

All the BDD used in thesis was provided by Element Six Ltd., Harwell, UK. Generally, electroanalysis grade BDD grown by MWCVD was used, which contains minimal sp² bonded carbon content, and contains ca. 3×10^{20} boron atoms cm⁻³, above the metallic threshold.¹ The BDD was grown to the desired thickness on a silicon wafer which is removed after growth to leave a freestanding BDD wafer. The growth face was then polished using the Scaife method to leave a ~nm roughness surface.² Where different processing to this was adopted, details are provided in the experimental section of each results chapter. Where HPHT BDD was used (chapters 3 and 4), this material was developed and produced at Element Six Ltd., as part of the research presented here, as detailed in chapter 3.

2.2.1 Laser micromachining

BDD electrodes were cut into desired geometries using a 355 nm Nd:YAG 34 ns laser micromachining system (E-355H-ATHI-0 system, Oxford Lasers, UK) at 100 % power, 20 kHz. The required shapes were drawn using Alphacam software (Vero Software, US) and exported as G-Code, a computer numerical control (CNC) programming language which instructs the laser system where to machine.

2.2.2 Acid cleaning

After laser micromachining, BDD electrodes were subjected to an oxidative acid cleaning treating.³ First, the BDD was boiled in concentrated H₂SO₄ supersaturated with KNO₃ (~0.75 g per ml), for 30 minutes. The solution was then left to cool to room temperature, before diluting the acid in room temperature water, disposing of this solution, and rinsing the BDD with water. Then, the BDD was boiled in concentrated H₂SO₄ only, for another 30 minutes, to ensure no residual KNO₃ was left on the surface. Again, this was then left to cool before diluting and decanting the acid, and thoroughly rinsing the BDD with water. Samples were then left to dry in air, ready for use/further processing. This acid cleaning procedure was adopted to ensure 1) that the resulting BDD surface is oxygen terminated and 2) removal of machining debris and sp² bonded amorphous carbon formed during the laser micromachining process.

2.2.3 Electrochemical contacting

To produce ohmic contacts on BDD electrodes, standard sputtering techniques were used. For polished BDD, the surface must first be roughened to improve adhesion. This was achieved using a 532 nm Nd:YAG laser micromachining system (A-Series, Oxford Lasers Ltd. UK) with a nominal pulse length of 15 ns and a fluence of ~20 J cm⁻¹. Layers of Ti and Au, 10 nm and 400 nm thick, respectively, were sputtered onto the roughened area using a magnetron sputtering system (MiniLab 060 Platform Sputter system, Moorfield, UK), at pressures below 1×10^{-5} mbar. After sputtering, the BDD was annealed in air at 400 °C for 5 hours to form titanium carbide which provides the ohmic contact to the BDD.⁴

2.3 Material characterisation

2.3.1 White light interferometry

White light interferometry (WLI) measurements were taken using a Bruker ContourGT (Bruker Nano Inc., USA) equipped with either a $\times 5$ or $\times 50$ objective lens. Data analysis and visualisation was performed, and surface roughness and depth profiles calculated, using Gwyddion 2.55.⁵ All surface roughness measurements presented were measured by WLI and are reported as root mean squared (RMS) values. RMS values were calculated using a 750 \times 750 µm region centred on each image, unless otherwise specified.

2.3.2 Raman spectroscopy

Raman measurements were performed using a Renishaw inVia Reflex Raman microscope with a 532 nm (2.33 eV) solid state laser, a laser power of 3.6 mW and a Leica N-Plan \times 50 objective with an NA of 0.75; giving a spot size of approximately 1 μ m, unless otherwise stated. The Raman spectrometer was turned on before use and left for 30 minutes to allow the CCD Detector to cool down and the laser to initialise. A silicon wafer was used to calibrate the system before measurements were recorded. Once calibrated, this wafer was removed and replaced with the sample of interest for data acquisition.

2.3.3 Electron microscopy

Throughout this thesis, several electron microscopy (EM) techniques were used to investigate the structure and composition of BDD surfaces. This includes FE-SEM, EDX, TEM, STEM, and EELS.

Where FE-SEM was used, images were recorded using the in-lens, SE2, and STEM detectors on a Zeiss Gemini FE-SEM 500 (Zeiss, Germany) operating at 3, 5, or 20 kV, as specified in chapters 3, 4, and 5. Working distances of 2-4, 7-9, and ~3.3 mm were adopted when the in-lens, SE2, and STEM detectors were used, respectively. In chapter 3, FE-SEM was used in combination with EDX. EDX measurements of BDD particles and compacts were recorded using the EDX unit (Oxford Instruments) attached to the microscope, and corresponding images taken using the SE2 detector, at a working distance of 8.5 mm with an accelerating voltage of 20 kV.

Both conventional TEM imaging (JEOL 2100, LaB₆ filament, JEOL, Japan) and STEM imaging (double aberration corrected JEOL ARM200F, Schotttky FE gun, JEOL, Japan) were utilised. Both microscopes were operated at an accelerating voltage of 200 kV. The JEOL ARM200F microscope was also equipped with a Gatan Quantum EELS spectrometer, for EELS data acquisition during STEM imaging. Image visualisation and analysis was carried out using Gatan's Digital Micrograph software. For some experiments, annular dark field (ADF) and high angle ADF (HAADF) imaging was carried out at the same time as the EELS mapping.

2.4 Electrochemical Characterisation

All electrochemical measurements were made using a commercial potentiostat, either an Ivium Compactstat potentiostat (Ivium Technologies, Netherlands) or a CHI potentiostat (600B, 760E, or 800B, CH Instruments Inc., US). Typically, CV (as described in section 1.1.2) was adopted with a standard three electrode setup where the WE, CE, and RE are dipped into a beaker containing electrolyte solution. Various BDD electrodes were used as the WE, with a Pt coil CE, and a SCE (CHI150, IJ Cambria Scientific) or a commercial Ag/AgCl as REs (DRIREF-2SH, saturated KCl, World Precision Instruments). All potentials are quoted with respect to the RE. The potentiostat is used to apply the desired potential at the WE, with respect to the RE, which is achieved by passing the current from the WE to the CE (see

section 1.1.1 for further details). For some experiments, where the nature and geometry of the BDD electrode did not lend itself to a dipped experiment, a three-electrode droplet cell setup⁶ (see section 3.2.5) was instead adopted.

2.4.1 Solvent window

The electrochemical solvent window reflects the potential range over which, for a given electrode material and electrolyte solution, the solvent is neither oxidised nor reduced. Solvent window measurements in this thesis were recorded in 0.1 M KNO3 at a scan rate of 0.1 V s⁻¹, typically over the potential range -2 V to +2 V. The potentiostat was used to sweep the potential from 0 V to -2 V and then between -2 V and + 2 V repeatedly, until a minimum of 3 full cycles were recorded. The first cycle was discarded, and the second CV converted to current density, considering the size and geometry of the active electrode area. Solvent windows are defined for a geometric current density of ± 0.4 mA cm⁻², unless stated otherwise. The presence of sp² bonded carbon on the BDD surface produces anodic peaks due to sp² bonded carbon oxidation, and cathodic peaks due to catalysing ORR which reduce the size of the solvent window.⁷ For high quality BDD electrodes, where the boron content is above the metallic threshold and minimal sp² bonded carbon is present, the solvent window measured in aqueous solutions is expected to be >3 V, with no additional peaks observed.8,9

2.4.2 Capacitance

The potential window was reduced significantly to probe the double layer capacitance of the electrode. It is important that this measurement is carried out over a potential range where no Faradaic processes are occurring. Capacitance measurements were recorded in 0.1 M KNO₃ at a scan rate of 0.1 V s^{-1} , typically over the potential range -0.01 V to + 0.01 V. The potentiostat was used to sweep the potential from 0 V to -0.01 V and then between -0.01 V and + 0.01 V repeatedly, until a minimum of 3 full cycles were recorded. Again, the first cycle was discarded, and the second CV used to estimate capacitance, C, using equation (2.1):
$$C = \frac{i_{av}}{vA} \tag{2.1}$$

where i_{av} is the average current magnitude at 0 V from the forward and reverse sweep, v is the scan rate (0.1 V s⁻¹), and A is the geometric electrode area.

2.4.3 Redox electrochemistry

The electrode response for the fast redox couple $Ru(NH_3)_{6}^{3+/2+}$ was also investigated by recording CVs of 1 mM $Ru(NH_3)_{6}Cl_3$ in 0.1 M KNO₃ at scan rates in the range 0.005 V s⁻¹ to 0.1 V s⁻¹. The potential was swept between +0.2 or +0.4 and -0.6 V. As discussed in section 1.1.2, for a single ET process at room temperature (298 K) the peak to peak separation, ΔE_p , should be 57 mV (=2.22*RT/F*), as predicted by classical theory.^{46,47} Ru(NH₃)₆Cl₃ was chosen as a mediator to investigate BDD material quality as it shows fast, outer sphere, electron transfer and is electroactive in a region which challenges p-type semiconducting BDD.

2.5 References

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3 Fabrication of heavily boron doped diamond micro- and nanoparticles for electrochemical applications

3.1 Introduction

Producing BDD in a powder (i.e., NPs or MPs) form reveals new possibilities for electrode fabrication which are not limited by electrode size or geometry.

BDD MPs are useful cost-effective building blocks for producing hierarchical 3D structures for a wide range of electrochemical applications requiring high surface areas, such as gas diffusion electrodes,¹ electrical double layer capacitors² *etc*. They are also a suitable precursor for processing down to the NP size.^{3,4}

BDD NPs could find use in PEMFC applications, where corrosion is a concern for other carbon based materials, and in screen printed devices, where low background currents and fouling resistance is desired. Encouraging preliminary studies for both of these applications have been undertaken,^{4–8} making use of CVD grown BDD, which is effective but unfeasible for high volume production. BDD NPs can be produced through mechanical milling of CVD grown BDD films, and current work in this area chiefly adopts this preparation method.⁹

Alternatively, HPHT synthesis¹⁰ with metal catalysts offers a lower cost, significantly higher volume alternative to the CVD approach, producing large volumes of micron to sub-mm diamond particles.¹¹ However, achieving homogenous boron doping at the levels required for metallic conductivity whilst retaining a well-defined crystallography is challenging in HPHT synthesis, as discussed in section 1.2.2. Of the limited research on the HPHT synthesis of BDD particles,^{12–19} the use of HPHT BDD as an electrode material has yet to be exhibited. Currently no published research describes the use of HPHT BDD particle based electrodes.

In this work, we determine HPHT experimental conditions which result in the synthesis of: (i) well-defined BDD MPs, with (ii) sufficiently high, uncompensated, boron levels which enables use as an electrode material, and (iii) use of the lowest P and T conditions to-date for similar materials.^{12–19} We

assess the material and electrochemical properties at both the single particle level and in compacted-particle, porous electrode form. To investigate compact electrode and porosity effects, scanning electrochemical cell microscopy (SECCM) was employed.²⁰ Preliminary studies have also been undertaken in mechanically milling, using a ball mill, CVD grown BDD wafers down to the NP size.

3.2 Experimental

3.2.1 Reagents and materials

HPHT BDD material was produced from graphite powder (S9, Morgan Advance Materials), carbonyl iron powder (Fe >99.5 CIP CN, BASF), carbonyl nickel powder (Ni >99.85%, type 123, Vale), AlB₂ (grade A, H. C. Starck), and US Mesh 100 diamond seed (1.60-1.77 μ m diameter, polycrystalline diamond micron grade 2, Element Six Ltd). CircuitWorks conductive silver epoxy (Chemtronics) was employed to fix HPHT compacts to Ti/Au coated glass slides for electrochemical characterization.

3.2.2 HPHT material preparation

10 g of a 'mastermix' was prepared containing 5 g of graphite powder (50 wt%), 3.5 g of iron powder (35 wt%), 1.5 g of nickel powder (15 wt%), and 0.002 g of diamond seed. A single steel ball (10 mm diameter) was added to the mastermix and the pot mixed for 30 minutes with a turbulent mixer. 1 kg batches of undoped powder were then prepared containing 500 g of graphite (50 wt%), 350 g of iron (35 wt%), 150 g of nickel (15 wt%), and 1.525 g of 'mastermix' (0.305 mg of diamond seed per kg). 200 g of steel balls (10 mm diameter) were added (1:5 mass ratio of steel balls to powder) and mixed for 3 hours using a cone blender. This ratio of metal powders was chosen as this is close to the eutectic ratio for a Fe/Ni/C system and thus allows synthesis at the lowest possible P/T conditions, whilst providing a wide P/T operating range. The undoped powder was then mixed with AlB₂, using two different concentrations of AlB₂ expressed as weight % (Table 3.1). Concentrations of AlB₂ were chosen to ensure an excess of B was available during growth i.e., to produce BDD with >10²⁰ B atoms cm⁻³ required for metal-like conductivity.

AIB ₂ (wt%)	AIB ₂ (g)	Undoped powder mix (g)	Total mass (g)
3.6	19.8	530.2	550
4.8	26.4	523.6	550

Table 3.1: Composition of boron containing powder mixes.

Steel balls (10 mm diameter, 1:5 ball to powder ratio) were added to these powders which were then mixed for 1 hour using a cone blender. The boron containing powder mixtures were sieved to remove the balls, compacted into cylinders (18 g per cylinder) and heated to 1050 °C under vacuum to remove oxygen and hydrogen impurities. Synthesis was then carried out at as low as possible P/T conditions, here ca. 5.5 GPa and 1300 °C in a cubic anvil HPHT apparatus.²¹

To remove residual metals, unreacted graphite and sp² bonded carbon formed on the BDD surface, the following cleaning treatment was applied. Specifically, two cylinders were first crushed into small pieces using a Weber press operating at 100 kN. The crushed particles were then heated at 250 °C in HCl (37-38%, 2.0 L) for 22 hours. When cool, the solution was decanted through an 80 µm sieve to remove any smaller graphitic residue, and the acid discarded. This process imposes a minimum size of 80 µm in the final particle size distribution. The remaining solids were then subjected to three rinses with deionised water and the BDD particles then boiled at 250 °C in a 3:1 mix of H₂SO₄ and HNO₃ (95-97%, 1.5 L and 68-70%, 0.5 L, respectively) for 22 hours. The solution was again decanted through an 80 µm sieve, the acid discarded, and the remaining solids rinsed three times with deionised water. The BDD particles were added to H₂SO₄ (95-97%, 0.5 L) and the solution heated to 300 °C. Once boiling, approximately 10 g of KNO₃ crystals were added and the solution left for an additional 30 minutes. Once cool, the solution was sieved and washed as previously. Finally, the BDD particles were added to 100 mL of deionised water in a beaker and placed in an ultrasonic bath (Branson 5510) for 20 minutes to remove any residual graphite. After this time, the wastewater was carefully decanted, and the process repeated until the water remained colourless after ultrasonication. This water was also decanted and the BDD particles left to dry overnight in a 60 °C oven.

To produce HPHT BDD compacted electrodes, herein referred to as "compacts" approximately 2 g of BDD particles were compacted at around 6.6

GPa and 1700 °C in a cubic anvil HPHT apparatus to produce BDD discs. Each compact was treated for 24 hours in a mixture of 50 mL HF (60%) and 50 mL HNO₃ (68-70%) to release the compacts from the capsule residue. In the absence of metal, at these temperatures, a small degree of BDD to graphite conversion is expected during HPHT compaction. Graphite formation will be prominent in areas where the pressure experienced by the BDD is lower than the nominal applied pressure, due to the microstructure of the compact.²²A surface de-graphitization treatment was applied by annealing for 5 hours at 450 °C in air,²³ before polishing one side of each compact to leave a smooth surface, rms roughness ca. 100-200 nm (measured by WLI, Bruker ContourGT). Polishing was achieved using a resin-bonded scaife, embedded with diamond grit particles, whilst rotating and translating the compacts to ensure multidirectional polishing of the surface.

All characterization was carried out on the polished side of the compact, which had a diameter of approximately 16 mm and a thickness of 2 mm. To carry out electrochemical characterization, a titanium (Ti:10 nm) /gold (Au:400 nm) contact was sputtered (Moorfield MiniLab 060 Platform Sputter system) on the unpolished side and annealed in air (400 °C for 5 hours) to create an ohmic contact.²⁴ Each compact was then placed on a Ti/Au coated glass slide with CircuitWorks conductive silver epoxy (Chemtronics) in contact with both the slide and the Ti/Au contact and left to dry in a 60 °C oven for at least one hour.

Electrodes were also fabricated from single BDD particles (4.8 wt% AlB₂ only). Metal contacts were sputtered onto one end of an individual BDD particle by embedding the particle into silicone WF Gel-Film (Gel-Pak), exposing a single face to the sputter target. Particles were removed from the Gel-Film after sputtering and then annealed as described above. CircuitWorks conductive silver epoxy (Chemtronics) was used to adhere individual particles to lengths of PVC insulated copper wire (RS Components) which had been polished with silicon carbide pads (Buehler) to a point. These were left to dry in an oven (60 °C) for at least one hour. These assemblies were then sealed using epoxy resin (Epoxy Resin RX771C/NC, Aradur Hardener HY1300GB, Robnor Resins), and dried at room temperature for 72 hours. After drying, excess epoxy was removed by carefully polishing with silicon carbide pads (Buehler) of decreasing roughness until the BDD particle was exposed to produce a single particle electrode (SPE).

3.2.3 CVD nanoparticle preparation

A film of freestanding CVD grown BDD of ~130 μ m thickness (2×10²⁰ - 5×10²¹ B atoms cm⁻³, Oliver Williams, Cardiff, Seki AX6500 series MPCVD), weighing 0.8354 g was broken by hand and split approximately into half to be milled into BDD NPs using two different milling ball materials: tempered steel and silicon nitride (Si₃N₄). The milling procedure for each half of the film was the same but with different milling balls used in each instance. The pieces of BDD film were placed into an 80 mL grinding bowl of a PULVERISTTE 7 premium line Planetary Micro Mill with 5 mL of deionised water, ~0.4 g BDD, and either 40 g of tempered steel milling balls (3 mm diameter) or 17 g of Si₃N₄ milling balls (3 mm diameter). The material of the grinding bowl was the same as the material of the milling balls used in each experiment. Different masses of milling balls were used in line with manufacturer instructions. Each sample was treated for 60 minutes at 11,000 rpm (revolutions per minute), which corresponds to a relative centrifugal force (RCF) of 95 g, comprised of 3 continuous cycles of milling for 5 minutes followed by a 15 minute rest period to prevent overheating. The resulting powder was flushed out with deionised water and left on a 60 °C hotplate to evaporate the water, leaving a dry powder of BDD NPs.

The BDD NPs were then washed to remove impurities that have been introduced by the milling process. The Si_3N_4 milled NPs were heated under reflux at 140 °C in 30 mL of 100% phosphoric acid for 24 hours. After cooling to room temperature, the acid was removed from the solution by several cycles of centrifugation and washing. Each centrifuge cycle was carried out for 15 minutes at 20,000 g using a Sigma 3-30KS centrifuge. The supernatant was then decanted and discarded and replaced with deionised water. This process was repeated until a pH of above 6 was reached. The tempered steel milled NPs were added to 30 mL of aqua regia and heated under reflux at 190 °C for 24 hours. The solution was then diluted fourfold with deionised water before the washing/centrifugation cycles were carried out in the same way as the Si_3N_4 milled NPs to remove the acid. Following the washing, both samples were left on a 60 °C hotplate to evaporate the water, and the dry BDD NPs collected. 0.1864 g of tempered steel milled BDD NPs, and 1.7907 g of Si_3N_4 milled BDD NPs were obtained.

A preliminary study was also undertaken to assess the suitability of facilities available at the University of Warwick to carry out the BDD NP preparation procedure; samples were milled at either Cardiff or Warwick, and then acid washed by centrifugation at either Cardiff or Warwick. For these experiments, freestanding CVD grown BDD of ~150 μ m thickness was provided by Element Six (>10²⁰ B atoms cm⁻³). The same general procedure was followed with the following modifications.

After breaking the BDD film by hand, the pieces were reduced further in size using an agate pestle and mortar, before passing through a 200 μ m sieve to ensure a constant size of BDD feedstock. This step was introduced to eliminate any potential effect of feedstock size on milling outcome. At Warwick, a Retsch PM 100 mill was used with a 25 mL stainless steel comfort grinding jar (Retsch), 10 mL of deionised water, ~0.5 g BDD film, and 50 g of stainless steel milling balls (3 mm diameter, Retsch). These samples were milled for 20 minutes at 650 rpm, which corresponds to a RCF of 33 g, comprised of 4 continuous cycles of milling for 5 minutes followed by a 15-minute rest period to prevent overheating. At Cardiff, total milling time was reduced to 20 minutes and the volume of water used during milling increased to 10 mL. For samples acid washed at Warwick, a Sigma 4-15 centrifuge was used, adopting cycles of 15 minutes at 17,120 g.

For inductively coupled plasma (ICP) based techniques employed to investigate potential Si (for Si₃N₄ milling) and Fe (for tempered steel milling) contamination introduced during milling, 5 mg of each BDD powder was added to 10 mL of 72% nitric acid in deionised water and placed in an ultrasonic bath for 20 minutes to solubilise any impurities present. These solutions were then diluted with deionised water to 4% total acid content. The final solutions were filtered through a 0.2 μ m filter to remove large particles which can disrupt particle flow and block sample tips within the spray chamber.²⁵

For TEM imaging, 1 mg of each BDD powder was added to 5 mL of ethanol. These solutions were then placed in an ultrasonic bath for 20 minutes to disperse the NPs. Next, 1 mL of each solution was centrifuged at 3000 rpm for 2 minutes in an Eppendorf MiniSpin to remove any large particles or agglomerates. 5 μ L of each solution was dropped onto a carbon film coated copper 200 mesh TEM grid (Agar Scientific, UK), and the grids left to dry

under a lamp. After 1 hour, another 5 μ L of solution was dropped onto the same grids and again left to dry. This step was repeated a further 3 times. The grids were then left to dry under a lamp for 24 hours before imaging.

Dynamic light scattering (DLS) samples were prepared at 2 mg ml⁻¹, unless otherwise stated, and placed in an ultrasonic bath for 20 minutes to disperse the NPs. These solutions were centrifuged for 15 minutes at 10,000 g using a Sigma 3-30KS centrifuge and then filtered through a 200 nm filter to remove any large particles or agglomerates. For NP tracking analysis (NTA) measurements, these samples were diluted tenfold with deionised water.

3.2.4 Material characterisation

(i) Raman spectroscopy measurements were performed using a Renishaw inVia Reflex Raman microscope with a 532 nm (2.33 eV) solid state laser, a laser power of 3.6 mW and a Leica N-Plan ×50 objective with an NA of 0.75; giving a spot size of approximately 1 µm. (ii) FE-SEM images of the BDD MPs and compacts were taken using the SE2 and InLens secondary electron detectors of a Zeiss Gemini FE-SEM 500 (Zeiss, Germany) operating at 5 kV and 3 kV, respectively. EDX measurements of the BDD particles and compacts were recorded using the EDX unit (Oxford Instruments) attached to the microscope, and corresponding images taken using the SE2 detector, at a working distance of 8.5 mm with an accelerating voltage of 20 kV. (iii) Inert fusion infrared and thermal conductivity detection (ON736 gas Oxygen/Nitrogen Elemental Analyzer; LECO Corporation, Michigan, USA) was used to determine the nitrogen content of the particles. (iv) Glow discharge mass spectrometry (GDMS; Evans Analytical Group SAS, Tournefeuille, France) was utilized to characterize the boron content of the HPHT BDD particles. (v) Secondary ion mass spectrometry (SIMS; Loughborough Surface Analysis Limited, Loughborough, UK) was employed to characterize the boron content of the compact disks. (vi) Four point probe measurements were recorded (Jandel RM300) using 100 µm probes arranged in a linear array with 1 mm spacing between probes to determine compact resistivity. (vii) ICP mass spectrometry and optical emission spectrometry (ICP-MS and ICP-OES, respectively) of the BDD NPs. ICP-MS measurements were taken with an Agilent LC-ICP-MS 7500cx using SCP28 standards (0, 50, 100, 250, 500, 1000, and 2500 ppb), ICP-OES measurements were taken with a PerkinElmer 5300DV ICP-OES using Agilent multiple element calibrations standards (0, 50, 100, 250, 500, 1000, and 2500 ppb). (viii) TEM images of the BDD NPs were recorded using a JEOL 2100 (LaB₆ filament; JEOL, Japan) microscope operated at 200 keV. (ix) DLS measurements were taken using a Malvern Zetasizer Nano ZS. (x) NTA measurements were taken using a Malvern NanoSight LM10.

3.2.5 Electrochemical characterization

CV was carried out using a potentiostat (CHInstruments 600B, 760E, or 800B). A three-electrode droplet cell setup²⁶ (Figure 3.1) was used with the BDD compact as the WE, a platinum coil as the CE and a SCE (CHI150, IJ Cambria Scientific) or a commercial Ag/AgCl as RE (DRIREF-2SH, saturated KCl, World Precision Instruments). All potentials are quoted with respect to the RE. All BDD electrodes were oxygen-terminated due to the cleaning procedures adopted prior to use. Each measurement was recorded for a 1 mm diameter circular area of the surface, achieved by masking with a piece of Kapton tape containing a 1 mm diameter circular hole, cut using a laser (A Series 532 nm Nd:YAG 15 ns pulse green laser, Oxford Lasers Ltd. UK). A droplet of the electrolyte solution ($\sim 100 \mu$ L) was placed on the electrode surface. The platinum CE was positioned as far away as possible from the electrode surface (ca. 5 mm) in the droplet cell set-up, sufficient to prevent CE electrolysis products interfering with the BDD electrochemical response on the measurement timescale. Before measurements, the surface of each BDD compact was electrochemically cleaned by running CVs between -2.0 V and



Figure 3.1: Schematic showing the three-electrode droplet cell set-up for electrochemical characterisation of the HPHT BDD compact electrode.

+0.2 V in 0.1 M H₂SO₄. A standard three-electrode cell set-up was used with the single particle BDD electrodes, with a platinum coil CE and a SCE RE.

Solvent window and capacitance measurements were run in 0.1 M KNO₃ at a scan rate of 0.1 V s⁻¹. Solvent windows are defined for a geometric current density of \pm 8.5 mA cm⁻² for compacts and \pm 2.0 mA cm⁻² for SPEs. Limits were chosen where water electrolysis first becomes evident above the background current measured. The electrode response for the fast redox couple Ru(NH₃)₆^{3+/2+} was also investigated by recording CVs of either 1 mM or 10 mM Ru(NH₃)₆ Cl₃, in 0.1 M KNO₃ electrolyte, at scan rates in the range 0.005 V s⁻¹ to 0.1 V s⁻¹. The BDD compact and BDD SPE, Pt CE, and Ag/AgCl RE were rinsed between different solution measurements.

For SECCM measurements to detect differences in local wetting across the compact electrode, nanopipettes were pulled from borosilicate glass single barrel capillaries (1 mm o.d., 0.5 mm i.d., Harvard Apparatus) using a Sutter P-2000 laser puller (Sutter Instruments, USA). After pulling, the inner diameter of the end of the nanopipettes were ca. 1 μ m. The outer walls were silanized by dipping the nanopipette in dichlorodimethylsilane (>99% purity, Acros), while flowing argon through to ensure the inside walls were not silanized. This treatment minimized solution spreading from the pipet onto the sample surface during SECCM measurements (*vide infra*).²⁷ The nanopipette was filled with solution containing 10 mM Ru(NH₃)₆Cl₃ and 10 mM KNO₃ and an AgCl-coated Ag wire quasi-reference-counter electrode (QRCE) inserted into the back of the nanopipette. A relatively low concentration of supporting electrolyte was used to prevent KNO₃ crystallization during measurements. The experimental setup is shown in

Figure **3.2**. A hopping mode was employed,²⁸ whereby the nanopipette was used to make a series of discrete voltammetric measurements across a 300 × 300 μ m area (pixel separation or 'hopping distance' of 5 μ m) of the HPHT BDD compact (4.8 wt% AlB₂) surface (WE). The uncompensated tip resistance under these conditions was determined to be 15 M Ω from an *I-V* curve measurement.²⁹ As discussed below, the resulting ohmic drop was relatively small, given the small currents measured. The potential applied to the QRCE was swept from +1 V to -1 V, then back to +1 V at a scan rate of 10 V s⁻¹, and the current at the surface was recorded. All data analysis was performed using Matlab (R2014b, Mathworks).



Figure 3.2: Schematic showing the SECCM experimental set-up used to measure the local electrochemical response of a HPHT BDD compact electrode, grown using 4.8 wt% AlB₂. A scan rate of 10 V s⁻¹ was used for the CVs recorded at each pixel location (n = 400, indicated by blue circles). The potential is applied to the Ag/AgCl QRCE in the nanopipette, with respect to the compact working electrode (grounded) and the current measured at the compact surface. The coloured surface represents an EBSD map of BDD crystallographic orientation.

A high quality CVD grown metal-like doped polycrystalline BDD electrode (350 µm thick, negligible sp² bonded carbon content, grown by a commercial microwave CVD process by Element Six Ltd, UK, mechanically polished to sub-nm surface roughness)³⁰ was used as a control. The crystal orientation of the compact surface for the SECCM scanned area was determined by electron backscatter diffraction (EBSD) using a Zeiss Sigma FE-SEM (Zeiss, Germany) equipped with a Nordlys EBSD detector (Oxford Instruments, UK).

In order to confirm porosity of the intrinsic material, the polished surface of a HPHT BDD compact was electrochemically coated with a thin, uniform, pinhole free, insulating film of poly(oxyphenylene),³¹ and the electrochemical response observed. This was achieved by the electropolymerisation of a freshly made solution containing 60 mM phenol, 90 mM 2-allyphenol, and 160 mM 2-n-butoxyethanol in water/methanol (1:1 by volume).³¹ The pH of the

monomer solution was adjusted by the addition of ammonium hydroxide, dropwise, until a pH of 9.2 was reached. A voltage of +2.5 V against a silver wire QRCE was applied for 20 minutes. After deposition, the surface was rinsed in 1:1 water/methanol, and the copolymer film heat cured for 30 minutes at 150 °C. To remove the polymer coating, the HPHT BDD compact surface was gently polished using alumina micropolish (0.05 μ m, Buehler) with a cotton bud, before rinsing with distilled water (Figure 3.3).



Figure 3.3: Cross sectional schematic to show the process of void (pore) filling a HPHT BDD compact by electrodeposition of a poly(oxyphenylene) film. The yellow colour represents the voids, and the blue represents the insulating polymer. During polishing the top surface of the compact is revealed.

3.3 Results and discussion

3.3.1 HPHT microparticles

As described in section 3.2.2, HPHT synthesis methods were used to produce both BDD MPs and BDD MP composite porous electrodes, suitable for electrochemical applications. Thorough material and electrochemical characterisation was carried out for the HPHT BDD in both particle and composite electrode form.

3.3.1.1 Material characterisation

FE-SEM was employed to investigate the morphology and size of the BDD particles produced via HPHT. To the best of our knowledge, this is the first time crystallographically well-defined HPHT single crystals, which contain BDD at sufficiently high doping levels for electrochemistry, have been observed, as shown in Figure 3.4 a and Figure 3.4 b, for 3.6 wt% and 4.8 wt% AlBr₂, respectively. From the FE-SEM images recorded (n = 3), the growth process resulted in HPHT BDD particles of sizes 80 - 190 µm (3.6% AlB₂) and 80-180 µm (4.8% AlB₂). 80 µm was a minimum size imposed by the sieving process employed during particle recovery (see section 3.2.2). The crystals are

typically octahedral in shape with the triangular {111} face dominant (Figure 3.4 a, pink arrow). This is result of a difference in growth rate between crystal faces, where {111} < {100}, and is explained by the bald point model (Figure 3.5).¹⁵



Figure 3.4: FE-SEM images showing morphology of HPHT BDD particles made with a) 3.6 wt% AlB₂ b) 4.8 wt% AlB₂.



Figure 3.5: Schematic to show the dangling bonds present when boron (blue) is substituted for carbon (black) on the {111} and {100} growth faces of diamond. Image generated using Avogadro (version 1.2.0).³²

On the {111} diamond face, each carbon atom forms bonds with three neighbouring carbon atoms, leaving a single dangling bond through which the crystal extends during growth. Conversely, on the {100} diamond face, each carbon atom forms bonds with two neighbouring carbon atoms, leaving two dangling bonds through which the crystal extends during growth. In metallic doped BDD, boron atoms substitute ~1 in 1000 carbon atoms. As boron only has three valence electrons (as opposed to carbon's four) when a boron atom sits in place of a carbon atom on the {111} face, there is no dangling bond for carbon atoms to bond to (Figure 3.5) and so no further growth can occur from

this point, leaving bald-points on the $\{111\}$ surface. However, when a boron atom sits in place of a carbon atom on the $\{100\}$ face, there is a single dangling bond for carbon atoms to bond to (Figure 3.5), and thus crystal growth continues.¹⁵

Defects on the surfaces of the crystal faces were observed for both boron concentrations (Figure 3.6).¹⁵ Similar types and density of defects were observed, regardless of boron concentration, these included small holes and triangular features (green circles), the latter observed predominantly on the {111} face, Figure 3.6 a. Other more irregularly shaped pits (blue rectangles), Figure 3.6 a, were also noted, although in some locations these could be the result of closely spaced triangular pits. Triangular etch pits are expected on {111} faces.^{33,34} Some deformation from perfect crystallinity was observed, particularly evident at the corners of the individual crystals (Figure 3.6 b, see also Figure 3.4 a and b) along with small crystallite nucleation and growth on the faces of the larger crystals, typically at defect sites (red arrow, Figure 3.6 b).³⁵



Figure 3.6: FE-SEM images surface defects of HPHT BDD particles made with a) 3.6 wt% AlB₂ (close up of {111} face) and b) 4.8 wt% AlB₂. Red arrows indicate surface nucleation. Green circles and blue rectangles indicate triangular pits and irregularly shaped holes, respectively.

EDX measurements indicated that the surfaces of the particles were also free from residual Fe and Ni catalytic metallic impurities (Figure 3.7), although it is possible Fe and Ni may still be present in small quantities as internal inclusions buried within the particles. However, these will not affect electrochemical properties as electrochemical processes occur only at the electrode-electrolyte interface. The EDX spectra shown in Figure 3.7 clearly shows a very strong peak for carbon and a small peak for boron, as is expected for BDD. Signals for Fe, Ni, Co, and Al (potential contaminants) are not present. This is also shown in the EDX maps, whereby carbon and boron signals strongly correlate with BDD particle location, and Fe, Ni, Co, and Al signals are negligible.

FE-SEM images were also taken of the polished surface of the HPHT BDD MP compacted "compact" electrodes (Figure 3.8). In polycrystalline CVD grown BDD, differences in SEM contrast between grains has been observed due to varying levels of boron uptake in different crystallographic faces.³⁶ In Figure 3.8 a and b, the black regions represent voids between compressed particles, as no binder is present during compaction to fill these gaps. Metal binders, such as Co and Ni,³⁷ are deliberately excluded here to avoid metallic interferences to the electrochemical response.



Figure 3.7: a) EDX spectrum of HPHT BDD particles grown using 4.8 wt% AlB₂, with the EDX measurement area outlined in white in inset FE-SEM image. b) Elemental EDX maps of area shown in a) for C, B, Fe, Ni, Co and Al.



Figure 3.8: FE-SEM images showing surface structure of the polished compact electrodes produced from HPHT BDD particles synthesized using a) 3.6 wt% AlB₂ and b) 4.8 wt% AlB₂.

Importantly, within and between particles the contrast varies minimally suggesting homogenous boron doping throughout, not unexpected given the prevalence of octahedral {111 faces}. Between the large, clearly distinguishable particles are poorly defined areas consisting of much smaller particles. During compaction, some of the larger particles will fracture and fill appropriately sized gaps between particles. A greater extent of connection, with fewer and smaller holes between particles was observed for the 4.8 wt% AlB₂ additive (Figure 3.8 a) compared to 3.6 wt% AlB₂ (Figure 3.8 b) where BDD particles appear more isolated and distinct. Tentatively this could suggest that the higher doped BDD particles fracture more easily under the high pressures applied, producing the smaller fragments/particles required to fill the gaps.

To provide information on boron doping levels, Raman spectra were taken of the two differently boron doped compacts (Figure 3.9) and compared to the spectrum obtained for an HPHT single diamond crystal (contains nitrogen at doping levels typically 200 - 300 ppm;³⁸ ca. $3 - 6 \times 10^{19}$ N atoms cm⁻³). The presence of boron in the diamond lattice is confirmed by peaks at ~550 cm⁻¹ and ~1200 cm⁻¹, a signature of highly doped BDD and not observed in the diamond crystal.³⁹ The 550 cm⁻¹ peak has been attributed to the local vibration modes of boron pairs within the lattice.⁴⁰ The broad 1200 cm⁻¹ band corresponds to a maximum in the phonon density of states which arises from the disorder introduced by boron doping.⁴¹



Figure 3.9: Raman spectra of (a) HPHT diamond, and HPHT BDD compacts at (b) 3.6 wt% and (c) $4.8 \text{ wt\%} \text{ AlB}_2$ additive. BDD peaks observed at 550 cm⁻¹ and 1200 cm⁻¹, along with an asymmetry due to Fano resonance and redshift in the intrinsic diamond peak at 1330.83 cm⁻¹ (3.6 wt% AlB₂) and at 1329.15 cm⁻¹ ($4.8 \text{ wt\%} \text{ AlB}_2$).

The BDD Raman line is also red-shifted slightly relative to the diamond line (1332.5 cm⁻¹; Figure 3.9 a), occurring at 1330.83 cm⁻¹ and 1329.15 cm⁻¹ for 3.6 wt% AlB₂ and 4.8 wt% AlB₂, respectively. This shift is due to boron impurity scattering which causes a tensile residual stress.⁴² The larger magnitude shift is observed for the 4.8 wt% AlB₂ compact, indicating a higher boron doping level than for the 3.6 wt% AlB₂ compact, as expected. A slight asymmetry of this peak is also observed due to a Fano resonance,⁴³ indicative of metal-like conductivity.⁴⁴ No graphite peaks are present (the *G* and *D* peaks lie at ca. 1560 cm⁻¹ and 1360 cm⁻¹ respectively)⁴⁵ indicating removal of any sp² bonded carbon impurities introduced either during growth or the compaction process, within the resolution of the measurement.

Raman spectra for the individual HPHT BDD particles were also obtained (Figure 3.10) and the same key features observed. As the Raman spot size (ca. 1 μ m) was significantly smaller than the size of a particle, spectra can be recorded on individual particles. No significant difference was seen between particles. This again is supportive of the observation that the vast majority of particles grown are of the same crystallographic orientation.



Figure 3.10: Typical Raman spectra recorded on an individual HPHT BDD particle grown using (a) 3.6% AlBr₂ and (b) 4.8% AlB₂. BDD peaks are observed at 550 cm⁻¹ and 1200 cm⁻¹, along with an asymmetry due to a Fano resonance and red shift in the intrinsic diamond peak at 1330.8 cm⁻¹ (3.6% AlB₂) and at 1329.2 cm⁻¹ (4.8% AlB₂).

SIMS and GDMS analysis of the two differently boron doped compacts are given in Table 3.2 and provide information on the total boron and nitrogen dopant levels. Both compacts are above 10^{20} B atoms cm⁻³,⁴⁶ with higher [B_{total}] for the larger wt% of AlB₂ added. With no concern for nitrogen doping these would be indicative of suitable boron dopant levels for metal-like conductivity. However, in HPHT growth nitrogen doping must also be considered. The measured nitrogen content was found to be more than one order of magnitude lower than the boron content (Table 3.2). The data indicates nitrogen compensation effects will not be significant, also concluded from the Raman data in Figure 3.9 and Figure 3.10, which show BDD peaks with accompanying Fano resonances.

Table 3.2: [B_{total}] from glow discharge and secondary ion mass spectrometry (GDMS and SIMS, respectively), [N_{total}] from LECO nitrogen elemental analysis.

AIB ₂ (wt%)	[B _{total}] from GDMS (atoms cm ⁻³)	[B _{total}] from SIMS (atoms cm ⁻³)	[N _{total}] (atoms cm ⁻³)
3.6	$2.0 \pm 0.4 \times 10^{20}$	$1.3 \pm 0.1 \times 10^{20}$	$7.7 \pm 0.4 \times 10^{18}$
4.8	$2.9 \pm 0.6 \times 10^{20}$	$1.9 \pm 0.1 \times 10^{20}$	$4.2 \pm 0.1 \times 10^{18}$

3.3.1.2 Macroscopic electrochemical measurements

Electrochemical characterization of the polished surface of the two differently doped BDD compacts was performed. Data for the 3.6 wt% AlB₂ compact are shown in blue, and data for the 4.8 wt% AlB₂ compact are shown in red, Figure 3.11. The solvent windows, for each material (Figure 3.11 a) in 0.1 M KNO₃ at 0.1 V s⁻¹, were wide and featureless, with values of 2.64 V and 2.95 V for 3.6

wt% AlB₂ and 4.8 wt% AlB₂ (for a given geometric current density of \pm 8.5 mA cm⁻²) respectively. To calculate the electrochemical capacitance, C, the voltage window was decreased to 0 V \pm 0.1 V (Figure 3.11 b) and equation (3.1) was used:

$$C = \frac{i_{av}}{vA} \tag{3.1}$$

where i_{av} is the average current magnitude at 0 V from the forward and reverse sweep, v is the scan rate (0.1 V s⁻¹), and A is the geometric electrode area. The sloping response of the CV in Figure 3.11 b indicates both a significant resistive contribution, as well as a capacitive component.



Figure 3.11: CVs recorded in 0.1 M KNO₃ at a scan rate of 0.1 V s⁻¹ at the polished HPHT BDD compacts with 3.6 wt% AlB₂ (blue) and 4.8 wt% AlB₂ (red). Shown are (a) solvent windows, (b) typical capacitance curves recorded to calculate capacitance, and electrode response in (c) 1 mM and (d) 10 mM $Ru(NH_3)_6^{3+/2+}$.

For polished CVD-grown BDD a C of $\leq 10 \ \mu\text{F} \text{ cm}^{-2}$ is typical.³⁰ The C values for the compact electrode are almost three orders of magnitude larger, 3.1 mF cm⁻² for 3.6 wt% AlB₂ and 2.6 mF cm⁻² for 4.8 wt% AlB₂. In accordance with the FE-SEM images in Figure 3.8, this suggests that there is an almost three orders of magnitude larger electrochemically accessible surface area, due to the porosity of the compact. For some electrochemical applications, e.g., electrochemical supercapacitors, high specific capacitance materials are desired;^{47,48} although not the focus this could be explored in the future.

Four-point probe measurements of sheet resistance, R_s , were recorded to calculate the resistivity, ρ , of two HPHT BDD compact electrodes, one grown using 3.6 wt% AlB₂ and the other 4.8 wt% AlB₂, taking into account electrode geometry. Four measurements were taken per compact, two in the forward direction and two in the reverse direction. ρ was calculated for each measurement using equation (3.2):

$$\rho = R_s t f_1 \tag{3.2}$$

where *t* is the compact thickness and f_1 is a finite thickness correction factor, given in Table 3.3 where *s* is the spacing between probes.^{49,50} The average of these four ρ values were taken to give 959 ± 96 m Ω cm and 646 ± 129 m Ω cm for 3.6 wt% AlB₂ and 4.8 wt% AlB₂, respectively. The resistance of the compacts, *R*, when operated as an electrode, was calculated using the equation for the resistance of a truncated cone, equation (3.3):

$$R = \frac{\rho L}{ab} \tag{3.3}$$

where, *L* is the length of the cone, and *a* and *b* are dimensions depicted in Figure 3.12. In this case, *a* is the radius of the exposed top surface of the compact electrode (a = 0.5 mm), *b* is the radius of the bottom surface of the compact electrode and *L* is the thickness of the compact. Again, four values were calculated for each compact and the average taken to give 0.48 ± 0.06 Ω and 0.27 ± 0.03 Ω for the two compacts, 3.6 wt% AlB₂ and 4.8 wt% AlB₂, respectively.

t/s	f ₁
2.50	0.520
2.55	0.515
2.60	0.510
2.65	0.495
2.70	0.480
2.75	0.475
2.80	0.470

Table 3.3: Finite thickness correction factor values.



Figure 3.12: Schematic to show the key dimensions used to calculate the resistance of a truncated cone from resistivity measurements.

These values demonstrate that the compaction process is successful at producing a low-resistance, well-connected BDD particle to BDD particle, HPHT electrode. The ohmic drop (iR) contribution, assuming just these resistance values, will be negligible when considering the currents passed in Figure 3.11 c and Figure 3.11 d. However, the CVs in Figure 3.11 b, show non-zero, approximately linear gradient backgrounds, suggesting a significantly higher resistance when the electrodes are immersed in the electrolyte solution: $15.4 \pm 9.5 \text{ k}\Omega$ and $10.0 \pm 5.4 \text{ k}\Omega$ for 3.6 wt% AlB₂ and 4.8 wt% AlB₂ compact electrodes, respectively (taking the voltage range 0.0 - 0.1 V and simply applying Ohm's law). We attribute this resistance to solution porosity; solution trapped within the small pores results in significant, high solution resistance, manifested in the electrochemical measurement.

To provide information on the electrochemical performance properties of the material, the one-electron reduction of $Ru(NH_3)_{6^{3+}}$ was studied by CV. Due to the large background currents, the reduction and oxidation peaks for CV of 1 mM $Ru(NH_3)_{6^{3+}}$ are difficult to discern (Figure 3.11 c) over the background at this scan rate (0.1 V s⁻¹). Note that for an identical cell set-up and CV scan

conditions on planar CVD-grown BDD, the Ru(NH₃)₆³⁺ response is close to reversible (diffusion-controlled), with a 62 mV peak to peak separation, $\Delta E_{\rm p}$ (Figure 3.13). Increasing the concentration of $Ru(NH_3)_{6^{3+}}$ to 10 mM (Figure 3.11 d), improves the CV response of the composite electrodes, with ΔE_p values of 125 mV and 104 mV for 3.6 wt% AlB₂ and 4.8 wt% AlB₂, respectively. The larger ΔE_p values, compared to the response of the CVD BDD electrode in 1 mM Ru(NH₃)₆³⁺ (Figure 3.13), again indicates uncompensated resistance (ohmic drop). However, the apparent uncompensated resistances in these CVs are significantly less than would be deduced from the resistance values derived from the capacitive curves in Figure 3.11 b. This is because as the pore solution resistance increases with increasing solution penetration depth there will be a concomitant decrease in the driving force for the redox process. This results in a natural depth limit at which the redox reaction can no longer occur for a given applied potential range. A major component to the redox process is thus from the top surface of the electrode (planar diffusion), exposed directly to the solution, where ohmic drop contributions are less significant.



Figure 3.13: CV recorded in 0.1 M KNO₃ and 1 mM Ru(NH₃) $_{6^{3+/2+}}$ at a scan rate of 0.1 V s⁻¹ to show the electrode response of CVD grown BDD, using a droplet electrochemical cell set-up as described in section 3.2.4. A peak to peak separation, ΔE_p , of 62 mV is observed.

3.3.1.3 Local electrochemical measurements

To further understand porosity and pore solution resistance contributions to the electrochemical response of the compact electrodes, SECCM measurements were performed using a 1 μ m-diameter pipette. This pipette was sufficiently small such that it was possible to make measurements on individual crystal faces of the compact. CVs were recorded in 10 mM $Ru(NH_3)_{6^{3+}}$ and 10 mM KNO₃. A typical voltammetric response, on a (111) facet of a 4.8 wt% AlB₂ HPHT compact, identified using EBSD analysis (vide infra), is shown in Figure 3.14 a. This response is compared to a typical CV obtained under the same conditions but using a CVD-grown polished polycrystalline BDD electrode, Figure 3.14 b.



Figure 3.14: Typical CVs recorded in 10 mM $Ru(NH_3)_6Cl_3$ and 10 mM KNO_3 at 10 V s⁻¹ with a 1 μ m sized nanopipette on a) a (111) facet of the 4.8 wt% AlB₂ HPHT BDD compact and b) a high quality CVD grown BDD sample with schematics to show how electron transfer is occurring at each electrode surface.

In all cases, the SECCM tip was landed at a WE potential of 1 V vs QRCE. Immediately upon meniscus contact with the substrate (but no contact of the pipette), the voltammetric scan commenced, at a fast rate of 10 V s^{-1} to prevent significant wetting on the timescale of the scan, given the hydrophilic nature of oxygen terminated BDD.²⁷ For the compact, at the start of the scan (1 V vs QRCE), the current is close to zero, but as the potential is scanned cathodically, a reduction current begins to flow at approximately -0.3 V and increases monotonically as the potential is scanned further in the negative direction. At -1.0 V vs QRCE, the scan direction is reversed and the current decreases in magnitude towards 0 nA, before an anodic peak is observed in the potential range -0.2 V to +0.5 V. Notably, the reduction current magnitudes for the HPHT electrode (Figure 3.14 a i) are much higher when compared to the CVD sample (Figure 3.14 b i). A different CV shape is also observed; the reduction peak of Ru(NH₃)₆³⁺ at -0.75 V is pronounced for the CVD electrode but not observed for the HPHT electrode.

An estimation of the electron transfer kinetic rate constant, k_0 , for CVD grown BDD was obtained based on the peak to peak separation of *ca*. 0.6 V in Figure 3.14 b i using DigiElch software.⁵¹ The conditions of these SECCM experiments differ from conventional macroscopic experiments due to an enhanced mass transport originating from radial diffusion in the tip orifice.⁵¹ However, because a fast scan rate was used in the reported experiments to minimise the contact time of the SECCM meniscus on the surface and solution wetting during each measurement, mass transport will predominantly be transient (planar diffusion) as evident from the CV response in Figure 3.14 b i. It should be noted that mass transport is by migration as well as diffusion, as the concentration of Ru(NH₃)₆³⁺ and supporting electrolyte (10 mM KNO₃) was similar to prevent crystallization and blocking at the tip orifice. Thus the DigiElch calculations (planar diffusion) are approximate, but can be used to estimate the intrinisic rate constant, k_0 , from the SECCM experiment (diameter of the WE $d = 2.5 \pm 0.2 \ \mu m$, scan rate $v = 10 \ V \ s^{-1}$, and an uncompensated resistance of 15 M Ω from the nanopipette tip) giving a k_0 of 5 \times 10⁻³ cm s⁻¹. This is slightly lower than earlier reported calculations for BDD but reasonable given the approximations employed.³⁰

The larger current magnitudes in the reduction sweep are indicative of porosity effects. During the $Ru(NH_3)_{6^{3+}}$ reduction process (O to R in Figure

3.14 a and b ii), there is solution ingress into the body of the electrode, as shown schematically in Figure 3.14 a ii. This results in high mass transport as a result of solution flow into the electrode and a larger accessible electrode area, compared to the corresponding planar surface (Figure 3.14 b ii). The current magnitude increases during the forward (cathodic) scan, but for this measurement location, does not peak. This indicates that, overall, there is insufficient driving force for transport-controlled electrolysis of $Ru(NH)_{6^{3+}}$ at some parts of the electrode (deep within the pores) due to the high solution resistance.

As the potential scan direction is reversed in the anodic direction, solution will continue to flow into the porous BDD, carrying the product, $Ru(NH)_{6}^{2+}$ (O in Figure 3.14 a ii), which is re-oxidized on the return sweep. The peak current for the compact electrode (Figure 3.14 a i) is smaller and much broader than that for the planar surface (Figure 3.14 b i), indicating re-oxidation occurs mainly within the resistive body of the electrode. As the scan area for each CV is typically much smaller than the average particle size, these data indicate that the individual crystal faces are also porous, likely due to sub-micron sized fractures created during compaction, in addition to voids present between particles, as seen in Figure 3.8.

Porosity of the intrinsic material was also confirmed by electrochemically compact with an coating the HPHT BDD insulating layer of poly(oxyphenylene)³¹ and observing the electrochemical response (Figure 3.3 and Figure 3.15). Prior to coating with poly(oxyphenylene), the CV for 1 mM $Ru(NH_3)_{6^{3+}}$ is shown in Figure 3.15 (black line). As the coating method is electrochemical, all accessible wetted areas of the electrode should be available for insulation by the polymerized insulating material. This was confirmed by the absence of an electrochemical response when the insulating coating was applied, (orange line). After gentle polishing and removal of the insulating polymer predominantly from the top surface, the CV (pink line) is now clearly defined, smaller in current and significantly reduced in capacitive contributions compared to the CV recorded on the bare compact. This is likely due to the coating filling the sub-surface pores and thus limiting the exposed BDD area to only the top surface of the compact. A peak to peak separation in 1 mM Ru(NH₃)₆³⁺ of 0.105 V was determined.



Figure 3.15: CVs recorded in 1 mM $Ru(NH_3)_6^{3+/2+}$ and 0.1 M KNO₃ at 0.1 V s⁻¹ of a HPHT BDD compact grown using 4.8% AlB₂ before and after coating with poly(oxyphenylene), and after polishing of the coating.

A key aspect of SECCM for polycrystalline electrode materials is that the spatial distribution of electrochemical processes can be investigated as a function of surface structure.⁵² EBSD demonstrates that the surface of a compact electrode now comprises different crystallographic regions (Figure 3.16 a). Whilst the compact is predominantly formed using octahedral {111} crystals, polishing of the compact surface results in different regions being exposed. Most are due to well-defined low index crystal planes, although there are areas where the plane orientations are less well-defined on the spatial resolution of EBSD. These areas contain much smaller BDD particles, created during HPHT grit compaction, and voids, both previously observed in the FE-SEM images in Figure 3.8.

Detailed analysis of all CVs on the 4.8 wt% AlB₂ HPHT BDD compact is provided in Figure 3.16 (vide infra). A map of onset cathodic potential as a function of tip position, defined as the potential where the current was twice the standard deviation of the background current (= -0.24 nA) is shown in Figure 3.16 b. The map does not reveal any correlation of onset potential with crystallographic orientation (Figure 3.16 a). This is not unexpected given that the boron dopant density is likely to be fairly uniform across the surface as the compact is formed mainly from {111} crystals. Voltammetric responses from four marked locations in Figure 3.16 b are shown in Figure 3.16 c. They are typical of those obtained at different locations across the surface. The full dataset of CVs recorded is provided along with a MATLAB data reading script which can be downloaded from Elsevier where this work is published and



Figure 3.16: a) EBSD image and b) map of onset potentials of the SECCM scan area on the 4.8 wt% AlB₂ HPHT BDD compact. Onset potential was defined as the potential (E) at -0.24 nA on the cathodic sweep. Black squares in b) indicate the locations where the CVs shown in c) were recorded. The CVs for each pixel in the image are provided in ESI 10. All CVs were recorded in 10 mM Ru(NH₃)₆Cl₃ and 10 mM KNO₃ at 10 V s⁻¹. Arrow indicates initial scan direction. d) Correlation between the potential at -0.24 nA on the cathodic sweep of all recorded CVs.

allows the reader to visualise the CV response for each pixel (n = 400) in Figure $3.16 \text{ b}.^{53}$

Response 3 most closely resembles that shown in Figure 3.14 a. For those curves which show higher cathodic activity on the forward reduction sweep (1 and 2), there is a limiting cathodic current and higher anodic activity on the reverse sweep. Moreover, the larger the forward cathodic current magnitude, the more negative the potential of the anodic peak. A detailed analysis of all 400 CVs in Figure 3.16 d further highlights this correlation by plotting the onset potentials for the cathodic and anodic sweep of each curve (defined as - 0.24 nA on the cathodic and +0.24 nA on the anodic). A linear line slope of ca.

2.5 results, i.e., the less cathodic the process the less anodic the reverse process (smaller separation), and the more facile (less resistive) the electrochemical response. Facile electrochemistry is attributed to solution ingress into less resistive, more open, internal structures, which in turn give rise to larger current magnitudes and a transport-limited steady-state response on the cathodic scan (see Figure 3.14).Local capacitance values were estimated from equation (3.1), at 0.95 V, free from faradaic contributions, from the forward sweep only, measured immediately upon contacting the electrode surface with the nanopipette. The exposed geometric electrode area, A, during individual measurements was estimated to be $6.8 \pm 2.0 \ \mu\text{m}^2$, calculated from meniscus residues observed in FE-SEM secondary electron images (n=24, Figure 3.17). Extracted capacitance values were $12 \pm 3.6 \mu F \text{ cm}^{-2}$, two orders of magnitude lower than the macroscopic measurements previously detailed, and close to those recorded for a planar CVD BDD electrode ($\leq 10 \ \mu F \ cm^{-2}$).³⁰ When measuring the capacitance after a 1 second contact, compared with that measured upon immediate contact of droplet to electrode, the mean value increased approximately fourfold to 56 \pm 17 μ F cm⁻² (Figure 3.18). This again supports the idea of significant substrate porosity: on a relatively short time scale solution leaks into pores, the accessible electrode area increases, and so does the local capacitance.



Figure 3.17: FE-SEM secondary electron images of the SECCM scanned region shown in Figure 3.16 of the HPHT BDD compact, grown using 4.8 wt% AlB₂. Meniscus residues are clearly visible in both images indicating the spatial locations of the capillary. The large salt crystal visible in the upper left corner of a) is residual KNO₃ from deliberately crashing the nanopipette tip into the surface to aid location detection



Figure 3.18: Typical capacitance CVs recorded in 0.01 M KNO₃ at 10 V s⁻¹ during an SECCM scan of a HPHT BDD compact, grown using 4.8 wt% AlB₂ after a) immediate contact of droplet to electrode surface and b) after a 1 second delay. The values of capacitance estimated from capacitance CVs recorded at each pixel over the whole SECCM scan area (n=400) are a) 12 ± 3.6 μ F cm⁻² and b) 56 ± 17 μ F cm⁻².

3.3.1.4 Electrochemical characterisation of individual HPHT BDD particles

The electrochemical behavior of a single BDD particle was also investigated. Studies were performed on BDD particles grown using 4.8 wt% AlB₂. Figure 3.19 shows an FE-SEM image of the top surface of an alumina polished SPE with the {111} face of the BDD particle exposed. The electrode is irregularly shaped, ca. 1.3×10^{-4} cm² in geometric area, determined using ImageJ.⁵⁴ The white outline depicted in Figure 3.19 illustrates the BDD area that is exposed from the insulating epoxy resin by alumina polishing.



Figure 3.19: FE-SEM image showing an HPHT BDD particle of an SPE.

For this electrode, the solvent window of 2.93 V (defined by a geometric current density of \pm 2.0 mA cm⁻²), at 0.1 V s⁻¹, in aerated 0.1 M KNO₃, is flat and featureless (Figure 3.20 b). From the CV scan (Figure 3.20 c), a capacitance value of 46 μ F cm⁻² is determined, using equation (3.1). This is likely to be an overestimation as FE-SEM shows the BDD surface is not featureless and thus the geometric area underestimates the electrochemically accessible area. No electrochemical features associated with sp² bonded carbon are present.³⁰

Figure 3.20 d shows the CV response for 1 mM Ru(NH₃) $_{6^{3+/2+}}$ over the scan range 0.005 V s⁻¹ to 0.1 V s⁻¹. As the scan rate is decreased, the CV changes morphology from peak-shaped to almost sigmoidal in response, as expected for a microelectrode of this size: at the higher scan rates linear diffusion dominates, whilst an increasing radial contribution prevails at slower scan rates.⁵⁵ From the limiting current, $i_{lim} = 23.7$ nA, an approximate value for the electrode radius, a, (assuming a disk geometry and a diffusion coefficient, D, value for Ru(NH₃) $_{6^{3+}}$ of 8.8 × 10⁻⁶ cm² s⁻¹)⁵⁶ is 69.8 µm, calculated using equation (3.4):

$$i_{lim} = 4naFDc^*$$
(3.4)

where F is the Faraday constant, n (=1) is the number of electrons transferred, and c* is the bulk concentration of Ru(NH₃)₆^{3+,55,57} When the Tomes criterion of reversibility - which states that for a reversible charge transfer process the difference in quartile potentials, $|E_1/4-E_3/4|$, equals 56.4 mV for a one electron transfer process at 298 K - is applied to the CV recorded at the slowest scan rate of 0.005 V s⁻¹ (Figure 3.20 d red line), a value for $|E_1/4-E_3/4|$ of 54 mV is obtained.^{55,58} Note that $|E_1/4-E_3/4|$ is slightly below the Tomes criterion for reversibility because although the CV reaches a plateau, the mass transport rate is insufficiently high for the process to be at true steady-state during the course of the scan. For nominally steady-state techniques, the effect is to sharpen the voltammogram (smaller $|E_1/4-E_3/4|$) as seen here.⁵⁹ This result provides further compelling evidence that these particles are doped sufficiently to be considered metal-like for electrochemical applications and contain negligible sp² bonded carbon.



Figure 3.20: a) Schematic to show the structure of the HPHT BDD SPE. CVs recorded in 0.1 M KNO₃ at a scan rate of 0.1 V s⁻¹ at the HPHT BDD SPE (4.8 wt% AlB₂ additive showing b) the solvent window, c) a typical capacitance curve and d) the electrode response in 1mM Ru(NH₃)₆^{3+/2+} and 0.1 M KNO₃ at scan rates of 0.1, 0.05, 0.02, and 0.005 V s⁻¹.

3.3.2 CVD Nanoparticles

Ideally, to produce a lower cost and readily scalable alternative to CVD BDD NPs produced by milling, the HPHT BDD MPs described in section 3.3.1 should be used as a precursor to make NPs. As a first step towards this end goal, ball milling was carried out on fragmented pieces of CVD grown BDD material using milling facilities at both Cardiff University and the University of Warwick (see section 3.2.3). This initial work was essential to establish milling procedures for BDD and will allow future investigation into the ball milling of the HPHT BDD material, to produce NPs.

3.3.2.1 Material characterisation

After milling, the NPs were washed in acid to remove impurities introduced during milling, and then subjected to washing/centrifugation cycles to deacidify, as described in full in section 3.2.3. The resulting solutions (water and NPs) were dried on a hotplate to leave behind a dry NP powder.

The impact of the milling ball material on transfer of material from the ball to the milled BDD was first assessed, using either the tempered steel balls or the Si₃N₄ balls. The Si₃N₄ milling method produced almost ten times the mass (1.7907 g) as the tempered steel milling method produced (0.1864 g), from an equivalent starting mass of ~0.4 g BDD. This mass is also significantly greater than the starting mass of BDD film which was milled with Si₃N₄. These factors suggest that the product obtained using the Si₃N₄ milling method is not pure BDD, and therefore lots of impurities must be present, whereas the product obtained using the tempered steel milling method is likely to contain significantly less impurities.

Raman spectrometry was adopted to investigate further the chemical composition of the BDD powders. Measurements were taken by focusing the laser onto a small pile of each powder, placed onto the stage. As observed for the HPHT particles and compacts, the Raman spectra of both the tempered steel milled sample (Figure 3.21 a), and the Si₃N₄ milled sample (Figure 3.21 b), show the characteristic features of highly doped BDD. These include peaks at ~550 cm⁻¹ and ~1200 cm⁻¹,³⁹ a redshifted diamond peak (intrinsic diamond 1332.5 cm⁻¹) occurring at 1372.2 cm⁻¹ (tempered steel milled) and 1317.2 cm⁻¹ (Si₃N₄ milled)⁴³ with asymmetry due to a Fano resonance.⁴⁴

Differences in the spectra are also clear. Both samples contain some sp² bonded carbon, indicated by the graphene G peak at ~1580 cm⁻¹.⁴⁵ The increased relative intensity in this peak for the Si₃N₄ milled sample suggests it contains a larger amount of sp² bonded carbon. A second sp² bonded carbon peak, the graphene G' peak,⁴⁵ at ~2700 cm⁻¹ can also be observed in only the Si₃N₄ milled sample, again indicating higher levels of sp² bonded carbon impurities. The sp² bonded carbon present in these samples is either due to sp² bonded carbon content in the grain boundaries of the polycrystalline BDD film as grown, or due to production of sp² bonded carbon during the milling process. As both samples were produced from the same starting CVD material, the former of these possible origins of the sp² bonded carbon observed in the

Raman spectra should be equal for both samples. The latter is therefore likely the most significant factor as to why the Raman spectra indicates greater sp² bonded carbon in the Si₃N₄ milled sample. For electrochemical purposes, sp² bonded carbon content should be minimised as this will affect the electrode response. A post-milling anneal in oxygen at 600 °C for 5 hours was trialled on the Si₃N₄ milled sample which has been previously demonstrated to minimise sp² bonded carbon introduced during laser micromachining of CVD BDD.⁶⁰ Similar treatments have also been used to minimise the sp² bonded carbon found in detonation nanodiamond as by-products of synthesis, including amorphous carbon, carbon onions, fullerenic shells, and graphite ribbons.^{23,61} After annealing, a substantial decrease in the amount of sp² bonded carbon present in the sample was observed (Figure 3.21 c), with the G' peak disappearing completely and the G peak significantly reduced in intensity. This data suggests this treatment successfully removes a significant amount of the sp² bonded carbon from the BDD NPs.

The Si₃N₄ sample (Figure 3.21 b) also shows an additional triplet peak centred at 200 cm⁻¹ which has previously been assigned as hexagonal β -Si₃N₄.⁶² The presence of this peak therefore indicates that the phosphoric acid clean did not sufficiently remove Si₃N₄ impurities introduced during milling.



Figure 3.21: Raman spectra of a) tempered steel milled BDD nanoparticles and b,c) Si₃N₄ milled BDD nanoparticles, a) before and b) after annealing in oxygen for 5 hours at 600 °C.

As Si/Fe contamination can be introduced during milling from the Si₃N₄ and tempered steel balls and the grinding chamber (where the chamber and balls are made of the same material), respectively, ICP-MS (Fe) and ICP-OES (Si) were used to determine the concentrations given in Table 3.4. To remove any impurities residing on the NPs for ICP assessment, powder samples were

added to nitric acid and sonicated (as described in section 3.2.3). The nitric acid (containing any solubilised impurities) is then diluted for ICP analysis.

The tempered steel milled BDD NPs contained more Fe and less Si than the Si₃N₄ milled NPs, as expected. It is unclear where the relatively large amount of Si contamination found in the tempered steel sample originates from; it is possible this is residual contamination from Si₃N₄ milling balls being incorrectly used in the steel milling chamber in a previous experiment. It is important to note that these techniques only measure that which is solubilised during the sample preparation. As BDD is insoluble in nitric acid, these concentrations correspond to impurities which have been removed during the nitric acid clean, so any Fe or Si remaining on the BDD NPs is not measured. It is therefore possible that the actual concentration of Fe and Si contamination present in the BDD powders is higher than those reported here. The presence of Fe contamination is more problematic for electrochemical applications as Fe is electrochemically active, unlike semiconducting Si, however the Fe concentrations measured here are very low, and further cleaning procedures could be optimised to reduce this even further.

Table 3.4: Iron (Fe) and silicon (Si) concentrations of tempered steel milled and Si₃N₄ milled BDD nanoparticles, from ICP-MS (Fe) and ICP-OES (Si).

Milling ball material	[Fe] from ICP-MS (ppb)	[Si] from ICP-OES (ppb)
Tempered steel	186.4±1.17	1706±3.41
Si ₃ N ₄	11.2±0.46	2901±6.96

3.3.2.2 Morphology and size analysis

Representative BF-TEM images of both milled samples are shown in Figure 3.22. The tempered steel milled sample (Figure 3.22) contained many small spherical NPs with a diameter of 5-10 nm (Figure 3.22 a and b), with some larger and more irregularly shaped particles ~100 nm diameter (Figure 3.22 c). Conversely for the Si₃N₄ milled sample only large and irregularly shaped particles with ~200 nm diameter were seen, with no small or spherical particles observed (Figure 3.22 d). In BF-TEM, the thicker the sample is, the darker the image appears. As a heterogenous contrast is observed within single particles (Figure 3.22 d-f), the NPs are not completely spherical and are show a non-uniform thickness. This data suggests that milling with tempered steel produces BDD NPs of a smaller size and more uniform morphology than when milling with Si₃N₄.



Figure 3.22: BF-TEM images of the BDD nanoparticles at varying magnifications. a) b) and c) are images of the tempered steel milled BDD nanoparticles, and d) e) and f) are the Si_3N_4 milled BDD nanoparticles.

DLS measurements were taken before and after additional centrifugation and filtering steps (described in section 3.2.3, adopted to separate large clusters of aggregated particles and incompletely milled BDD) to investigate NP size. Before size separation, both samples clearly contain large particles and/or aggregates as large peaks are observed at ~615 nm and ~320 nm diameter for tempered steel (Figure 3.23 a, dashed line) and Si₃N₄ milled (Figure 3.25 b, dashed line) NPs, respectively. These large particles may be: large pieces of residual unmilled, or incompletely milled, BDD film, or agglomerates of smaller NPs which can occur if aggregation occurs during milling due to heat build-up in the solvent (in this case water).⁶³ The tempered steel milled sample, before size separation, shows an additional shoulder at ~164 nm diameter (Figure 3.23 a, dashed line). Both samples show a very wide size distribution. In DLS, the presence of large particles causes a great amount of light scattering which stops smaller particles from being detected, and thus smaller particles are likely present but not detected due to the high scattering intensity from the larger particles. For this reason, each sample was then centrifuged and passed through a 200 nm to filter to investigate whether smaller particles are present. After this size separation, smaller particles and a narrower size distribution were observed for both samples centred at ~79 nm

(tempered steel milled, Figure 3.23 a, solid line) and ~98 nm (Si₃N₄ milled, Figure 3.23 b, solid line). This shows that a narrow size distribution at around 100 nm can be achieved, but size separation steps are necessary to first remove larger particles and agglomerates from the NP solutions. The 5-10 nm tempered steel milled NPs observed in TEM imaging are not detected here as the scattering from the 100 nm NPs eclipses the signals produced.



Figure 3.23: Size distribution from DLS of a) the tempered steel milled and b) the Si_3N_4 milled BDD nanoparticles before (dashed line) and after (solid line) centrifuging and filtering.

Further size investigation was carried out using NTA, which visualises and analyses particles, in conjunction with a microscope, and determines particle size by the rate of Brownian motion of the particles in a liquid.⁶⁴ Dilute solutions are required for this analysis as if NP concentration is too high, the video frame can become saturated which results in the production of inaccurate results. NTA gave average NP sizes of 100.4 ± 6.3 nm and $77.3 \pm$ 2.7 nm for tempered steel (Figure 3.24 a) and Si₃N₄ milled (Figure 3.24 b) NPs, respectively. This is in agreement with both TEM and DLS analysis which also show that tempered steel milling produces smaller particles. Tempered steel milling (Figure 3.24 a) also produced a narrower size distribution than Si₃N₄ (Figure 3.24 b). It is important to note that these size distributions have been obtained after centrifuging and filtering to remove larger particles and agglomerates, which from the DLS results is evidently a key step if a small size, of around 100 nm, and narrow size distribution is desired. An advantage of using NTA in comparison to DLS is that the particle motion is analysed by video which allows the user to select and vary measurement parameters by eve and thus achieve a more accurate measurement. One limitation of this


Figure 3.24: Size distribution from NTA of a) the tempered steel milled and b) the Si₃N₄ milled BDD nanoparticles after filtration.

technique is that the detection limit of NTA is around 30 nm. This is due to the presence of background scattering which prevents the scattering from smaller NPs from being detected as signal.

To ascertain the suitability of facilities available at the University of Warwick for carrying out BDD NP preparation, a comparative study was undertaken. The mass of milling balls used (40 g at Cardiff or 50 g at Warwick) was selected based on manufacturer guidance for each mill, and the mass of BDD film varied (~0.4 g at Cardiff or ~0.5 g at Warwick) to maintain a constant ball to powder ratio (100:1, by mass). Full milling conditions are described in section 3.2.3 and were chosen to provide minimum variation between the comparable systems used. For these studies the same CVD BDD material was used as the starting material (~150 μ m thickness, >10²⁰ B atoms cm⁻³, Element Six). It should be noted that this is a different source of CVD BDD to that used in the data presented prior to this point (~130 μ m thickness, >10²⁰ B atoms cm⁻³, Oliver Williams, Cardiff).

Two equivalent BDD NP samples were milled at Warwick. For the first sample, 0.4971 g of BDD film was milled, the product acid washed at Warwick, and 0.1949 g of BDD NPs recovered (39 % yield). For the second sample, 0.5008 g of BDD film was milled, the product acid washed at Cardiff, and 0.3279 g of BDD NPs recovered (65 % yield). A single sample was milled at Cardiff from 0.4004 g of BDD film. After recovery from the mill, but before acid washing, the sample was split in half. One half of this was acid washed at Warwick, and

0.1291 g of BDD NPs recovered (64 % yield). The other half was acid washed at Cardiff, and 0.1167 g of BDD NPs recovered (58 % yield).

DLS analysis was carried out on these samples, prepared at concentrations of 2, 3, and 4 mg mL⁻¹, with measurements taken after centrifugation and filtration as previously described. This concentration range was deemed appropriate as the measured particle size was found to be independent of sample concentration. Average particle size (corresponding to peak position) was noted for each sample, at each concentration, to compare material produced and worked up at both locations (Figure 3.25).



Figure 3.25: Comparison to determine any effect of milling and acid washing locations on BDD NP particle size, determined by DLS measurements.

The samples milled at Warwick were found to have a slightly smaller particle size with a narrower sized distribution, reflected in the smaller error bars. For both samples milled at Cardiff, one of the concentrations showed two populations of different sized particles. This suggests that the Cardiff milled samples contain more large particles/agglomerates. No effect was observed of acid washing location. Though this study involved a small number of samples only, the preliminary data implies that it is possible to prepare small BDD NPs with a narrow size distribution with the facilities available at Warwick, despite the reduced maximum RCF of both the planetary ball mill and the centrifuge employed during acid washing of the NPs.

3.4 Conclusion

Well-defined crystallographic (octahedral with {111} faces dominant) BDD MPs (< 200 μ m in size) containing negligible sp² bonded carbon and suitable for electrochemical applications, were synthesized using HPHT. SIMS, GDMS, and Raman experiments showed that boron doping levels were above those required for metal-like conductivity. Synthesis of these particles represent an exciting step forward in the large scale, cost-effective production of electrochemically-viable BDD particles. Such materials can function as building blocks for both the bottom-up production of cheaper BDD-based electrodes and the top-down production of smaller BDD NPs. The use of a Fe-Ni carbide forming catalyst aided in enabling lower temperatures and pressures than previously reported, ~5.5 GPa and 1200 °C, whilst AlB₂ functioned as both a source of B and nitrogen sequester.

HPHT compaction was shown to be an effective method for creating macroscopic high surface area, low material resistance, porous electrode structures from the BDD particles. Changing the compaction conditions, including P and T, run time, and particle size, will be one way to manipulate electrode porosity in the future. We envisage, such BDD electrodes will be of great interest for applications where high double layer capacitance or electrode porosity is required, with the added benefits of corrosion stability and a large aqueous solvent window e.g., gas porous electrodes, electrocatalyst or enzyme support structures. CV analysis proved useful at assessing the impact of electrode porosity at the macro-level, showing three orders of magnitude increase in double layer capacitance compared to a planar non-porous CVD-grown electrode.

SECCM was employed as a new method to detect and fingerprint electrode porosity at the micro-level. For porosity mapping, the voltammetric waveshape was shown to be diagnostic of the ingress of electrolyte solution into the porous electrode and a qualitative mark of the local pore dimensions. There are further ways in which SECCM could be developed for porosity mapping in the future, including measuring capacitance alongside the redox process to reveal the internal electrode surface area, which would allow more detailed analysis of the redox process. The use of different voltammetric scan rates or chronoamperometry could also be beneficial in quantifying porosity as a function of solution ingress.

Highly doped 'metallic' BDD NPs were also successfully produced by milling BDD film grown by MPCVD. The material of the milling balls used was found to influence the size and morphology of the BDD NPs produced, with tempered steel milling producing smaller and more spherical particles, and Si₃N₄ milling producing larger and more irregularly shaped particles. It is also clear that milling with Si₃N₄ introduces a larger number of impurities, predominantly residual Si₃N₄, even after acid cleaning. sp² bonded carbon impurities are also introduced by milling, though these can be removed almost entirely by annealing in air.

Large particles and agglomerates were found to be present in both samples, though centrifuging and filtering easily removes these to give narrow size distributions (100.4 \pm 6.3 nm for tempered steel milled BDD NPs and 77.3 \pm 2.7 nm for Si₃N₄ milled BDD NPs). Further investigation into the effect of milling parameters should be undertaken to achieve the optimum yield and size of NPs. Electrochemical characterisation and testing of milled NPs will also be a key step in proving the promise of this material in powder based electrochemical applications. Further work will look to combine HPHT BDD MPs with milling procedures as a means to producing high volumes of BDD NPs.

3.5 References

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4 Ozone generation on boron doped diamond electrodes

4.1 Introduction

Dissolved ozone in water is an environmentally clean and powerful oxidant, with an absence of harmful residues, with applications including sterilisation and sanitisation,¹ deodorisation,² and decolourisation.³ This is seen commonly in both waste and potable water treatment, as ozone oxidises contaminants to harmless products.^{4,5} In water, ozone decays rapidly in water with a half-life of ca. 20 minutes,⁴ and therefore for all water based applications must be either generated on site.

Traditionally ozone generators produce ozone in the gas phase via corona discharge, where a high voltage is applied between two electrodes in the presence of air or oxygen.⁶ Drawbacks to this method include high energy use, expensive set-up cost, and the ozone gas must then be dissolved in the water for use.^{7–9} EOP has therefore gained in popularity as dissolved ozone can be produced simply by electrochemical oxidation of water. EOP offers the advantages of a facile, small-scale, and robust experimental setup, low voltage operation, high current efficiency, no need for gas feedstocks¹⁰ and direct generation of dissolved ozone in water. Recent global events such as the COVID-19 pandemic have highlighted the need for new and/or effective disinfection methods which are more environmentally friendly and less susceptible to interruption of supply than traditional disinfectants. Small ozone EOP generation cells suitable for use in handheld and portable sterilisation devices are currently commercially available from a variety of companies and use tap or deionised water as the electrolyte.^{11–13}

BDD is an extremely attractive anode material for EOP with many advantages over other materials as discussed in detail in section 1.3.2.^{14–20} Typical commercial EOP cells contain two perforated CVD BDD electrodes sandwiched together with a Nafion® solid electrolyte proton exchange membrane between them.^{18,19} As discussed in section 1.3.2, perforated electrodes have been used to allow solution access to the Nafion® membrane and maximise the triple-point contact area between the Nafion® membrane, anode, and the solution.^{17,19} HPHT grown BDD has yet to be realised for EOP. The mechanism of EOP is believed to proceed via the electrochemical generation of surface bound hydroxyl and oxygen (O·) radicals (see section 1.3.2 for full EOP mechanism).²¹ When solid, freestanding, BDD electrodes are employed, laser cutting of the BDD from the wafer, is required to produce the desired electrode geometry. This process has been shown to introduce nondiamond, sp² bonded carbon, in undoped diamond, as a result of thermal damage from the laser beam, which results in the solid-to-solid conversion of diamond to graphite and amorphous carbon.^{22,23} Sublimation of this graphite can also occur during machining.²⁴ There is limited work which suggests that sp² bonded carbon from the CVD growth process can improve ozone production, however, there are other papers which point at the importance of having a pristine BDD surface for EOP.^{16,19,25}

In this chapter, the role of sp² bonded carbon in BDD on EOP on BDD, is investigated, using CVD grown BDD electrodes. As the electrodes are cut using laser micromachining, first there is an investigation into the nature and properties of the sp² bonded carbon introduced at the surface of the BDD, pre and post oxidative acidic cleaning treatments. The impact of the % of sp² bonded carbon present on the surface of the BDD for EOP is then investigated. Secondly, electrodes fabricated by compaction of HPHT grown BDD MPs, as highlighted in chapter 3, are assessed for suitability for EOP. Under the same cell conditions and using the same freestanding electrode geometries the performance properties of the compacted HPHT versus CVD BDD electrodes are also directly compared for EOP in terms of ozone output and current efficiency.

4.2 Experimental

4.2.1 BDD electrodes

CVD BDD electrodes were produced from polycrystalline freestanding CVD BDD wafers grown (6 inch diameter, Element Six (E6) Ltd., Harwell, UK; Electrochemical Processing Grade) on a silicon support. The wafers were grown to the desired thickness (200 μ m, 320 μ m, 420 μ m, or 700 μ m) and then removed from the support. The boron content of the wafers was 1.9×10^{20} boron atoms cm⁻³, with a material resistivity of 60 m Ω cm.^{26,27} Perforated BDD electrodes were cut into their desired geometries by laser

micromachining. The growth face was either left "as-grown" with a roughness of ~ 15 μ m RMS, or polished to give a much smoother finish (RMS ~ 6.5 nm). The rear "nucleation" face has a roughness of ~ 100 nm RMS. Lapping of the nucleation face, increases the surface roughness to ~ 560 nm RMS. All surface roughness values were measured using WLI (with a ×5 magnification objective lens). For the CVD BDD electrodes used to compare against HPHT BDD electrodes, each of these surface finishes was present in the final CVD cell assembly as discussed further in section 4.3.3. For the CVD BDD electrodes were inserted into the cell bodies with the "as-grown" face Nafion facing, and the nucleation face solution facing.

Freestanding HPHT BDD electrodes were produced using a binder-free HPHT compaction process (at 6.6 GPa and 1700 °C in a cubic anvil press) of HPHT synthesised BDD MPs. The MPs were grown from a Fe/Ni/C melt with 4.8 wt% AlB₂ as the boron source, as described in detail in section 3.2.2.²⁸ This method produces freestanding cylindrical compacted electrodes, herein referred to as "compacts" with a diameter of approximately 16 mm, a thickness of 2 mm, and a boron content of ca. $2-3 \times 10^{20}$ B atoms cm⁻³. The compact used for all experimental work in this chapter had a resistivity of ca. 520 m Ω cm, calculated from four-point probe resistivity measurements (in air), as previously described. The 2 mm thick compact were sliced using electrical discharge machining (EDM) to give multiple ~ 500 µm thick electrodes. The HPHT electrodes were either left "as-cut" (RMS ~ 6 µm,) or mechanically abraded (lapped) to give a smoother finish (RMS ~ 3 µm).

To ensure the cut edges were perpendicular to the face of the BDD a trepan system was used to widen the laser spot diameter to 50 μ m in order widen the cut trench and prevent the beam interfering with the trench sides removing the need for kerf on cuts. Cutting was performed in two passes with a fluence of 760 J cm⁻¹. The electrodes were cut into 12 mm or 8 mm diameter rounds with a rectangular tab (3 × 2 mm) for ease of electrical contacting. The larger 12 mm diameter electrode size was adopted for the investigation of sp² bonded carbon content on CVD grown BDD electrodes. The smaller 8 mm diameter electrode size was adopted for the HPHT and CVD comparison study (section 4.3.3) due to the limited size of the HPHT BDD compacts. The BDD electrode was perforated with through holes of different geometries, cut from the central

region of each electrode. The impact of electrode design on EOP will be discussed in section 4.3.2.

The 12 mm diameter electrodes were cut with varying geometries, discussed further in section 4.3.2. The 8 mm diameter electrodes contain 8 slots that are each 300 μ m wide, with each slot separated by 300 μ m wide BDD pillars, cut with varying lengths to maintain a constant distance of 1 mm from the edge of the electrode. In total, the patterned area encompassed a 6 mm region of the electrode.

Identical pairs of each electrode geometry were produced to provide an equivalent anode and cathode. As explained further in section 4.2.2, the cell design allows either electrode to be connected as the anode or cathode, and polarity can be switched between the two. The solution facing sides of the contact tabs on the CVD electrodes were roughened using laser micromachining. This was performed to increase the surface roughness which improves adhesion of the electrical Ti/Au contacts. This treatment was not applied to the HPHT electrodes as the electrode faces for contacting were already much rougher (HPHT faces, RMS ~ 3 μ m cf. CVD faces, RMS ~ 100 nm).

To produce a pair of minimal sp² bonded carbon containing electrodes for comparison, the electrodes were exposed to a hydrogen plasma prior to measurements. The electrodes were laid onto a molybdenum holder and placed into a Carat Systems SDS6U MWCVD plasma reactor. The microwave power and pressure conditions were 5.5kW and 85 torr, respectively. The gas flow was maintained at 300 standard cubic centimetres per minute (SCCM) of H₂ sourced from a F-DGSi COSMOS.MF.H2.1000 hydrogen generator. The power and pressure in the system were ramped up in 2.5 minutes in a hydrogen atmosphere followed by a hold time of 90 minutes at the set conditions. At the end of the 90 minutes, the power and pressure in the chamber were slowly ramped down over 3 minutes, whilst maintaining a hydrogen atmosphere. This treatment was carried out firstly with the "asgrown" faces in contact with the hydrogen plasma, the electrodes flipped, and then the treatment repeated with the nucleation faces in contact with the hydrogen plasma. Taking into account the ramp up and ramp down time, the total hydrogen plasma exposure time for the electrodes was 95.5 minutes for each face.

To confirm removal of the sp² bonded carbon content, for electrochemical quinone surface coverage (QSC) measurements, the electrode was cycled in 0.1 M sulphuric (H₂SO₄) acid as described previously to ensure a consistent oxygen surface termination.²⁹ Γ was measured in a pH 2 (measured using a SevenEasy pH meter, Mettler Toledo) Carmody buffer, prepared using boric acid (99.97%, Sigma Aldrich), citric acid (≥99.5%, Sigma Aldrich) and tertiary sodium phosphate (≥95%, Sigma Aldrich).³⁰

All BDD electrodes were then acid cleaned at ~200 °C in concentrated H₂SO₄ saturated with KNO₃ for 30 mins, then rinsed with water and cleaned in concentrated H₂SO₄ at ~200 °C for 30 min, to remove debris introduced during laser micromachining.³¹ A titanium (Ti:10 nm)/gold (Au:400 nm) contact was sputtered (Moorfield MiniLab 060 Platform Sputter system) onto the rectangular tab of each electrode (on the solution facing side). The electrodes were then annealed in air (400 °C for 5 h) to create an ohmic contact.³²

For a comparison experiment, a pair of GC electrodes were cut from a 300 μ m thick sheet (SIGRADUR G, HTW, Germany) into the same geometry as one of the CVD BDD electrode designs, for direct comparison, using the same laser parameters. After laser cutting the electrodes were not acid cleaned due to stability concerns. Electrical contact sputtering was also deemed unnecessary due to the higher electrical conductivity of GC compared to BDD. Cell assembly was performed in the same way as for the BDD EOP cells.

For investigation of the effect of laser micromachining and acid cleaning on the surface of the HPHT BDD MP compacts, an additional two 3×3 mm squares were laser micromachined from an HPHT BDD MP compact. Each square had a small ca. 1 mm diameter circular area in the middle of the square roughened by laser micromachining, to mirror the nature of a laser cut edge. One square was acid cleaned, and one square was left as-lasered. Raman spectroscopy measurements were recorded on both squares, in the lasered circle and on the bulk, unlasered, compact surface. Raman spectroscopy measurements were performed using a Renishaw inVia Reflex Raman microscope with a 532 nm (2.33 eV) solid state laser, a laser power of 3.6 mW and a Leica N-Plan ×50 objective with an NA of 0.75; giving a spot size of approximately 1 μ m.

4.2.2 EOP cell design and assembly

The cell bodies were designed in Fusion 360 (Autodesk, USA) with each ozone cell being made up of two separate half cells which each accommodate one BDD electrode. Identical pairs of BDD electrodes were produced so that each cell has an electrode with equivalent geometry in each half cell. Each half cell comprises of a recess for the electrode to be adhered, a recess for a 3D printed elastomeric gasket, a slot for an external copper contact, and a channel for solution flow across the backside of the electrode.

The cell bodies were 3D printed in a UV curing clear polymethylmethacrylate (PMMA) resin (FormLabs Standard Clear, FormLabs, USA) at 50 µm layer height on a Form 3 (FormLabs, USA). After printing, a 10-minute wash in isopropyl alcohol was used to remove excess resin (Form Wash, FormLabs USA), followed by an additional UV cure for 20 minutes at 60°C (Form Cure, FormLabs, USA). After removing the 3D printing support material the faces of each cell body were polished to ensure they were flat. The electrodes were adhered into each half cell using additional UV resin (FormLabs Clear, FormLabs, USA) and electrical contact was made using a conductive silver epoxy (Conductive Epoxy, CircuitWorks, Chemtronics, USA) and a copper tab.

This process results in two individually addressable half cells, labelled A and B. Both side of the cell can be connected as either the anode or cathode. For all experiments, initially A was connected as the anode (for EOP) and B as the cathode, before reversing the polarity.

Prior to cell assembly, the BDD electrodes were polished with alumina MPs (0.05 μ m, Buehler, Germany) on a microcloth pad (Buehler), and then rinsed to remove any residual alumina. Elastomeric 3D printed gaskets (FormLabs Elastic 50A, FormLabs, USA) were positioned in the main cell assembly and the two half cells bolted together with a Nafion® (Nafion® 424 reinforced with poly(tetrafluoro-ethylene) fiber, 0.33 mm in thickness, Sigma-Aldrich) sandwiched between them. The Nafion® membrane was cut by hand into a 2 cm diameter round circle.

Figure 4.1 shows the perforated electrode cell. The position of the Nafion® membrane with respect to the BDD electrode is shown in the schematic of one



Figure 4.1: a) Render to show the front view of one half cell, b) photograph of one half cell (the contact and solution inlet can be seen at the back) prior to cell assembly, and c) render to show the flow profile and cross-sectional view through the assembled ozone generation cell.



Figure 4.2: Schematic to show an example flow profile of the EOP cell. BDD electrodes are in black, the Nafion membrane® is in light grey, the 3D printed cell body is in dark grey, the copper contacts in orange, the solution in blue, and the flow path indicated by the blue arrows.

half cell (Figure 4.1 a). Figure 4.1 b is a photograph of one half cell prior to assembly, and Figure 4.1 c shows the cross-sectional view through the assembled ozone generation cell, with the flow profile indicated for each distinct half cell. Figure 4.2 is a close up schematic of the electrodes within the cell, showing the flow profile in more detail.

4.2.3 Nafion® membrane pretreatment

Perfluorosulfonated membranes are a standard in PEMFCs, most frequently Nafion® membranes are used due to their high proton conductivity and superior chemical stability.³³ The ionic conductivity, and thus performance, of

Nafion[®] membranes is highly dependent on many factors including temperature and water content.³⁴ As a consequence, a pre-treatment procedure is commonly employed to protonate and hydrate the Nafion[®] membrane before use and to achieve an optimal and consistent performance output. Typically this is achieved by heating in acid (commonly H₂SO₄, HNO₃, HCl, or H₃PO₄) for a short time period.³⁴

For all experiments in this chapter, membranes (Nafion® 424 reinforced with poly(tetrafluoro-ethylene fiber, 0.33 mm in thickness, Sigma-Aldrich) were cut from a flat sheet into the desired geometry, as previously described, and sandwiched between the two cells. Acid pre-treatments were investigated, however, immersing the membranes into aqueous solutions for extended periods of time (ca. 60 mins) was found to cause a tight curling of the membrane, making them unsuitable for insertion into the EOP cell. To avoid running acidic solutions through the experimental set-up, due to corrosion concerns, an electrochemical pre-treatment was instead employed.¹⁹

Cells were first run at ~ 0.3 A for 5 mins for the 8 mm diameter perforated electrodes, and at ~ 0.6 A for 5 mins for the 12 mm diameter perforated electrodes. A lower current was adopted for the smaller electrodes to produce a roughly equivalent current density as the electrode area is smaller. This pretreatment was applied with the A side BDD electrode connected as the anode. Triplicate calibration plots were recorded. The pre-treatment was then applied again but this time with the B side BDD electrode connected as the anode. Triplicate calibration plots were again recorded with side B as the anode. The pre-treatment condition selected always produced a stable response between calibrations, producing consistent current/voltage repeated and current/ozone output data (as reflected in the relatively low errors reported in the experimental data).

4.2.4 Ozone UV-Vis calibration plots

Following the Nafion® electrochemical pre-treatment, plots of applied current vs ozone concentration, referred to herein as calibration plots, were recorded and UV-Vis employed for ozone quantification.

For all UV/Vis measurements, a UV/Vis spectrometer (Lambda 850, Perkin Elmer) was employed with quartz cuvettes. The UV absorption spectrum of ozonated water contains an absorption peak at ~258 nm.^{35,36} For static

measurements, a high precision quartz cell (Hellma Analytics) was employed, whilst for long term testing, a type 45FL flow-through cell (FireflySci) was employed, both with an optical path of 1 cm.

Calibration plots of applied current vs ozone concentration were recorded over an applied current range of 0 - 0.6 A in approximately 0.1 A intervals, using a benchtop power supply unit (VLP-2602 OVP, Voltcraft) in a current limited regime. Water was flowed into the ozone generation cell from a 1 L reservoir via a 6 V DC diaphragm pump (SC3701PW, Skoocom Electronic Co. Ltd), as shown in Figure 4.3.



Figure 4.3: Schematic to show experimental setup for recording calibration plots. The 1 L reservoir was refilled when required.

A 2 mL aliquot was taken from the cell outflow when each required applied current was reached (Figure 4.3). Static UV/Vis measurements of these aliquots were taken with the absorption spectra recorded between 350 to 200 nm, at a spectral resolution of 1 nm and a scan speed of 266.75 nm min⁻¹. Maximum absorption values at ~258 nm, were taken for each sample and used to calculate ozone concentration, *c*, using equation(4.1):

$$A = \varepsilon c l \tag{4.1}$$

where *A* is the measured maximum absorbance, ε is the molar absorption coefficient, 2900 M cm⁻¹,³⁷ and *l* is the pathlength of the cuvette (1 cm).³⁸ The exact value for the molar absorption coefficient is a matter of continuing debate, with values from 2000 to 3600 M cm⁻¹ reported in the literature,³⁹ however 2900 M cm⁻¹ has been adopted herein in agreement with similar work in the field.⁴⁰ Following the electrochemical pre-treatment (section 4.2.3), calibration plots were run from low to high current, with A as anode (*n* =3).

Cell polarity was then reversed, and the process repeated for B as anode (n = 3). The flow rate of solution through the cells was typically 300-330 ml min⁻¹.

4.2.5 Long term stability testing

For long term cell stability testing of EOP cells, the UV absorbance at 258 nm was recorded as a function of time while the cells were continuously operated for 20 h at a constant current of ~ 0.3 A. Calibration plot triplicates were collected for both sides of the cell before and after long term testing following the procedure described in section 4.2.4, including the Nafion® electrochemical pre-treatment.

In order to deal with the large volumes of solution required for the 20 h experiment, water from a 10 L reservoir was recirculated through the system using a diaphragm pump (Figure 4.4). It was however necessary to remove the electrogenerated ozone prior to recirculation back into the cell; this was achieved through use of an in-house built "ozone destroyer". Solution was flown through a high surface area quartz tube system placed in-between two 254 nm UV lamps; at 254 nm dissolved ozone is converted to oxygen.⁴¹ The flow rate through this system was typically 200-250 ml min⁻¹.



Figure 4.4: Schematic showing experimental set-up for long term EOP stability testing.

4.2.6 Transmission electron microscopy investigation of the impact of laser micromachining and oxidative acid cleaning on the BDD surface

Square BDD plates, 1×1 mm in size, were cut from a 370 µm thick CVD wafer, and laser micromachined in air on the growth face. The BDD wafer consisted of a polished growth face (~ 100 nm RMS) and a lapped nucleation face (~ 560 nm RMS). A circular pit with a diameter of 400 µm and a depth of 5 µm was machined into the centre of each plate on the polished face. Machining parameters adopted were: i) a pulse frequency of 100 Hz, or one ns-pulse per 0.01 s ii) a fluence of 15 J cm^{-2} and iii) a speed of 0.3 mm s⁻¹. These parameters were chosen as they are typical of those used in the laser micromachining of BDD electrodes, specifically to laser cut wafers into desired electrode shape.^{42,43} Two identical BDD plates were fabricated in this way for TEM analysis (Figure 4.5): (1) with no further treatment (Figure 4.5 i) and (2) after an oxidative acid treatment as described below (Figure 4.5 ii).



Figure 4.5: Schematic showing the different FIB lamallae produced for TEM imaging, and associated processing routes for the BDD plates.

For the oxidative acid treatment, the BDD plate was heated at ~200 °C in concentrated H₂SO₄ (98%) saturated with KNO₃ for 30 min. This time was chosen to be sufficient to exhaust all of the KNO₃ in solution. When the KNO₃ is added to the H₂SO₄, nitric acid is generated *in-situ*, resulting in a more strongly oxidising environment.

From the two differently treated laser micromachined BDD plates, a single TEM lamellae was cut for TEM imaging. This was achieved using standard FIB lift-out procedures on an FEI Scios DualBeam FIB Microscope. For each sample, the electron beam transparent region produced was typically $5 \ \mu m \times 3 \ \mu m \times 100 \ nm$: length × height × thickness. During FIB lift out processing, sample surfaces commonly experience some damage from the ion beam. To avoid mistaking beam damage for structural changes induced by the

BDD processing steps, protective layers of Pt and/or Al were deposited onto the surface of the laser micromachined BDD plate before lamellae were cut. Pt was deposited was by FIB, and Al was sputtered/evaporated onto the surface (MiniLab 060 Platform sputter/evaporator, Moorfield Nanotechnology) prior to FIB processing. The Al layer acts both as an additional/alternative surface protection layer, but also separates the BDD surface from the FIB deposited Pt layer. This is useful as FIB deposited Pt typically contains a high carbon content from the breakdown of the Pt precursor gas.⁴⁴ The presence of an sp² bonded carbon signature in the Pt lay may provide misleading information during mapping of the sp² bonded carbon in the BDD plate by EELS analysis.

The cross-section specimens were examined using conventional TEM in a JEOL 2100 LaB₆ and scanning TEM (STEM) using a double-aberration corrected JEOL ARM200F (Schotttky FE gun) equipped with a Gatan Quantum EELS Spectrometer, at an accelerating voltage of 200 kV. Samples were tilted so that the electron beam lay parallel to the interface between the regions of interest to minimise projection effects. Standard Spectrum Imaging (SI) methodology⁴⁵ was utilised for EELS data acquisition with a beam current of ~75 pA in a <0.1 nm probe, convergence angle of 16 mrad and a collection semi-angle of 25 mrad. EELS spectra were acquired from individual image pixels (size of pixel stated in text). Background subtraction, deconvolution, and subsequent analysis was carried out using standard routines found in Gatan's Digital Micrograph software. ADF and HAADF imaging was carried out at the same time as the EELS mapping. Both ADF and HAADF imaging detects electrons which have been scattered from the optical axis and as such both techniques are sensitive to atomic number (often called Z-contrast). However, HAADF imaging detects electrons which have been scattered to larger angles than ADF imaging. This makes HAADF more sensitive to Zcontrast and less susceptible to other mechanisms which can contribute to image contrast, such as diffraction.

4.3 Results and discussion

4.3.1 Assessment of laser micromachining and subsequent acid oxidation on the surface properties of BDD

It is widely understood that during laser cutting of synthetic diamond wafers, sp² bonded carbon is deposited onto the laser cut edges.^{27,46} Compared to sp³ bonded carbon (i.e., diamond), sp² bonded carbon electrodes typically have shorter solvent windows, higher background currents, and higher electroactivity for many redox processes, including ORR and OER. For many applications, it is desirable to remove this sp² bonded carbon material. To date, little is known about the exact nature of this material on a laser cut BDD surface, both prior to and post acid cleaning of a laser cut surface.

Figure 4.6 shows a cross section through the BDD surface after ns laser micromachining, imaged using the HAADF detector. Due to the small size of the lamella, compared to the grain size of the polycrystalline BDD (typically 10's of μ m), the region imaged is within a single grain, and no grain boundaries are visible in any of the images shown in this chapter.

Several distinct layers can be identified within the laser machined sample and are labelled in Figure 4.6 a. The bottom layer is the BDD plate, and the top layer is the FIB deposited protective Pt layer which appears white. Between the BDD and the Pt layers, two additional layers are visible, labelled I and II, which are clearly not Pt or BDD. The interface between layer I and II is not clearly defined. The difference in density of the BDD layer, layer I, and layer II, is reflected in the contrast difference in the HAADF image Figure 4.6 a. The brighter the image (i.e., BDD), the denser the material, as there is more scattering of the electron beam to larger angles. In contrast, the Pt layer appears brighter as a result of elemental contrast, where the higher Z-number and thus heavier atoms Pt appear brighter in the micrograph. The contrast difference between BDD layer, layer I, and layer II can be confidently attributed to density rather than Z-number as these regions only contain carbon and trace boron. The bright Pt layer can also be seen penetrating through layer II, indicating that this layer (and this layer alone) is deeply fissured.



Figure 4.6: a) HAADF STEM image with white rectangle indicating EELS spectrum image area, pixel size = 33 nm. b) EELS spectra of BDD (green), graphite (blue) and amorphous carbon (red), obtained from the BDD substrate, layers I and II respectively. Spectra have been scaled to fit the axis. c) Multilinear Least Squares fitting of the 3 spectra in b), showing the distribution of BDD, graphite and amorphous carbon.

The sp²/sp³ bonded carbon character of the BDD layer, layer I, and layer II was interrogated using EELS (over the area defined by the white box in Figure 4.6 a). Figure 4.6 b shows the averaged EELS spectra of each layer within this area, calculated at each individual pixel of 33 × 33 nm. The BDD layer (green line), layer I (blue line), and layer II (red line) are consistent with the spectra expected for diamond, graphite, and amorphous carbon, respectively. The peak observed at 285 eV in the EELS spectra of graphite (layer I) and amorphous carbon (layer II) is a result of a 1s $\rightarrow \pi$ * transition.^{47,48} This transition is only observed in sp² bonded carbon and thus indicates the presence of sp² character in these layers. Between 280 and 330 eV, the structure of the carbon K-edge is clearly different for each material type; this provides information regarding the local density of states which differs because of the different local bonding configuration of carbon atoms in each layer.⁴⁹

The EELS data can also be used to map out the spatial distribution of each carbon type (diamond, graphite, and amorphous carbon). This is achieved using multiple linear least squares (MLLS) fitting of the EELS spectra image (SI, the white box in Figure 4.6 a), using Gatan Digital Micrograph software. This is calculated by fitting the EELS spectrum at each pixel using a linear combination of the diamond, graphite and amorphous carbon spectra (Figure 4.6 b). The generated MLLS fit coefficients are then plotted in a false colour image (Figure 4.6 c) to show the distribution of each carbon phase (BDD in green, graphite in blue, and amorphous carbon in red) at the laser ablated surface.

Layer I, which is approximately 200 nm in thickness and sits directly on top of the BDD layer and is almost purely graphitic in nature (Figure 4.6 c). This layer is likely the product of a solid-solid phase transition of BDD to graphite that is induced during ns laser micromachining. High magnification BF-TEM imaging of the interface between the BDD layer and layer I (Figure 4.7) also reveals lattice fringes in layer I with a spacing of 0.34 nm (the distance between the basal lattice planes of graphite)⁵⁰, further supporting the EELS analysis. At the interface, both parallel and perpendicular orientations of the graphite layer are observed, with the perpendicular planes curving as the distance from the interface increases, into a hemispherical shape. Due to this curving, at further distances from the interface, the graphite planes are predominantly oriented at ~45° to the BDD over 100's nm; this suggests that crystallization occurs over relatively long timescales, much longer than individual ns laser pulses. In contrast, the BDD layer does not appear to show any preferential crystallographic orientation.

Looking back at the MLLS fit spatial orientation map (Figure 4.6 c) but now focusing on layer II, we see a gradual change from graphite to amorphous carbon over a distance of several hundred nm. This corresponds to the poorly defined interface between layer I and layer II (Figure 4.6 a). The top section of layer II is almost purely amorphous carbon. Layer II is a likely a product of



Figure 4.7: High magnification BF TEM image showing lattice fringes in layer I that confirm graphitic composition.

plasma phase re-deposition of carbon from the graphitic material, due to either sublimation or vaporisation,²² which is a common occurrence during laser ablation of diamond. In fact, the composition of all the damage layers observed here on highly doped BDD are comparable to those found on laser ablated undoped diamond, indicating that the boron content does not affect the damage mechanism.²²

An equivalent ns laser micromachined BDD sample was subjected to an oxidative acidic treatment (30 mins at ~200 °C in sulphuric and nitric acid), after which a cross section was again analysed by TEM. This procedure was chosen as it is a commonly adopted treatment for cleaning diamond samples.^{27,46} Figure 4.8 a shows a HAADF STEM image of a cross section through the BDD surface after ns laser micromachining and the oxidative

acidic treatment. This sample was prepared with an Al/Pt protective capping layer, as indicated in Figure 4.8 a. Between the BDD plate and Al layer, a thin dark layer with varying thickness (up to 40 nm in height) is seen, in contrast with layer I/II (up to a micron in height) seen in the sample that was not acid cleaned (Figure 4.6). The dark layer appears to be continuous cover the BDD surface with a minimum thickness of ~5 nm, with clusters where this material is thicker, up to 40 nm.



Figure 4.8: a) HAADF STEM image of ns laser micromachined BDD after acid cleaning, Inset: shows the MLLS fit using the diamond, graphite and amorphous carbon spectrum. b) EELS spectrum (pixel size = 5.9 nm) obtained from the graphite cluster (blue) and the spectrum from the amorphous shell (red). Spectra rescaled to plot on same axis. c) High resolution BF TEM image showing the graphite cluster with basal planes perpendicular to the BDD interface and a thin amorphous top layer. Inset shows the amorphous shell-graphite interface. d) BF TEM image showing the graphite-BDD interface.

Figure 4.8 b shows the averaged EELS spectra of each layer within the area defined with a white box in Figure 4.8 a, calculated at each individual pixel of 5.9×5.9 nm. MLLS fitting of the EELS data was again used to map out the spatial distribution within this area of carbon type. This shows the thick clusters are primarily comprised of graphitic carbon. The averaged EELS

spectra for the cluster (Figure 4.8 b, blue line) follows a similar shape to that of layer I in the previous sample (Figure 4.6 b, blue line). Further high magnification TEM imaging of these clusters (Figure 4.9) confirmed the structure as highly oriented graphite and revealed that they are oriented with the graphite basal plane perpendicular to the BDD surface. A number of clusters were imaged, and this observation was consistent throughout. This suggests that the orientation of the graphite with respect to the BDD surface is a key component in this material's ability to survive the oxidative acid treatment.

Due to the considerable difference in thickness of the new graphitic layer and layers I/II prior to the acid oxidation (Figure 4.6), it is clear that all of layer II (the amorphous and fissured carbon) has been completely removed. The remaining clusters are remnants of layer I (highly oriented graphitic carbon) that have survived the oxidative acid treatment. Crucially, it appears only perpendicularly orientated graphite clusters were able to survive. The MLLS fit also shows that these cluster are encapsulated by a thin shell of amorphous carbon (~5 nm in thickness, Figure 4.8 a inset). It is speculated that the amorphous shell forms as a result of the acid oxidative etch of the graphite (layer I). Again, this shell was observed for all clusters imaged and therefore it is believed to be responsible for these clusters withstanding complete removal by the oxidative acid treatment. To differentiate this material with other amorphous carbons, e.g., layer II which is fissured and etches easily in acid, from herein this will be referred to as diamond stabilised non-diamond carbon (DSC).

Using the approach of Bruley et al.,^{51,52} it is also possible to calculate the sp² bonded carbon fraction of each distinct region from the EELS spectra. The graphitic layer (layer I) from the ns laser micromachined sample (Figure 4.6) was used as a reference material for 100% sp². The encapsulating amorphous shell was found to be approx. 70% sp² bonded carbon, compared with the amorphous, fissured, carbon layer in Figure 4.6 (layer II) which was found to be approx. 80% sp² bonded carbon. Analysis of the thinner parts of the dark layer, between the thicker clusters, was inconclusive, and thus is speculated to also be DSC. Based on the TEM cross sectional images obtained, an approximate density of ~108 cm⁻² clusters was calculated.



Figure 4.9: Additional BF TEM images of graphite clusters on the BDD surface following the oxidative acid treatment.

The studies described herein on the differently treated BDD allow us to postulate the following steps for the transformation of carbon at the surface of BDD due to ns laser micromachining and oxidative acid cleaning, Figure 4.10. Of course, due to the structure of this graphitic cluster containing layer, it is the encapsulating amorphous shell of DSC that is in contact with the electrolyte solution, not the graphite itself. Whilst the robustness of this remaining layer towards complete removal by acid oxidation is somewhat surprising, producing this material will be really important for applications which require a robust and stable hybrid sp²-sp³ bonded carbon electrode.^{42,43,53} This is especially true of applications where oxidative environments are unavoidable,⁵⁴ or when positive potentials must be consistently applied. The latter is the case for EOP generation cells.



Figure 4.10: Schematic showing BDD processing and layers identified from TEM imaging of FIB lamellae produced at each stage. Not to scale.

4.3.2 BDD electrode optimisation for EOP

sp²/sp³ bonded carbon hybrid electrodes can be produced by deliberately incorporating sp² bonded carbon into the BDD during growth.^{16,25} This is a particular useful approach when adopting thin film BDD electrodes deposited onto a support mesh as no laser machining is required to create perforation. However, because the sp² bonded carbon content will be distributed throughout the BDD and not just at the surface, only relatively low levels can be incorporated before significant damage to the diamond character is noticed.¹⁶ Increasing the sp² bonded carbon content in the bulk material also raises stability concerns, especially considering the high potentials and long run times desired for EOP devices. Whilst previous work looked at changing CVD growth conditions to incorporate sp² bonded carbon into the BDD material, even the highest B/C ratio trialled is likely to have only achieved a low surface coverage of sp² carbon (<1%).^{16,25} To investigate the impact of sp² bonded carbon on EOP, the above laser machined, and acid treated hybrid material will be ideal, as the sp² bonded carbon content at the electrode surface can be easily manipulated from very low to high levels (up to 80% sp² bonded carbon herein). This is achieved by laser machining different perforated electrode geometry structures (or even the surface of the BDD). The laser machined surface contains sp² bonded DSC, whilst the bulk electrode material remains sp³ bonded BDD, resulting in a high sp² bonded carbon content electrode without loss of diamond properties.

Figure 4.11 shows the different BDD electrode designs employed in this study. As the Nafion® is compressed against the BDD surface, a perforated design was chosen (typically achieved with vertical slots) in order to enable solution to come into contact with both the BDD and Nafion®, an approach also used by others.^{18,19} All the BDD electrodes used had a diameter of 12 mm and thickness of 420 μ m, unless otherwise stated.



Figure 4.11: Geometries of all the EOP CVD BDD electrodes used in this section.

In order to calculate percentage of sp² bonded carbon in contact with electrolyte solution during EOP, the following definitions were used. In the EOP cells, the face of the BDD that is pressed against the Nafion® membrane (front face) is considered to be solution excluded, contacting the membrane only. The total accessible area of each electrode is therefore equal to the sum of the area of the wetted (back) face of the electrode plus the internal edge area of the laser micromachined slots (henceforth referred to as slot edge area), as described by equation (4.2):

$$Total accesible area = wetted face area (4.2) + slot edge area$$

The sp² bonded carbon content, expressed as a %, is calculated as a ratio of the slot edge area to the total solution accessible area \times 100, equation (4.3):

$$\frac{sp^2 \text{ bonded}}{carbon \text{ content}} = \frac{slot \text{ edge area}}{total \text{ accesible area}} \times 100 \quad (4.3)$$

Figure 4.12 shows a graphical representation of these areas. It is likely that the calculated sp² bonded carbon content will be a slight underestimate, as only the laser induced material is considered; sp² bonded carbon introduced into the BDD during CVD growth is ignored. However, the amount of the latter will be minimal compared to the amount of the former, and thus this approximation will not impact the conclusions drawn.





Table 4.1 lists the electrodes depicted in Figure 4.11 and shows their material thickness, sp^2 bonded carbon content (as calculated by equation (4.3)), solution accessible area (as calculated by equation (4.2)), and geometry.

	Thickness (µm)	sp ² bonded carbon content (%)	Solution accessible area (cm ²)	Geometry
а	420	5	0.57	1.4 mm ø hole
b	420	30	0.71	300 µm slots
с	420	40	0.78	300 µm slots
d	420	50	0.86	300 µm slots
е	420	60	0.67	600 µm slots
f	420	69	0.85	400 µm slots
g	420	70	1.01	300 µm slots
h	420	80	1.51	100 µm slots
i	420	H plasma	1.01	300 µm slots
j	200	53	0.64	300 µm slots
k	320	63	0.81	300 µm slots
I	700	80	1.49	300 µm slots

Table 4.1: Comparison of electrode properties and geometries all the EOP CVD BDD electrodes depicted in Figure 4.11.

In order to evaluated and compare the performance of EOP cells, two different metrics will be assessed: (1) the ozone output gradient, and (2) the peak current efficiency. The ozone output gradient (mg L⁻¹ A⁻¹, or mg L⁻¹ A⁻¹ cm²) is calculated by applying a least-squares linear fit of the applied current, or current density (in A, or A cm⁻², respectively), y axis, vs. measured ozone concentration (in mg L⁻¹), x axis, for three repeats. For all cells, the ozone concentration was measured in 0.1 A increments from 0.1 A to 0.6 A. As the electrodes differ in geometry and thus area, in some cases it is also necessary to normalise the applied currents with respect to the solution accessible area to compare across data sets. This is why current density is plotted on the y axis rather than current. A higher/steeper ozone output gradient means that for a given increase in current or current density more ozone is produced, and therefore the more efficient the cell is.

Current efficiencies (ϵ) were calculated using equation (4.4):

$$\varepsilon = 2 \times \frac{100 \times nF\nu C}{iM} \tag{4.4}$$

where *n* is the stoichiometric number of electrons transferred (n = 6),¹⁶ *F* is the Faraday constant in C mol⁻¹, *v* is the solution flow rate in L s⁻¹, *C* is the concentration of dissolved ozone in mol L⁻¹, *i* is the applied current in A, and *M* is the molecular weight of ozone in g mol⁻¹ of ozone.¹⁹ For each cell, the current efficiency was calculated at every applied current point in the calibration plot. The highest value was then chosen as the peak current efficiency, as is common in the literature.

Previous work on EOP has focused on cells which split the anode products (i.e., dissolved ozone) from the cathode products.^{16,19} This modality allows variation and optimisation of parameters for the anode and cathode separately (for example the supporting electrolyte and flow rates used) as the flow streams are isolated and do not mix. All the data presented in the thesis was collected by combining the anode and cathode product streams, although the EOP cell design does allow for separation of products. This setup was chosen as it is experimentally more facile and reflects combine product cells used currently in commercially available handheld EOP devices. As dissolved ozone is produced solely on the anode, combining the two flow streams dilutes the maximum ozone output of the cell by a factor of two. For this reason, a factor of two was introduced in equation (4.4) to account for this.

The overall results of this study are shown in Figure 4.13, with some example electrode geometries depicted. As the sp² bonded carbon content increases from 5% to 60%, a small increase is observed in the ozone output gradient (0.88 to 1.99 mg L⁻¹ cm² A⁻¹) and peak current efficiency (17.8% to 23.6%). From 60% to 80% the sp² bonded carbon content, however, increases more rapidly, with an increase in ozone output gradient from 1.99 (60% sp²) to 4.00 (80% sp²) mg L⁻¹ cm² A⁻¹. The peak current efficiency from 60% sp² bonded carbon content and above is relatively constant, indicating that 60% is a key threshold to hit for maximum efficiency. It is important to note here that the peak current data (Figure 4.13 b) does not take into account the different total accessible areas of each electrode (a result of the different geometries adopted to vary electrode sp² bonded carbon content). However, the ozone output



Figure 4.13: a) Ozone output gradient, normalised to electrode solution accessible area, in mg L^{-1} cm² A^{-1} and b) peak current efficiency versus the solution accessible sp² bonded carbon content of the perforated 420 μ m thick CVD BDD electrodes. Insets, schematics of some electrode geometries, schematics of all geometries can be found in Figure 4.11.

gradient data (Figure 4.13 a) does take this into account as the gradients are normalised for area, and the same trend is observed. This data clearly indicates the importance of sp² bonded carbon for EOP on BDD electrodes, with a ratio of around 60% sp² bonded carbon content a critical ratio for maximising efficiency of perforated BDD electrode EOP cells. Due to the nature of the perforated electrode geometry, achieving greater than 80% sp² bonded carbon content is challenging as removing more material to create the slots makes the electrodes increasingly fragile.

The peak current efficiencies achieved here were compared with those previously reported, given in Table 4.2. The peak current efficiency demonstrated here is only ~10 % lower than the highest value reported in the literature, 47%, achieved by Arihara et al. using freestanding perforated CVD BDD electrodes.¹⁹ However, note comparison of current efficiencies does not take into account changing experimental conditions.

The data indicates that a purely a sp² bonded carbon electrode material such as GC, should be very efficient for EOP. To investigate this further, an electrode with identical geometry to the 70% sp² bonded carbon content BDD electrode (Figure 4.11 g) was cut from 300 μ m thick GC (slightly thinner than the 420 μ m thick BDD) and an EOP calibration measurement made. However, the electrode was unable to complete a single calibration without sustaining

Table 4.2: Comparison of the peak current efficiency and maximum ozone concentrations achieved between the CVD BDD electrodes used in this work and other reported electrodes, where deionised water was used as the feedstock solution.

Anode (EOP) material	Cathode material	Cell design	Peak current efficiency (%)	[O₃] _{max} (mg L⁻¹)	Current for [O ₃] _{max} (A)	Flow rate at anode (mL min ⁻¹)	Ref
Freestanding perforated CVD BDD	Pt mesh	Zero gap cell with Nafion membrane	47	9	10	2000	19
Thin film CVD BDD deposited on perforated Si wafer	Thin film CVD BDD deposited on perforated Si wafer	Zero gap cell with Nafion membrane	42	8	5	1100	16
Freestanding perforated CVD BDD	Freestanding perforated CVD BDD	Zero gap cell with Nafion membrane	37	1.64	0.6	335	-
Thin film CVD BDD deposited on perforated Nb mesh	Thin film CVD BDD deposited on perforated Nb mesh	Zero gap cell with Nafion membrane	24	4.25	5	667	17
PbO ₂ deposited on multilayer perforated Ti mesh	Pt deposited on multilayer perforated Ti mesh	Zero gap cell with Nafion membrane with Pt deposited on cathode side	12	120	10	550	55
PbO ₂ deposited on perforated Ti mesh	Pt deposited on Nafion	Membrel water electrolyzer cell	15	30	30	833	56
Thin film CVD BDD deposited on Nb rod	Stainless steel wire	Nafion membrane and cathode wound around anode	7	6	0.75	40	20

substantial corrosive damage which was obvious to the naked eye (Figure 4.14). This again points to the stability of the DSC formed on the BDD surface after the laser cut and oxidative acid treatment.

The proposed mechanism for EOP, detailed in section 1.3.2, highlights the role of adsorbed hydroxyl and oxygen radicals. BDD electrodes are unique in that hydroxyl radicals are known to be very weakly absorbed on the electrodes surface, resulting in them being able to detach from the electrode with relative ease and react with species in solution.^{57,58} It is as a result of this property that



Figure 4.14: a) Photograph and b) optical microscope image of a 300 μ m thick GC electrode used as the anode in an EOP cell after half a calibration plot run, electrode operating for less than 10 minutes.

BDD electrodes are widely studied for advanced oxidation.⁵⁹ This radical detachment will result in a lower overall current efficiency as hydroxyl radicals no longer contribute to either ozone production or OER and instead react with solution components. It is therefore proposed that the inclusion of the DSC regions on the BDD electrode surface contains favourable sites for hydroxyl/oxygen radical absorption. This in turn results in a higher concentration of absorbed radicals, ultimately producing more ozone and becoming more current efficient.

BDD thickness was also investigated as a method of producing BDD electrodes with varying sp^2 bonded carbon content, without changing the electrode geometry. This removes any possible impact on ozone output and efficiency that may be a result of employing different electrode geometries. Perforated electrodes with 300 µm slots were cut from 200, 320, 420, and 700 µm thick BDD with resulting sp^2 bonded carbon content varying from 53-80%. Ozone output gradient and peak current efficiency data obtained for these electrodes is shown in Figure 4.15 (see Figure 4.11 and Table 4.1 for a full list of electrode thickness and sp^2 bonded carbon content).

Increasing the thickness of the slotted electrode from 200 to 700 μ m results in a linear increase in the ozone output gradient. This provides the case where the cell design and electrode geometry remain constant whilst the sp² bonded carbon content of the electrodes is increased, leading to improvements in EOP cell performance.



Figure 4.15: a) Ozone output gradient, normalised to electrode solution accesible area, in mg $L^{-1} A^{-1} \operatorname{cm}^{-2}$ and b) peak current efficiency versus the electrode thickness for a single perforated electrode geometry (inset). sp² bonded carbon content is also given for each electrode.

The peak current efficiency plot however follows a different trend, where all thickness but 420 μ m have similar efficiencies, with 420 μ m slightly higher (although also with greater error). The origin of these observations is likely because of the change in flow profile over the electrode as a result of the change in aspect ratio of the slots, which are 300 μ m wide in this design. This data suggests that although increasing the thickness is a valid way of increasing the sp² bonded carbon content a good rule of thumb is to have perforations of a similar width to the material thickness in order to prevent solution and gases becoming trapped on the electrodes surface.

This data is also interesting because it appears to disputes the triple-point theory discussed in current literature initially proposed by Kraft et.al.¹⁷ As discussed in section 1.3.2, the triple-point theory suggested that only the parts of the BDD electrode that are in contact with both the Nafion membrane and the solution are active for the generation of ozone. Since all four of the electrodes shown in Figure 4.15 have an identical slot length (and therefore triple-point length, which is 170 mm for this design), if this theory held, it would be expected that the ozone output gradient and peak current efficiency would be independent of material thickness; this is clearly not the case.

Although the data presented so far in this chapter strongly indicates the relationship between sp² bonded carbon content and EOP output/efficiency, it has so far been challenging to isolate this as the sole changing variable. For the data presented in Figure 4.13, the electrode geometry is also variable, and

for the data presented in Figure 4.15, the flow profile is also altered slightly. To isolate the effect of sp² bonded carbon content only and further substantiate these results, a 70% sp² bonded carbon BDD electrode cell was fabricated. To significantly reduce the sp² bonded carbon content, this electrode was subject to a hydrogen plasma treatment (Figure 4.11 i).^{60,61} In the plasma, hydrogen gas (H₂) decomposes to atomic hydrogen, which can easily react (with an activation energy of 7-9 kcal mol⁻¹, compared to 50-80 kcal mol⁻¹ for H₂) with sp² bonded carbon on to produced CH4 and thus preferentially etch the sp² bonded carbon from the BDD surface.⁶² Following the hydrogen plasma

The BDD electrode surface will be oxygen-terminated after the acid clean (an oxidative treatment), resulting in the presence of a variety of different functional groups on the sp^2 bonded carbon surface. This includes electroactive quinones; it has previously been shown QSC correlates with surface sp^2 bonded carbon content.²⁹ Thus, QSC measurements were made to verify the reduction in sp^2 bonded carbon (Figure 4.16). The incidence of the peak between 0.2 and 0.6 V in Figure 4.16 a indicates the presence of quinone surface groups, and thus sp^2 bonded carbon. After the hydrogen plasma treatment (Figure 4.16 b), the peak is scarcely observable, indicating the removal of the sp^2 bonded carbon. The hydrogen plasma treatment therefore produced a geometrically identical electrode, but with minimal sp^2 bonded carbon content.



Figure 4.16: Quinone response of the 70% sp² bonded carbon BDD electrode a) before and b) after hydrogen plasma treatment and acid clean.

The ozone output gradients and current efficiency achieved with this cell can then be compared to the 70% electrode with sp^2 bonded carbon present (electrodes i and g depicted in Figure 4.11 and Table 4.1), Figure 4.17. The electrode containing 70% sp^2 bonded carbon content significantly outperforms the H plasma treated carbon electrode in ozone output gradient and current efficiency. This data both validates the realised importance of surface sp^2 bonded carbon, and as with the varying thickness data (Figure 4.15), disputes the triple-point theory proposed by Kraft et.al.¹⁷ Once again, for the data given in Figure 4.17, the electrodes of both cells have the same slot length, and thus triple-point length (170 mm here), and exhibit different ozone output gradients (ozone concentration produced at each applied current value) and current efficiency. It therefore must be the entire internal slot area that contributes to the observed increase in EOP, and this is due to the presence of sp^2 bonded carbon, not geometric effects e.g., slot design, length, and material thickness.



Figure 4.17: a) Ozone output vs current for the 70% sp² bonded carbon and H plasma treated electrodes. b) Peak current efficiency versus current for both electrodes. Inset, schematics of both electrode geometries.

The 70% sp² bonded carbon content 420 μ m thick cell was then subjected to long term stability testing, by running at an applied current of 0.3 A for 20 h with the A side as anode and continually monitoring the UV absorbance measured, Figure 4.18 a. The large amounts of unavoidable spiking in the absorbance data is from the presence of ozone and oxygen gaseous bubbles in the flow system, produced during EOP. Over the 20 hour experiment, the UV absorbance (and thus dissolved ozone produced) measured (Figure 4.19 a)


Figure 4.18: UV absorbance at 258 nm over 20 hours with the A side as anode for the 70% sp² bonded carbon content electrode cell. The flow rate was $192 \pm 2 \text{ mL min}^{-1}$. Data was smoothed using a Savitzky-Golay filter with a points of window=500.

remains relatively constant, reflecting the long term operating stability of BDD electrodes.

A calibration plot was recorded both before the long term testing (Figure 4.19 a, black line), and again after (Figure 4.19 a, red line). No significant differences were observed, with both plots retaining good linearity with adjusted R² of 0.9823 and 0.9936 for before and after the 20 hours continuous run time, respectively. Likewise, the maximum concentration of dissolved ozone produced did not change considerably, at the maximum current applied of 0.6 A. The ozone output gradient (Figure 4.19 b) also remained relatively constant, with 2.6 ± 0.2 and 2.4 ± 0.1 mg L⁻¹A⁻¹ recorded before and after long term testing, respectively. The difference between these two values is minimal and lies within the usual errors noted in these cells when comparing data, for example, obtained on different days. Peak current efficiencies (Figure 4.19 c) of 29% and 25% before and after long term testing, respectively, were obtained. This slight reduction in performance would be acceptable for applications such as a handheld spray, where 20 hours is likely to be approaching the duration of use for the device's lifetime.



Figure 4.19: a) Ozone concentration and b) current efficiency for the 70% sp^2 bonded carbon content electrode cell before (black line) and after (red line) 20-hour testing. The flow rate was 329 ± 9 mL min⁻¹ before the long term stability testing, and 336 ± 2 mL min⁻¹ after. The A side of the cell operated as the anode.

This data demonstrates the long term stability and efficiency, with optimum performance maintained, of BDD electrodes for EOP. Again, this validates the hypothesis that the DSC layer produced on the BDD surface as a result of oxidative acid cleaning post-laser micromachining is incredibly robust in its constancy and attachment to the diamond. Consequently, these BDD electrodes have great potential to facilitate long product lifetimes, without performance drop off.

4.3.3 EOP on HPHT BDD compacted microparticle electrodes

As discussed in section 1.2.2 and chapter 3, producing conductive diamond electrodes via HPHT synthesis could provide a low cost, large scale fabrication method, unattainable with CVD synthesis. Freestanding, compacted HPHT BDD MP electrodes have yet to be realised as an alternative diamond electrode material. As the data presented in section 4.3.2 shows, it is the sp² bonded DSC laser machined surface that is responsible for the high output and efficiency for EOP demonstrated by perforated BDD electrodes. Because compacted HPHT BDD MP electrodes are a novel material, Raman spectroscopy was first utilised to investigate the nature of the compact surface before and after laser micromachining (Figure 4.20).



Figure 4.20: Raman spectra of the a) un-lasered and b) laser micromachined surfaces of a HPHT BDD MP compact electrode. Solid lines represent the surfaces as-lasered, and dotted lines represent the surfaces after acid cleaning.

As seen in section 3.3.1.1, the untreated compact surface (Figure 4.20 a, solid line) shows obvious signatures of highly doped BDD; a peak at ~550 cm⁻¹,⁶³ a slight red-shift in the diamond line (from 1332.5 cm⁻¹ to 1327.3 cm⁻¹),⁶⁴ and an asymmetry of this peak due to a Fano resonance.⁶⁵ Additional peaks at ~700 cm⁻¹ and ~1560 cm⁻¹ are observed, which can be attributed to sp² bonded amorphous carbon⁶⁶ and the *G* graphite peak, ⁶⁷ respectively. After acid cleaning (Figure 4.20 a, dotted line), a similar response is observed, with the 1200 cm⁻¹ BDD peak also now measurable.⁶³ However, the amorphous carbon peak can no longer been seen and the *G* graphite peak is reduced, indicating removal of sp² amorphous carbon from the compact surface during acid cleaning, as is observed with CVD BDD (section 4.3.1).

The lasered compact surface (Figure 4.20 b, solid line) also shows the amorphous carbon peak at ~700 cm⁻¹, along with very intense and broad peaks at ~1560 cm⁻¹ and ~1360cm⁻¹, the *G* and *D* graphite peaks,⁶⁷ which dominate and obscure the diamond line. Now the response after acid cleaning (Figure 4.20 b, dotted line) is notably different. The BDD peaks, diamond line, and Fano resonance are clearly visible, with the graphite *D* peak no longer observed and the graphite *G* peak minimised.

This data suggests that laser micromachining and acid cleaning treatments effect the surface of compacted HPHT BDD MP electrodes in a very similar way to CVD BDD electrodes. Laser micromachining introduces a large amount of sp² bonded carbon to the surface, which can be largely removed by oxidative acid cleaning, leaving a thin layer of robust DSC intimately bonded to the BDD. Similar TEM/STEM/EELS studies to those presented in section 4.3.1 could also be undertaken for the compacted HPHT BDD MP electrode material to confirm the presence of DSC.

For the experiments presented herein, an EOP cell with HPHT compacted BDD electrodes was compared against an analogous CVD BDD electrode cell. The exact same electrode geometry was used (see section 4.2.1. for details, also shown in the inset of Figure 4.21), designed to have >70% sp² bonded carbon, calculated according to equation (4.3). As the thickness of the two materials differs slightly (500 μ m for the HPHT electrodes compared to 420 μ m for the CVD electrodes), there was a minor difference in the resulting sp² bonded carbon, whilst the CVD electrodes contained 79% sp² bonded carbon.

Figure 4.21 details the BDD surface finishes used for both cells and their positions in the final cell assemblies. These final positions allowed investigation of the impact of surface roughness of the Nafion® facing BDD electrode surface on EOP cell performance.

Figure 4.22 shows a typical compacted HPHT BDD freestanding perforated electrode containing eight slots of 300 μ m diameter and of varying lengths. Importantly, as Figure 4.22 a shows, the HPHT compaction conditions employed were sufficient such that the material did not fall apart during the lasering process. Figure 4.22 b displays the concentration of dissolved ozone produced for both the HPHT cell (red line) and the CVD cell (blue line), in water, for applied currents in the range 0.1 to 0.6 A. Also shown in Figure 4.22 c are the corresponding current efficiencies for both cells over the same current range.



Figure 4.21: a) Schematic (not to scale) to show cross-sectional view through the cell, and electrode surface positions in each half cell. Inset shows BDD electrode geometry, scale bar is 5 mm. White light interferometry measurements of the BDD electrode surfaces and their positions in b) the HPHT cell, where i, ii and iv) are lapped faces, RMS: $3.4 \,\mu\text{m}$ and iii) is an "ascut" face, RMS: $6.1 \,\mu\text{m}$, and c) the CVD cell, where i) is a polished growth face, RMS: $6.5 \,\text{nm}$, ii) is a lapped nucleation face, RMS: $560 \,\text{nm}$, iii) is an "asgrown" face of unprocessed CVD, RMS: $15 \,\mu\text{m}$, and iv) is a nucleation face of unprocessed CVD, RMS: $99 \,\text{nm}$. Scale bar in b) and c) i-iv) is $200 \,\mu\text{m}$.



Figure 4.22: a) Photo of the compacted HPHT electrode laser cut into the desired geometry and adhered into a half cell. Also evident is the tab onto which electrical contact is made. Plots show, b) dissolved ozone concentration versus applied current (n=3) and c) current efficiency vs. applied current (n=3) for the A (lapped) side anode of the CVD BDD electrode cell (blue line) and the A (lapped) side anode of the HPHT BDD electrode cell (red line). The flow rates were 335 ± 4 and 302 ± 6 mL min⁻¹ for the CVD and HPHT cells, respectively.

For both cells, the amount of ozone generated can be seen to increase linearly as the applied current is increased, with ozone output gradients of 3.13 ± 0.06 and 2.23 ± 0.07 mg L⁻¹ A⁻¹ for the CVD and HPHT cells, respectively. The calibration plots for both cells show very good linearity, with an adjusted R² of 0.9945 for the CVD cell and 0.9882 for the HPHT cell. For the CVD cell, a maximum of 1.64 ± 0.03 mg L⁻¹ dissolved ozone was produced, at the highest applied current of 0.6 A, compared to the HPHT cell where a slightly lower maximum of 1.17 ± 0.07 mg L⁻¹ was produced. The small difference is most likely due to the lower resistivity of the CVD electrodes (ca. 60 m Ω cm),²⁶ compared to the higher resistivity HPHT electrodes (ca. 520 m Ω cm).²⁸ In the CVD material the grains inter-grow during synthesis forming a non-porous material, resulting in good electrical connectivity. In contrast, HPHT compaction can lead to the presence of voids both between neighbouring particles within the material, and at the surface of individual particles.²⁸

The current efficiency (ε) of the ozone generation process was again calculated using equation (4.4). Figure 4.22 c compares the current efficiencies between the HPHT and CVD cells for the different applied currents. For both, the current efficiency increases linearly with applied current from 0.1 to 0.3 A, at which point the ozone output gradient decreases and current efficiency begins to plateau. Between 0.4 and 0.6 A, the rate of increase in current efficiency with further applied current is significantly reduced, with a maximum efficiency of 37% and 23% reached for the CVD and HPHT cells, respectively.

As in section 4.3.2, calibration plots and current efficiencies were also measured before long term stability testing for both the CVD (Figure 4.23) and the HPHT cells (Figure 4.24), with the B side connected as the anode, and both sides compared. Whilst the A sides were lapped, the B sides were either "asgrown" (CVD) or "as-cut" (HPHT) and therefore considerably rougher (Figure 4.21 for RMS values). This enabled the effect of surface roughness on the ozone output gradient and current efficiency to be assessed. As shown in Figure 4.23 a and Figure 4.24 a for CVD and HPHT electrodes respectively, the ozone output gradients are identical, within error, for both CVD (lapped) = $3.13 \pm 0.06 \text{ mg L}^{-1} \text{ A}^{-1}$ compared with CVD ("as-grown") $3.21 \pm 0.10 \text{ mg L}^{-1} \text{ A}^{-1}$ ¹ and HPHT (lapped) = 2.23 ± 0.07 mg L⁻¹A⁻¹ compared with HPHT ("as-cut") = 2.24 ± 0.08 mg L⁻¹A⁻¹. With regards to current efficiency (Figure 4.23 b and Figure 4.24 b), the trends observed are also very similar. Though the smoother surface in the CVD cell shows marginally higher current efficiencies, the reverse is true for the HPHT cell, and thus no obvious dependence of cell performance on electrode surface roughness was observed. This is in contrast with current literature which suggests the contact area between the Nafion® and the electrode should be maximised for optimal ozone output.^{17,19}



Figure 4.23: Plots to show a) dissolved ozone concentration and b) current efficiency vs. applied current for the A (light blue) and B (dark blue) side anode (where the A side BDD electrode is lapped and the B side BDD electrode is "as-grown") for the CVD BDD electrode cell. The flow rate for the CVD BDD cell was $335 \pm 4 \text{ mL min}^{-1}$.



Figure 4.24: Plots to show a) dissolved ozone concentration and b) current efficiency vs. applied current for the A (red) and B (dark red) side anode (where the A side BDD electrode is lapped and the B side BDD electrode is "as-cut") for the HPHT BDD electrode cell. The flow rate for the HPHT BDD cell was $302 \pm 6 \text{ mL min}^{-1}$.

Both CVD and HPHT EOP cells were subject to long term stability testing, with the A sides functioning as the anodes, by running at an applied current of 0.3 A for 20 h and continually monitoring the UV absorbance measured, Figure 4.25 a (CVD) and Figure 4.25 b (HPHT). As discussed in section 4.3.2, the spiking in the absorbance data is an unavoidable consequence of bubbles in the system as ozone and oxygen is produced. However, it is possible to gauge average ozone output over time, as indicated by the solid lines in Figure 4.25 a and b generated by smoothing the data using a Savitzky-Golay filter with a smoothing window length of 500 points. Due to the heavy influence of chosen smoothing parameters on this data, these values should only be considered qualitatively where the trend over time is considered. For the CVD and HPHT BDD cells, the UV absorbance, and thus dissolved ozone concentration appear constant over the 20 hours, reflecting the long term operating stability of BDD electrodes.

Following the 20 h long term stability tests, ozone output calibration plots were again recorded (Figure 4.25 c) and compared to those recorded prior to long term testing (Figure 4.22 b), again with the A side functioning as the anode for both the CVD (red line) and HPHT (blue line) cells. For both, the ozone output gradients of the fitted calibration data were largely unaffected by the 20 hour run time i.e., for HPHT 2.23 \pm 0.07 mg L⁻¹ A⁻¹ (before) versus 2.30 \pm 0.08 mg L⁻¹ A⁻¹ (after) and for CVD 3.13 \pm 0.06 mg L⁻¹ A⁻¹ (before) versus 3.09 \pm 0.08 mg L⁻¹ A⁻¹ (after). Both CVD and HPHT calibration plots recorded after the long term stability test had excellent linearity, with adjusted R² values

of 0.9882 and 0.9817, respectively. For the CVD cell, a slight increase in the ozone output was observed, with the maximum dissolved ozone produced at 0.6 A increasing to 1.84 ± 0.07 mg L⁻¹ compared to 1.64 ± 0.03 mg L⁻¹. For the HPHT cell, the maximum ozone output of 1.19 ± 0.09 mg L⁻¹ at 0.6 A remained the same, within error. The data in Figure 4.25 a and b demonstrates that the robustness and long term EOP performance properties of the HPHT electrodes have not been impaired by the compaction process and compete favourably with the CVD electrodes. The long term stability of the CVD electrodes is also in agreement with the data collected for the 12 mm CVD electrodes used in section 4.3.2.



Figure 4.25: a,b) UV absorbance at 258 nm over 20 hours with the A side (lapped) as anode for the a) CVD BDD electrode cell and b) HPHT BDD electrode cell. The flow rates were 194 ± 1 and 193 ± 1 mL min⁻¹ for the CVD and HPHT cells, respectively. Data was smoothed using a first order polynomial Savitzky-Golay filter with a smoothing window length of 500 points. c,d) Plots to show, after long term stability testing, c) dissolved ozone concentration and d) current efficiency vs. applied current for the A (lapped) side anode for the CVD BDD electrode cell (blue line) and the HPHT BDD electrode cell (red line). The flow rates were 324 ± 4 and 304 ± 1 mL min⁻¹ for the CVD and HPHT cells, respectively.

Figure 4.25 d shows the current efficiencies of both cells, calculated using X, after long term testing. The current efficiency of the HPHT cell is very similar to that observed pre-long term testing (Figure 4.22 c), across the current range investigated. Again, a maximum current efficiency of 24% is obtained at 0.6 A. Interestingly, for the CVD cell, a change in response is observed. Whilst the maximum current efficiency achieved at 0.3 A is similar, 37% before long term testing, 43% after, we now observe a fairly constant current efficiency throughout the full range of applied currents. However, as the maximum current efficiency, ozone output gradient, and maximum ozone outputs remain the same, we do not believe this change in response reflects a significant difference in electrode behaviour, especially as it is only observed on one side of the CVD cell.

Measurements were also recorded after the long term tests but now with the rougher B side electrode functioning as the EOP anode for the CVD cell, Figure 4.26, and for the HPHT cell, Figure 4.27. A small difference was observed between the ozone output gradients when both A and B electrodes in the CVD cell were operated as the anode, with gradients of 3.09 ± 0.08 and 3.85 ± 0.07 mg L-1 A-1, respectively (Figure 4.26 a). For the HPHT cell, the ozone output gradients for both A and B electrodes functioning as the anode were again very similar (Figure 4.27 a). The current efficiency plots followed slightly different shapes (Figure 4.26 b and Figure 4.27 b); however, the maximum recorded current efficiencies were not significantly different between the A and B sides of each cell. It is not clear what caused the difference in gradient when the CVD A and B electrodes were operated as the anode after long-term testing. Some possible causes are degradation of one of the electrical contacts of the BDD electrodes. degradation of the Nafion[®] membrane, а surface roughness effect, or a combination of all these factors. Due to the limited data set combined with the large number of variables that can affect cell performance, it is complicated to elucidate the exact cause of this difference. As this difference was not observed prior to long-term testing, and only for the CVD cell after long-term testing, it is unlikely that electrode surface roughness plays a significant role in cell performance. All of the UV absorbance data used to calculate dissolved ozone concentrations throughout this section is given in Figure 4.28.



Figure 4.26: Plots to show, after long term stability testing, a) dissolved ozone concentration and b) current efficiency vs. applied current for the A (light blue) and B (dark blue) side anode (where the A side BDD electrode is lapped and the B side BDD electrode is "as-grown") for the CVD BDD electrode cell. The flow rate was 324 ± 4 mL min⁻¹.



Figure 4.27: Plots to show, after long term stability testing, a) dissolved ozone concentration and b) current efficiency vs. applied current for the A (red) and B (dark red) side anode (where the A side BDD electrode is lapped and the B side BDD electrode is "as-cut") for the HPHT BDD electrode cell. The flow rate was $304 \pm 1 \text{ mL min}^{-1}$.



Figure 4.28: UV absorbance spectra for the a-d) CVD BDD electrode cell and e-h) HPHT BDD electrode cell. Spectra were recorded prior to long term stability testing (a,b,e,f) and after long term stability testing (c,d,g,h), for both the A side (a,c,e,g) and B side (b,d,f,h) anode (where the A side BDD electrode is lapped and the B side BDD electrode is "as-grown" (CVD) or "ascut" (HPHT)).

4.4 Conclusion

In this chapter, freestanding compacted HPHT BDD MP electrodes have been used for EOP. Dissolved ozone was produced continuously for 20 hours of generation with no loss of performance. Compared to refined CVD BDD electrodes, the HPHT BDD electrodes only performed at a slightly lower ozone output and efficiency, which is an incredibly achievement considering the infancy of this material. Given the high volume production capacity of HPHT BDD, this work paves the way for the use of compacted HPHT BDD electrodes especially for electrochemical applications where large product volumes or large area electrodes are required.

To further understand the nature of EOP on BDD electrodes, TEM/STEM/EELS was used to nanoscopically interrogate the laser micromachined BDD surface, a technique employed to produce the perforated electrode geometries employed for EOP. It was demonstrated that laser micromachining produces an unstable sp² bonded carbon layer ~200 nm thick, which upon subjection to acidic oxidative cleaning treatments is transformed into a robust ~5 nm thick layer of DSC. This DSC layer has been shown to survive highly oxidative acid treatments and is robustly attached to the diamond lattice making it useful for long term use in EOP applications.

Further EOP studies confirmed the importance of sp² bonded carbon incorporation in perforated electrode BDD in EOP cells. Adding large amounts of sp² bonded carbon to an electrodes surface serves to increase its ozone output by four times, compared to diamond with only sp² bonded carbon created from growth present. The addition of this sp² bonded carbon also results in the current efficiency doubling from 18 to 36%, demonstrating significantly more efficient EOP is possible with sp² bonded carbon present. Our 70% sp² bonded carbon cell demonstrates a peak current efficiency of 30%, which is on par with those seen in previous BDD-EOP literature.

The reason for this increase in output and efficiency is due to the increased strength of bonding of OH and O radicals to sp² bonded carbon versus the purely sp³ bonded carbon in BDD. This increased binding strength increases binding time, and therefore radical density on the surface, ultimately resulting in a higher ozone production. The biggest value of this work is in the additional understanding of the importance of sp² bonded carbon on EOP on BDD. While

the cells built and tested are undoubtedly on a lab scale, the understanding of how to efficiently integrate sp² bonded carbon and treat it to form the highly robust DSC into BDD will no doubt assist in further BDD EOP optimisation work.

4.5 References

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5 Development of electron beam transparent BDD substrates for combined EC-TEM

5.1 Introduction

Commercial TEM grids consist of a thin (10-30 nm thick) film of amorphous sp² bonded carbon floated over a support grid, usually made from metal.¹ Carbon is an adventitious support material for TEM studies as it is low scattering so high resolution imaging can be achieved. It is also conductive, which is particularly beneficial for EC-TEM experiments where the grid is used both as the WE and as a support for imaging.

Sp² bonded carbon nanomaterials are also commonly employed as electrocatalyst supports in PEMFCs, and thus TEM imaging on carbon supports is especially desirable. For in depth mechanistic studies, IL techniques can be utilised, whereby a finder TEM grid is used to relocate a specific position or nanostructure. The advent of IL-TEM, though not without its challenges, has allowed the monitoring of single NPs during electrocatalysis and electrodeposition processes.^{2–4}

In the simplest approach, electrochemistry is performed on the TEM grid by dipping into electrolyte solution, with TEM imaging to examine the carbon film performed post-EC.^{5,6} However, this means the metal support grid is also immersed in solution and acting as the WE too which can cause contamination and inadequate results. Bespoke TEM grid holders and SECCM have been employed to circumvent such problems but can be challenging and not appropriate for all EC-TEM studies.^{7,8} Real time combined EC-TEM measurements can be carried out using *in-situ* electrochemical cells. Again, experimental problems are fairly common and electron beam scattering from the electrolyte solution means that atomic level resolution is yet to be achieved.^{9–12}

Although sp² bonded carbon has been widely used with great results, it does have some drawbacks as both an electrocatalyst support, and as a TEM support. For EC studies, the carbon support can electrochemically corrode at oxidising potentials. Prolonged TEM imaging in one location can also results in damage to the carbon film from the high energy electron beam.^{13,14} For thermal studies, the influence of interactions between the nanostructure and the carbon film must also be considered.¹⁵

BDD is an interesting alternative to sp² bonded carbon, as the sp³ bonded carbon results in high mechanical strength, and both chemical and electrochemical corrosion resistance. BDD is an ideal electrocatalyst support material due to its low capacitance and slow kinetics for electrocatalytic processes such as water electrolysis and oxygen.¹⁶ BDD has yet to be realised as an EC-TEM substrate due to the lack fabrication methods that can produce electron beam transparent (~10 to 100 nm thick) BDD in a robust, handleable format. In this chapter, novel procedures for the production of freestanding BDD EC-TEM substrates will be explored.

5.2 Experimental

5.2.1 PIPS method

The first methodology presented to produce BDD EC-TEM substrates adopts argon ion polishing using a precision ion polishing system (PIPS). In brief, bombardment of the BDD surface by the Ar⁺ beam slowly removes carbon atoms until electron beam transparent thinness of the BDD is achieved.

Where commercial TEM grids were used for comparison, amorphous carbon (sp²) film on 300 mesh copper or gold supports (Agar Scientific Ltd., UK) were used, and subjected to the same procedures as the BDD substrates, unless otherwise stated.

5.2.1.1 BDD EC-TEM substrate fabrication

Initially, freestanding polycrystalline BDD was synthesised using MWCVD, provided by Element Six Ltd., Oxford, UK. The material was suitably doped with boron (boron dopant level $>10^{20}$ B atoms cm⁻³) to ensure "metal-like" electrical conductivity is observed.¹⁶ The BDD was grown on a silicon wafer to a suitable thickness for it to be removed from the wafer as a freestanding BDD material.¹⁶ The surface was mechanically polished on both faces using the scaif method, to thin the material to a thickness of ~ 50 µm, with both sides showing a surface roughness finish of *ca*. nms on the surface of a grain (grain size *ca*. 2-8 µm), determined using AFM.¹⁷

The BDD wafer was then cut into disks of 3 mm diameter (suitable for insertion into the TEM holder) using laser micromachining and acid cleaned (immersed in concentrated H₂SO₄ at ~200°C saturated with KNO₃ for 30 mins, followed by rinsing with water before cleaning for 30 minutes in concentrated H₂SO₄ at ~200°C¹⁸) to remove machining debris. The material is thin enough such that it can be suitably handled for further processing, but not too thin that it curls up on itself. For EC-TEM applications, particularly where repeated EC and/or TEM experiments are required, ease of handling substrates is imperative. Naturally, when a support material reaches the thinness necessary for electron beam transparency, fragility becomes an issue.

The BDD rounds were argon ion polished to electron beam transparency using a GATAN PIPS. Due to the nature of PIPS milling, as described further in the succeeding paragraphs, the outside edges of the BDD EC-TEM substrate will remain ~ 50 μ m thick, and thus can be handled with no need for a secondary support structure. The BDD disk was mounted on a post support using glycol-phthalate bonding wax (Agar Scientific), allowing continuous milling as the sample rotated.

The bulk milling was carried out at an accelerating voltage of 6 kV and at an angle of incidence of $\sim 5^{\circ}$ from the top side of the disk. The highest accelerating voltage is used initially to produce the fastest milling rate to remove the bulk of the BDD. It is important to note that whilst milling at a high accelerating voltage, surface steps develop. A higher angle on incidence will remove material more quickly but at a steeper gradient resulting in a smaller region of electron beam transparent material produced - 5° was chosen as a middle ground. Each side of the BDD round was milled in turn (approx. 2-4 hours each side) until a small hole (ca. 50 - 150 µm in diameter) was formed in the centre of the BDD disk. This leaves a very thin area of BDD around the hole edge which has been milled to electron beam transparency. Typically, this was achieved by milling for 2.5 hours on one side, flipping the BDD disk and milling for 2 hours on the other side, and then milling for 15 minute intervals until light transmission through the centre of the BDD disk is visible i.e., a hole has formed. As the size of this hole increases with further milling, the size of the electron beam transparent area decreases, thus it is vital to stop milling as soon as the hole is formed (hence why shorter mill times are employed after bulk milling).

Following hole formation, the disk was then mounted in a clamp support for a final low energy polish of both sides of the disk simultaneously. This was achieved with a modulated ion beam at an accelerating voltage of 2 kV and an angle of incidence of ~4° from both the top and the bottom of the disk for 30 minutes to provide a smooth surface finish. This final step polishes away the surface steps introduced during the bulk milling leaving a smooth, electron beam transparent region surrounding the central hole. A lower angle of incidence is also used to maximise the size of the electron beam transparent region. It is important to note that the milling procedure detailed here results in the outer edges of the BDD disk remaining 50 μ m thick for ease of handling. To ensure removal of any salt contamination and oxygen termination of the surface, the BDD EC-TEM substrate was subjected to an acid clean following the ion milling, following the acid cleaning procedure previously described.

To make a good electrical contact to the BDD EC-TEM substrate for use an electrode, the BDD surface must be roughened. Typically this was achieved by laser micromachining the upper quarter of one of the edges, before acid cleaning (as previously described) to remove machining debris. A conductive layer must then be applied to the roughened area. Most commonly, a Ti (10 nm)/Au (400 nm) contact was sputtered (Moorfield MiniLab 060 Platform) onto the roughened area, followed by annealing the BDD EC-TEM substrate for 5 hr at 400 °C in air to create an ohmic contact. Alternatively, a C or Ag containing conductive ink (compatibility with the desired solvent for electrochemical experiments must be considered) can be instead hand painted onto the roughened area and left to dry according to the manufacturer's instructions. A glass slide can be placed over the bulk of the substrate during this process to minimise potential contamination from the conductive ink to the thin area of the BDD EC-TEM substrate. A Ti/Au sputtered contact must be removed by acid cleaning the BDD EC-TEM substrate, whereas a C/Ag ink contact can be easily rinsed off the substrate with common solvents. For the data presented herein, a total ground carbon conductive pen (MG Chemicals) was used to apply C contacts. Though not explored in this thesis, different geometries and sizes of roughened areas could be used. C/Ag/Au can be reapplied after many acid cleans to regenerate the contact and reuse the BDD substrate. After the Ti/Au contact has been removed by acid cleaning, a TiC layer may remain on the substrate. This can be removed by further laser micromachining; however, it must be considered that each time this process is applied to the substrate, BDD is removed, and the roughened area will get thinner and easier to break.

5.2.1.2 Electrochemical measurements

CV was carried out using a three-electrode setup controlled by a potentiostat (Ivium, Compactstat potentiostat, Holland) with a SCE (CHI150, IJ Cambria Scientific) used as a RE, and a Pt coil electrode as the CE. The BDD electrode was connected with a metal clamp to the Au contact and carefully dipped into the electrolyte solution using a micropositioner, ensuring that the hole was fully immersed in solution whilst the Au contact remained dry (Figure 5.1). It is important to ensure that the contact is not immersed into solution, regardless of contact type. All potentials stated are given with respect to the RE. After any electrochemical process, the BDD electrode was rinsed by gentle dipping in water and left to dry in a desiccator and then stored under vacuum before TEM imaging. For comparison with an unmilled BDD surface, a threeelectrode droplet cell setup was used (as previously utilised¹⁹ and described in full in section 3.2.5) with a 1 mm diameter circular area of the BDD exposed as the WE, an Ag/AgCl RE (DRIREF-2SH, saturated KCl, World Precision Instruments), and a Pt coil CE. A fresh 200 µL droplet of electrolyte solution was placed on the electrode surface for each measurement.



Figure 5.1: Schematic to show electrochemical setup. Inset shows schematic of milled BDD EC-TEM substrate with Au band that functions as an ohmic contact. Not to scale.

Solvent window and capacitance measurements were run in 0.1 M KNO₃ at a scan rate of 0.1 V s^{-1} . The electrode response for the fast redox couple $\text{Ru}(\text{NH}_3)_{6^{3+/2+}}$ was also investigated by recording CVs of 1 mM Ru(NH₃)₆Cl₃ in 0.1 M KNO₃ at a scan rate of 0.1 V s⁻¹. Solvent windows are defined for a geometric current density of ±0.4 mA cm⁻².

For long term electrochemical stability testing in acidic media, CV was conducted with a scan rate of 50 mV s⁻¹, for a total of 500 cycles from -0.20 to +1.05 V vs SCE, in 0.5 M sulphuric acid, following the approach of Abruña et al.⁴ This approach is designed to mimic the electrochemically corrosive environment of a PEMFC during start up and shut down conditions, which are known to corrode the electrocatalyst layer.

For investigating the *in-situ* TEM heating of manganese oxide, deposition was achieved a deposition time of 50 seconds at a deposition potential of +1.5 V (Ivium, Compactstat potentiostat, Holland). The manganese oxide electrochemical deposition solution was prepared from manganese chloride (MnCl₂, 0.1 M, Acros Organics) with potassium chloride (KCl 99%, 0.1 M,

Sigma Aldrich) as a supporting electrolyte, and acidified with hydrochloric acid (HCl 37%, 0.01 M, Sigma Aldrich).

5.2.1.3 Surface characterisation

The roughness of the surface before and after ion milling was measured by AFM (Innova AFM, Bruker, USA) at a scan rate of at a scan rate of 0.25 Hz in tapping mode. WLI profiles were also recorded (with a \times 50 magnification objective lens). For both AFM and WLI measurements, data analysis and visualisation was performed, and the surface roughness and depth profiles calculated, using Gwyddion 2.55.²⁰ Contact angle measurements were recorded using a Drop Shape Analyser (DSA100E, Krüss Scientific, Germany) with a water droplet of 50 µL. Measurements were recorded in triplicate, with the surface dried carefully inbetween using a lint free tissue. For the BDD sample, the disk was only PIPS milled on one side to produce a milled surface but without a hole (which would affect the wetting observed if contacted by the droplet).

FE-SEM was used to image a BDD EC-TEM substrate. Images were recorded using the in-lens, SE2, and STEM detectors on a Zeiss Gemini FE-SEM 500 (Zeiss, Germany) operating at 20 kV. TEM imaging on BDD EC-TEM substrates was carried out using JEOL JEM 2100 (LaB₆) at 200 kV. In-situ heating was also achieved using JEOL JEM 2100 (LaB₆) at 200 kV with a double tilt heating holder (model 652, Gatan Inc., US). The BDD EC-TEM substrate was heated in 50°C increments until crystallisation was observed (400°C). For long term electrochemical stability testing in acidic media, a BDD EC-TEM substrate was mapped around the hole edge using a double-corrected JEOL ARM 200F TEM, equipped with a Gatan Quantum spectrometer, operated at 200 kV. Multiple areas were selected, and ADF images were taken and compared before and after an electrochemical cycling. Electron energy loss spectroscopy (EELS) spectra were recorded during STEM imaging to estimate the change in thickness, if any, of the BDD EC-TEM substrate. EELS spectra were recorded with a probe convergence semi-angle of 32 mrad and a spectrometer semi-collection angle of 25 mrad, and a dispersion of 0.25 eV per channel. The energy resolution of the EELS measurements was 1.8 eV, as estimated from the full-width-half-maximum of the zero-loss peaks.

X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Analytical Axis Ultra DLD spectrometer with a monochromated Al K α X-ray

source (1486.69 eV) in a chamber with a base pressure below 1 x 10^{-10} mbar. Samples were mounted on to the sample bar using electrically conductive carbon tape. High resolution C1s spectra were collected using a pass energy of 20 eV (resolution of approximately 0.4 eV). Data from the BDD EC-TEM substrate were collected using an analysis area with a 55 µm diameter, to probe as close to the hole edge as possible. For the control sample (mechanically polished unmilled BDD), the data were acquired using a spot size of 110 µm diameter in order to increase the overall count rate, and two C1s spectra were obtained using a collection angle of 90° and 30° respectively. In order to investigate the different carbon chemical environments at the electrode surface, all data collected were fitted in CasaXPS using Lorentzian–Gaussian lineshapes and Shirley backgrounds, with asymmetry included for the sp² C-C peak.

5.2.2 Electrochemical etch method

The second methodology presented to produce BDD EC-TEM substrates adopts an electrochemical etch method. The generation of thin and uniform (intrinsic/undoped) diamond membranes is of great interest for optical, quantum and electronic device applications. A promising technique that has been proposed involves sub-surface ion implantation followed by annealing to convert the damaged diamond layer to graphitic carbon, followed by a graphite removal process, then diamond membrane lift-off.^{21–25} Electrochemical etching has been employed as a way to remove the damaged graphitic layer.^{22,23} This makes use of electrochemically generated radicals, and other oxidising species, from high conductivity solutions, at electrodes placed either side of the sample. It follows that a comparable synthesis route could be used to lift-off thin membranes of BDD, which could then be used as EC-TEM substrates.

The development of this novel synthesis route is very much still in its infancy; preliminary data is presented in this thesis, and further work will continue to optimise fabrication and demonstrate the suitability of lift-off BDD membranes as EC-TEM substrates.

5.2.2.1 BDD EC-TEM substrate fabrication

Polycrystalline electro-processing grade CVD BDD (490 µm thick, boron dopant level >10²⁰ B atoms cm⁻³, Element Six Ltd., Oxford, UK) with the front face mechanically polished to ~nm roughness, and the rear face lapped to ~µm roughness, was cut into a disk of 3 mm diameter (suitable for insertion into the TEM holder) using laser micromachining. The disk was then acid cleaned as previously described to remove machining debris. A 3 mm diameter support frame was also cut, with the same laser micromachining parameters, from a thinner wafer of polycrystalline BDD (70 µm thick, boron dopant level >10²⁰ B atoms cm⁻³, Element Six Ltd., Oxford, UK) with the front face mechanically polished to ~nm roughness, and the rear face lapped to ~µm roughness. The frame was glued onto the polished face of the BDD disk with a minimal amount of green overcoat epoxy (CircuitWorks Epoxy Overcoat, Chemtronics); this was achieved by applying epoxy to the frame, removing excess epoxy by blotting with filter paper, then placing the frame on top of the disk and pressing gently to adhere.

The polished face, with the frame adhered on top, was then implanted (Ion Beam Centre, University of Surrey, UK) with 2×10^{16} carbon atoms (@ 2 MeV) per square centimetre, to produce a damage layer 900 nm below the surface, and 400 nm thick, as calculated from a stopping range of ions in matter (SRIM) simulation using a damage threshold (D_c) of 2.8×10^{22} vacancies per cm² as chosen based on TEM studies conducted by Fairchild et.al.²⁶ Following implantation, the BDD disk was annealed under nitrogen at 1300 °C for 2 hours and then acid cleaned again; the annealing step converts the layer of damage, produced by ion implantation, into a layer of graphitic, sp² bonded carbon.

The choice of etch solution is key, as this plays a substantial role in the creation and stabilisation of the highly oxidising species, including radicals, which are responsible for the electrochemical etching of the graphitic layer. Potassium sulphate (K₂SO₄, Pure, Acros Organics, US), was chosen for the etch solution as this was previously demonstrated to produce a fast etch rate (compared to other commonly used etch solutions such as boric acid).²⁷

The electrochemical etch was carried out in a custom designed 3D printed (Lulzbot Taz 6) polyethylene terephthalate (PET) cell, adopting an experimental setup designed and optimised by Tully et al.²⁷ The electrodes

used were 2 cm of 0.75 mm diameter platinum wire (for a total area of 0.5 cm²), with a spacing of 6 mm between them. A variable DC power supply (Elektro-Automatik GmbH, EA-PS 9750-04) was used to apply a potential between the two electrodes, operating in a potential limiting mode at 30 V, with a current value of ~ 0.4 A, for 5 hours. To maintain constant solution composition and temperature, a flow system was used with a temperature-controlled reservoir of 25 °C. The experimental setup adopted for the electrochemical etch is shown in Figure 5.2. The etch solution (0.25 M K₂SO₄ with a solution conductivity of 42 mS cm⁻¹) was circulated from this reservoir into the cell and returned via an outflow. After etching, the BDD sample was removed from the electrochemical etch cell, rinsed in DI water, and left to dry in air.



Figure 5.2: Schematic of the etch cell setup, not to scale. Arrows show solution flow.

5.2.2.2 Surface characterisation

FE-SEM was used to image the resultant BDD membrane. Images were recorded using the in-lens detector on a Zeiss Gemini FE-SEM 500 (Zeiss, Germany) operating at 5 kV.

5.3 Results and Discussion

5.3.1 PIPS method

Achieving electron beam transparent BDD EC-TEM substrates is challenging. The starting point for fabrication was the production of freestanding and double sided polished (~ nm surface roughness) polycrystalline BDD substrates, as thin as possible but with the caveat that the material could be suitably handled. For this reason, freestanding BDD substrates of thickness in the range 50-80 μ m were initially produced, and cut into disks of 3 mm diameter to make them suitable for insertion into the TEM holder. To achieve electron beam transparency the substrate was argon ion milled and then argon ion polished, Figure 5.3. The aim was to produce a large an area as possible of electron beam transparency but still be able to handle the freestanding substrate. Initially the highest accelerating voltage was used (6 kV) to produce the fastest milling rate to remove the bulk of the BDD, using an angle of incidence in the middle range of that possible with the system (5°). If the angle was set to the highest value, whilst material was removed more quickly, a smaller region of electron beam transparent material resulted. A middle value was found to be a time efficient compromise (~2.5 hrs each side, see experimental details).



Figure 5.3: Schematic illustration of a) the PIPS ion milling setup, b) the inside of the PIPS milling chamber, and c) the PIPS milling procedure employed to thin the centre of the BDD disk to electron beam transparency.

The PIPS milling technique, as described in section 5.2.1.1, produces 3 mm diameter disks of freestanding and electrically conductive BDD, approximately 50 μ m thick at the edge, with a small hole in the centre of the disk around which exists an area of electron beam transparent BDD (Figure 5.4). A note should be considered with regards to the PIPS mill used. The fabrication procedure described here was initially developed using the original PIPS

system, also referred to as PIPS I. Milling parameters (e.g., ion beam angle and milling times) were optimised for this system. During the evolution of this project, an enhanced PIPS mill has become available, known as PIPS II. PIPS II offers improved low energy milling, which creates a smoother surface finish with reduced step edges. As a result, the final low energy polish, can be carried out at an accelerating voltage of 1 kV or lower to create a smoother surface finish. This is likely to produce larger areas of electron beam transparent BDD, free of surface steps, and thus should be employed for future BDD EC-TEM substrate fabrication. Adequate BDD EC-TEM substrates can be fabricated using either PIPS system, but to produce the best substrates, at least a final low energy polish on a PIPS II system will be required.



Figure 5.4: Schematic to show a PIPS milled BDD EC-TEM substrate (credit to Haytham Hussein for this image).

To apply a suitable electrical contact two approaches were adopted and assessed, each one offering different advantages. For all BDD EC-TEM substrates prepared the top quarter of the disk was first laser roughened (and acid cleaned), on top of the BDD surface, onto which an electrical contact could be placed. The two contacts investigated were a sputtered and annealed Ti/Au contact and conductive carbon ink (see section 5.2.1.1 for further details). The former is commonly used to make an ohmic electrical contact to BDD²⁸ but in this application, it can be very difficult to avoid Au contamination on the BDD EC-TEM substrate entirely during sputtering due to the concave profile of the BDD EC-TEM substrate. In contrast, the carbon ink can be simply painted onto the area of interest, but, to the best of our knowledge, has not been used before with BDD electrodes.

To assess the impact of both contacts on electrochemical performance, the uncompensated resistance, R_u , was measured for two BDD EC-TEM substrates dipped into solution (0.1 M KNO₃ electrolyte) with the two different electrical contacts; Ti/Au or a conductive carbon ink (838AR, MG Chemicals). Very similar areas were immersed (both faces and approximately three quarters of the disk, ~ 0.11 cm²) and the distance between the BDD EC-TEM substrate and RE was kept constant. In a potential range where no faradaic reactions occur, the electrode can be treated as ideally polarisable, and conforms to equation (5.1):²⁹

$$i(t) = \frac{\Delta E}{R_u} e^{-t/R_u C}$$
(5.1)

where ΔE is the pulse width (V), R_u is the uncompensated resistance (Ω), t is the total time (s), and C is the capacitance (F). The uncompensated resistance measurements were made using chronoamperometric pulses of 0.1 V width (-0.30 V to -0.20 V vs SCE) for 5 ms. Five separate pulses were recorded, and each pulse was fitted according to equation (5.2) following the Levenberg Marquardit iteration algorithm:

$$y = ae^{bx} (5.2)$$

where *b* is equal to $-1/R_uC$. R_u can then be calculated via equation (5.3), where *a* is the pre-exponential term from the fitted function, equation (5.2), and ΔE is the pulse width (0.1 V):

$$R_u = \frac{\Delta E}{a} \tag{5.3}$$

Figure 5.5 shows an example of the current-time responses (black line) recorded, with the corresponding exponential fit (red line) used to calculate R_u , for a BDD EC-TEM substrate with a C ink contact.



Figure 5.5: Example current-time response (black) and corresponding exponential fit (red) of a BDD EC-TEM substrate with a C ink contact.

Table 5.1 shows the fitted a parameter and calculate R_u values for five repeat measurements of each contact. For both electrodes, R_u values of 1.340 ± 0.006 k Ω (Ti/Au) and 0.958 ± 0.004 k Ω (carbon ink) were obtained, indicating that the carbon ink contact resistance is not high enough to be dominating the R_u value measured. The small difference in R_u may be due to not having exactly the same area of each grid in solution.

Table 5.1: Fitted a parameter and the corresponding R_u values from 5 chronoamperometric pulses, the average R_u , and the standard deviation.

	a (×10 ^{–5})	R _u (kΩ)	Average R _u (kΩ)	Standard Deviation (kΩ)
	7.51	1.3316		
BDD TEM	7.48	1.3369		
Au/Ti	7.47	1.3387	1.340	0.006
contact	7.44	1.3441		
	7.41	1.3495		
	10.5	0.9524		
BDD TEM	10.5	0.9524		
C ink	10.4	0.9615	0.958	0.004
contact	10.4	0.9612		
	10.4	0.9615		

5.3.1.1 Fabrication troubleshooting

There are a number of tips and tricks that can be adopted to maximise both the size of the electron beam transparent area, and the lifetime of the BDD EC-TEM substrates. As the milling time and fabrication process is time consuming, it is important to get as much use out of a single substrate as possible. As the electron beam transparent region of the BDD is very thin, small areas can snap off from around the hole edge. This is also worsened by the polycrystalline nature of the BDD EC-TEM substrate, where grain boundaries containing defect sites and sp² bonded carbon can fracture easily. Within grains, applied force can also result in cleavage along crystallographic planes of the BDD. The best way to avoid this is to exercise extreme caution when handling the BDD EC-EM substrates; ensuring they are not dropped, and avoid touching the hole edge with e.g., tweezers, the stream from a water bottle, other electrodes. It is often evident when areas have broken off where very straight edges, or areas missing from the original edge coastline, around the hole are observed in FE-SEM imaging. This is shown in Figure 5.6, where Figure 5.6 a shows a fresh BDD EC-TEM substrate, and Figure 5.6 b shows a heavily used BDD EC-TEM substrate with many areas around the hole edge snapped off. If other thin areas are still present (e.g., the top right segment of the dashed red circle in Figure 5.6 b), these areas can be utilised, and the substrate still used.



Figure 5.6: In-lens FE-SEM images of a) a freshly milled BDD EC-TEM substrate and b) a used BDD EC-TEM substrate where some areas around the hole edge have broken off. The red dashed circle shows the orginal edge coastline. Inset shows straight edges around the hole edge, where the substrate has snapped.

If many areas have snapped off, it may be difficult to locate large areas that are thin enough for high resolution imaging. This may also occur as a result of PIPS milling for too long and is also sometimes indicated by a larger than usual central hole, visible by eye. In these cases, in order to reuse the BDD EC-TEM substrate, an additional low angle, short timescale, PIPS clean can be undertaken, e.g., angle of incidence of ~1-2° from both the top and the bottom of the disk simultaneously at 1-2 kV for 1-5 minutes. Another issue that can occur is due to the method of creating an electrical contact to the BDD EC-TEM substrate. As mentioned in section 5.2.1.1, the BDD surface must be roughened by laser micromachining before either a Ti/Au sputtered contact or a C or Ag conductive ink contact is applied. During the roughening process, BDD material is removed from the \sim 50 µm thick edge of the substrate. This can lead to the roughened area snapping off of the BDD EC-TEM substrate along the edge of the lasered area. This tends to happen when multiple laser roughening treatments have been used, to regenerate used BDD EC-TEM substrates for further use. To avoid this, the number of laser roughening treatments used on a BDD EC-TEM substrate should be minimised where possible. If the roughened area does snap off, another part of the substrate outside edge can be used instead for contacting.

5.3.1.2 Surface characterisation

An exemplary BDD substrate fabricated via PIPS milling is shown in Figure 5.7. The central hole measures approximately 129 μ m in diameter with an electron beam transparent region (appears darker in Figure 5.7 a and brighter in Figure 5.7 b) extending to ca. 20 µm back from the hole edge with thickness increasing from the hole edge to the bulk BDD. In Figure 5.7 c, the very edge of the hole can be seen. In some locations around the hole edge, the BDD is milled so thin that holes form at the very edge. This is often observed in very thin areas, although absence of holes does not mean the BDD is not thin. Holes such as these can indicate that the surrounding areas are very thin and thus are good locations for high resolution imaging. Thinner areas allow higher resolution imaging because scattering from the BDD background is reduced and thus contrast of the nanomaterial being imaged increased. In general, the smaller the central hole, the larger the area of electron beam transparent material. For this reason, it is important to stop the bulk PIPS milling as soon as a hole is observed. Figure 5.7 d shows a high resolution DF-TEM image of a BDD-TEM electrode, showing the atomic structure of the 100 surface. A homogeneous, predominantly 110 surface of the BDD is revealed after mechanical and ion polishing.



Figure 5.7: FE-SEM (a,b) and STEM (c) images of an exemplary BDD EC-TEM substrate recorded at 20 KV using the a) In-lens, b) SE2, and c) STEM detectors. d) DF-STEM image of the surface of a BDD EC-TEM substrate, inset: electron diffraction pattern showing the [110] crystallography of the surface.

The maximum thickness at which electron beam transparency, and thus TEM imaging, can be achieved depends on the operating accelerating voltage of the microscope; for an operating accelerating voltage of 100 kV, the maximum sample thickness is around 200 nm,³⁰ so for typical TEMs that operate at 100-300 kV, a few hundreds of nms is commonly quoted as the limit for imaging.³¹ That being said, the thinner the sample, the better resolution images that can be recorded as with increasing thickness, the number of inelastically scattered electrons also increases, which reduces the achievable spatial resolution.

The topography of the milled BDD EC-TEM substrate was investigated using WLI and AFM. An overview is shown in Figure 5.8, where Figure 5.8 a shows WLI data and Figure 5.8 b shows AFM data. WLI has a resolution of 176 μ m × 176 μ m × 0.001 μ m in *x*, *y*, and *z*, respectively; thus, WLI has the advantage of accessing larger areas than AFM but with a reduced *x*,*y* scan spatial resolution. WLI across the bulk of the substrate Figure 5.8 a, where white corresponds to the highest areas, with green areas lower, and blue areas lower still, with the hole depicted as a centre black circle) shows topography with a radial symmetry around the hole, a results of sample rotation employed during



Figure 5.8: a) WLI and b) AFM topography data of a BDD EC-TEM substrate after PIPS milling, showing i) images obtained and ii) corresponding depth profiles of the surface, where y is the vertical sample height and x is the horizontal distance across the red and black lines marked in i). The AFM image was recorded 125 nm from the hole edge and is representative of the BDD surface in close proximity to the hole.

PIPS milling. The corresponding depth profile, an example of which is shown in Figure 5.8 a ii, shows BDD thickness increasing as distance from the hole edge increases. This thickness increase follows a shallow sigmoidal relationship. The difference in thickness between the bulk BDD (500 μ m from the hole edge) and the hole edge is approximately 18 μ m. As a result of inhomogeneous BDD material removal during milling, the resulting surface of the bulk BDD surface has a wavelike pattern, observed both in FE-SEM imaging (Figure 5.7 a), in AFM measurements (Figure 5.8 b i and Figure 5.9), and in higher magnification WLI measurements (Figure 5.10 a).

Figure 5.9 shows the phase and amplitude measured by AFM over the area shown in Figure 5.8 b i. The phase image (Figure 5.9 a) clearly shows the edges created by the milling process between flat regions of BDD. The grain structure of the polycrystalline BDD is also clearly observed, as the variation in B content between grains, and thus mechanical hardness (which decreases as B content increases³²), causes a change in the phase measured. Again, the wavelike structure, is qualitatively observable in the amplitude image (Figure 5.9 b).

The surface roughness was also measured both on the macroscale, by WLI, and on the nanoscale, by AFM. Figure 5.10, using WLI over consecutive areas of $20 \times 40 \ \mu\text{m}$, shows an increasing surface roughness from ~200 nm RMS at the edge of the hole to ~300 nm RMS ca. 200 μm away from the hole. The AFM data (Figure 5.9) shows that despite the wavelike structure, over a line profile of 20 μm (red line), the surface height only fluctuates ± 13 nm, with this fluctuation lessening as the area over which the measurement is taken is reduced; over a line profile of 5 μm (black line), this fluctuation is reduced to only ± 5 nm. This is key because for high resolution TEM imaging, only very small areas of the BDD EC-TEM substrate (e.g., < 1 × 1 μm) will be imaged at a single time, and as such the surface can be considered as 'flat', with approximately nm RMS. An RMS roughness of 52.25 nm was measured over the entire 20 × 20 μm area shown in Figure 5.9 b i.



Figure 5.9: AFM images of a) phase and b) amplitude, recorded over a 20 \times 20 μ m area 125 nm from the hole edge (representative of the BDD surface in close proximity to the hole).



Figure 5.10: a) WLI image and b) corresponding surface roughness, reported as root mean square (rms) values, calculated using Gwyddion $2.55.^{20}$ over successive areas of $20 \times 40 \ \mu m$ beginning at the hole (shaded grey in a) edge and tracking horizontally in a straight line away from the hole

BDD electrode surfaces are typically used as-grown or mechanically polished (and acid cleaned). Here the surface has been ion polished (and acid cleaned). XPS was used to examine the surface chemistry of the ion polished (and acid cleaned) BDD EC-TEM substrate compared with an un-milled, mechanically polished (and acid cleaned) surface, Figure 5.11 a-c. The latter is referred to hereafter as BDD control and is also the starting surface prior to ion milling. For the ion milled BDD EC-TEM substrate, measurements were made at the hole edge and obtained using a ssapot size of 55 µm. Auger spectra were also recorded on both the BDD control and the BDD EC-TEM substrate (Figure 5.11 d) which is more surface specific, to probe the differences between different penetration depths.^{33–35} Using the inelastic mean free path calculator (IMFP-TPP2M, S.Tougaard⁵⁴), which contains data for the inelastic electron mean free path formula from Tanuma et al.,⁵⁵ we are able to estimate the penetration depth of the C1s and Auger spectra in carbon. For C1s data, the penetration depth is 9.9 nm, for a collection angle of 90°, and half of this, 4.5 nm,⁵⁶ for a collection angle of 30°, whereas the Auger data has a penetration depth of 3.9 nm.

Figure 5.11 gives fittings of the C1s data for both substrates expressed as percentages of the total fitted envelope. There is a shift of approximately 0.9 eV in the absolute binding energy of the C1s peak, and thus of the binding energies of each assigned peak in the fitting, for the BDD TEM when compared to the BDD control. Because of this, binding energies have been considered relative to the assigned sp³ peak for each sample, as we observed consistent


Figure 5.11: a-c) Fitted C1s XPS spectra of a) unmilled, mechanically polished BDD (BDD control) at 90° collection angle, b) BDD control at 30° collection angle and c) ion milled BDD EC-TEM substrate measured 55 μ m away from the edge of hole (BDD TEM) at 90° collection angle. d) Derivative C KLL Auger XPS spectra of BDD control (black) and BDD TEM (red) with associated d parameters.

peak shape and position, despite the offset in absolute binding energy positions (Table 5.2).

The fitting of the C1s spectra of BDD control (Figure 5.11 a) indicates an sp³ contribution of approximately 72%, with an sp² character of 20% (Table 5.2). The C-O contribution, which is the expected surface termination of oxidatively acid cleaned diamond,³⁵ is approximately 7%. There are minimal (< 1% of the fitted peak) contributions from adventitious carbon signals, which have therefore not been displayed on Figure 5.11 a for clarity. The sp² peak was unexpectedly high (at 21%) so the collection angle was then adjusted to 30° (Figure 5.11 b), to lessen the X-Ray interaction depth and thus provide greater surface sensitivity.³⁶ The sp² component drops from 21% to 9% of the fitted envelope at this more surface sensitive collection angle (9.9 nm vs 4.5 nm penetration depth for 90° and 30° collection angles, respectively). This

indicates a subsurface sp² damage layer, which is not unexpected when the material has been subject to mechanical polishing.³⁷ There are also minimal (< 1%) $\pi - \pi^*$ interactions, typically found in graphite, indicating potential graphitisation of the surface is negligible.^{38,39}

	Assigned functionality	Absolute binding energy (eV)	Binding energy shift relative to sp ³ peak (eV)	Relative composition of fitted envelope (%)	
BDD control 90° (Fig. 1.10a)	sp ² C – C	284.1	-0.7	20.83	
	$sp^{3}C - C / C - H$	284.8	0	71.59	
	C – O	286.4	+1.6	6.96	
	Pi – Pi *	290.7	+5.9	0.62	
BDD control 30° (Fig. 1.10b)	sp ² C – C	284.0	-0.8	9.26	
	$sp^{3}C - C / C - H$	284.8	0	77.69	
	C – O	286.2	+1.4	12.77	
	Pi – Pi *	290.5	+5.7	0.28	
BDD TEM 90° (Fig. 1.10c)	sp ² C – C	284.8	-0.9	10.19	
	$sp^{3}C - C / C - H$	285.7	0	77.15	
	C – O	286.9	+1.2	12.35	
	Pi – Pi *	291.5	+5.8	0.31	

Table 5.2: C1s fittings of BDD control and BDD TEM expressed as percentages of the total fitted envelope.

When the BDD control data is compared to the BDD TEM spectra (Figure 5.11 c), both with a collection angle of 90°, the same functional groups are retained on the surface, but in different proportions. There is a clear decrease in the measured sp² character from 21% to 10%. This suggests that the sp² bonded carbon containing diamond observed in BDD control has been removed by ion milling.

From the recorded Auger spectra, which is more surface sensitive (3.9 nm penetration depth) than C1s at both 30° (4.5 nm penetration depth) and 90° (9.9 nm penetration depth) collection angles,^{33–35} the second derivative of the C KLL regions were obtained and fitted for both BDD control and BDD TEM (Figure 5.11 d). The d-parameter was calculated as per the approach of Lascovich et al (Figure 5.11 d).^{41,42} This can be converted to sp² content as a linear variation in d-parameter is observed between 23.1 eV for 100% sp² character surfaces (i.e., graphite) and 13.2 eV for 100% sp³ character surfaces (i.e., diamond).^{41,42} The calculated d-parameter for the BDD control sample was 13.8 eV (corresponding to 6% sp² character) compared to the BDD TEM

sample which had a d-parameter of 14.4 eV (12% sp² character). This data is broadly in agreement with the above XPS data but as the Auger spectra are more surface sensitive,^{33–35} it indicates that the ion milling process may cause a small increase in the sp² carbon character of the BDD surface.

XPS measurements were also obtained on a commercial amorphous sp² bonded carbon Au backed TEM grid (Figure 5.12) and have also been previously recorded by others.⁴⁰ The sp² and sp³ content were found to be 62% and 27% respectively (Table 5.3), and with a more significant contribution from C = O, O = C – O and $\pi - \pi^*$ on this sample (2% of the envelope each), indicating different surface functionality on an amorphous carbon TEM substrates compared to the BDD substrates.



Figure 5.12: Fitted C1s spectra of commercial amorphous sp² carbon film on an Au support mesh.

Table 5.3: C1s fittings of a commercial amorphous sp² carbon film on an Au support mesh expressed as percentages of the total fitted envelope.

	Assigned functionality	Absolute binding energy (eV)	Relative composition of fitted envelope (%)
	sp ² C – C	284.3	61.99
	sp ³ C – C / C – H	285.0	26.88
sp² carbon	C – O	286.8	4.60
TEM grid	C = 0	287.8	2.27
	O = C - O	288.8	2.39
	Pi – Pi *	290.7	1.87

As described by the XPS data, the overall surface chemistry of the BDD is retained after the ion milling process (albeit with slightly different proportions of each functional group). Another common surface property of BDD that can vary significantly due to surface chemistry, is hydrophobicity. Contact angle measurements to compare the hydrophobicity and wetting of a BDD (sp³ bonded carbon) vs a commercial amorphous carbon (sp² bonded carbon) coated TEM substrate (Figure 5.13). As discussed in section 5.2.1.3, for this experiment the BDD disk was only PIPS milled on one side to produce a milled surface but without a hole (which would affect the wetting observed if contacted by the droplet). The contact angles measured were $62.2 \pm 0.5^{\circ}$ and $83.6 \pm 1.1^{\circ}$ for the sp³ and sp² substrates, respectively. This suggests that the sp³ BDD surface is less hydrophobic than the sp² amorphous surface, and thus will wet more readily in aqueous solutions. The value recorded for the BDD EC-TEM substrate is in agreement with previously reported values of up to 65° for oxygen terminated BDD surfaces.^{16,43,44}



Figure 5.13: Triplicate repeat contact angle measurements of a 50 μ L water droplet on a) a PIPS milled BDD (sp³ bonded carbon) disk and b) an amorphous carbon (sp² bonded carbon) coated gold backed commercial TEM grid.

Prior to using the BDD EC-TEM substrate as an electrode, basic electrochemical characterisations such as determining the solvent window (i.e., potential values of the solvent/electrolyte decomposition) and electrode capacitance were performed of a PIPS milled BDD surface (again milled on a single face to avoid hole interference) and compared with an unmilled BDD control surface. Measurements were recorded using a droplet setup as described in section 5.2.1.2. This experimental setup was adopted to avoid edge contributions from laser micromachining. Data is shown in Figure 5.14. The solvent windows for both samples in 0.1 M KNO₃ at 0.1 V s⁻¹ were wide

and featureless (Figure 5.14 a), with values of 3.18 and 3.54 V (for a given geometric current density of ± 0.4 mA cm⁻²) for the milled and unmilled samples, respectively. To calculate the electrochemical capacitance, *C*, the voltage window was decreased to $0 V \pm 0.1 V$ (Figure 5.14 b) and equation (5.4) was used:

$$C = \frac{i_{av}}{vA} \tag{5.4}$$

where i_{av} is the average current magnitude at 0 V from the forward and reverse sweep, v is the scan rate (0.1 V s⁻¹) and A is the geometric electrode area.

Capacitance values of 13.4 and 8.5 µF cm⁻² for the milled and unmilled samples, respectively, were measured. For polished CVD grown BDD a C of $\leq 10 \ \mu F \ cm^{-2}$ is typical.⁴⁵ The one-electron reduction of Ru(NH₃)₆³⁺ was also studied by CV (Figure 5.14 c). For the unmilled sample, a peak to peak separation, ΔE_p , of 65 mV was measured compared to 70 mV for the milled sample. These responses are close to reversible (diffusion controlled); as discussed in section 1.1.2, for an n=1 electron transfer reaction, a ΔE_p of 57 mV is predicted by classical theory.^{46,47} This data suggests that milling of the BDD surface leads to a very small decrease in solvent window, and a similarly small increase in capacitance and Ru(NH₃)_{6³⁺} ΔE_p value, and does not significantly change the electrochemical response of the material. The advantageous properties of BDD, such as low capacitive current and a wide and featureless solvent window, are retained. It is important to note that all surface characterisation measurements reflect a single face of the BDD EC-TEM substrate only, though due to the nature of the PIPS milling, the BDD surface will be analogous on both sides.



Figure 5.14: CVs recorded in 0.1 M KNO₃ at a scan rate of 0.1 V s⁻¹ on a PIPS milled BDD surface (red) and an unmilled BDD surface (black). Shown are (a) solvent windows, (b) typical capacitance curves recorded to calculate capacitance, and (c) electrode response in 1 mM 10 mM Ru(NH₃)6^{3+/2+}.

5.3.1.3 Applications

To assess the electrochemical, corrosion stability of the BDD EC-TEM substrate, the electrode was subject to a long term electrochemical stability test in 0.5 M sulphuric acid following the approach of Abruña,⁴ designed to mimic PEMFC conditions which cause corrosion of the sp² carbon electrocatalyst support. The total run time of this experiment is ca. 7 hours, during which the potential was continuously swept from -0.20 to +1.05 V vs SCE, and then back to -0.20 V, for a total of 500 full cycles at a scan rate of 50 Vs⁻¹. This experiment was carried out with the BDD EC-TEM substrate dipped into solution, as described in section 5.2.1.2. Finding an identical location on the BDD EC-TEM substrate in different imaging sessions was possible by finding unique and recognisable features around the hole edge, Figure 5.15. In



Figure 5.15: Convergent beam electron diffraction images of the hole edge a,c) before and b,d) after electrochemical stability testing. Scale bar in a,b) is 7 μ m and in c,d) is 4.5 μ m. Red rectangles indicate areas shown in Figure 5.16 a and b. The blue arrow indicates where a small area of BDD has snapped off between imaging.

Figure 5.15 a and b, the BDD EC-TEM substrate is intentionally defocussed to maximise the field of view to help locate identifying features. Once the desired region is found, indicated here by a red rectangle, the sample is brought into focus for further imaging and analysis (Figure 5.15 c and d).

Figure 5.16 shows HAADF images of the hole edge before (Figure 5.16 a and c) and after (Figure 5.16 b and d) electrochemical stability testing. Figure 5.16 c and d shower higher magnification HAADF images of the region indicated in Figure 5.16 a and b with a blue rectangle. In order to estimate the change in thickness of the BDD EC-TEM substrate, EELS spectra were acquired for the regions imaged in Figure 5.16 c and d, and the BDD thickness at each pixel measured in Gatan digital micrograph using the absolute log ratio method.⁴⁸ The thickness was calculated in low-loss spectra using the log-ratio method with the thickness, *t*, is given by equation (5.5):

$$\frac{t}{\lambda} = ln(\frac{I_t}{I_0}) \tag{5.5}$$

where λ is the total mean free path for all inelastic scattering, I_0 is the area under the zero loss peak, and I_t is the total area under the whole spectrum.⁴⁹ An absolute value of the thickness is given in this work by assuming $\lambda = 97.61$ nm.⁵⁰ This gave an average thickness over the area within the blue rectangle of 44.2 nm before cycling, and 43.8 nm after. The difference in these values is within experimental error of the calculation, which is estimated to be approximately 5 %.⁴⁸ Representative line profiles of BDD thickness were also recorded, and the data presented in Figure 5.17; again, no significant difference was observed. The purple dashed lines in Figure 5.16 c and d show the position of where the line profile data shown in Figure 5.17 was measured.



Figure 5.16: High magnification HAADF images of BDD EC-TEM substrate a,c) before and b,d) after electrochemical cycling. Scale bar in a,b) is 1 μ m and in c,d) is 100 nm. Red rectangles correspond to areas indicated in Figure 5.15, blue rectangles indicate area selected for EELS acquisition, and dashed purple line indicates EELS line profile taken.



Figure 5.17: Representative 275 nm horizontal line profile from 2D EELS spectra acquired over area highlighted with purple dashed lines in a) Figure 5.16 c (before electrochemical stability testing) and in b) Figure 5.16 d (after electrochemical stability testing).

This TEM observation of BDD surface stability during electrochemical cycling was also supported by the stability of the electrochemical response (Figure 5.18). The initial electrochemical response shows that in the cathodic sweep the hydrogen evolution reaction (HER) is occurring, indicated by an increase in current from 0.4 to -0.2 V. In the anodic sweep, the current again increases from 0.4 to 1.05 V, indicating the onset of OER. At both limits of the solvent window, the current measured drops over the first 5 cycles, from -150 to -100 nA at the cathodic limit and from 125 to 75 nA at the anodic limit. As the number of cycles increases further through to 500, both currents drop further, although the magnitude of this change decreases throughout the experiment; between cycle 100 and cycle 500, a minimal change in current is observed. This behaviour is likely due to electrochemically cleaning the BDD surface in the first few cycles. A very small peak was also observed in cycles 1 and 5 at ca. 0.75 V but has disappeared by cycle 10; this indicates a surface contaminant that has been electrochemically cleaned off during cycling. In general, a stable response is observed, reflecting the stability of the BDD EC-TEM substrate.



Figure 5.18: CV response from electrochemical stability testing of BDD EC-TEM substrate. Cycles 1, 5, 10, 20, 100, 500 shown from the total 500 cycles, over a potential window of -0.2 V to +1.05 V vs. SCE, in 0.5 M H₂SO₄, at scan rate of 50 mVs⁻¹. A Pt coil was used as a counter electrode. Black arrows show scan direction.

For comparison a commercial Au backed sp² bonded amorphous carbon TEM grid was subjected to the same electrochemical cycling experiment on 0.5 M H₂SO₄. Now, the CV response changes dramatically over the initial 10 cycles (Figure 5.19 a), with large currents measured during cycle 1, indicative of surface oxidation. Figure 5.19 b shows that, unlike BDD, the sp² bonded carbon surface is still changing by 100 cycles, albeit less drastically than during the first 10 cycles. By the 100th cycle, a peak is evident at ~0.7 V vs. SCE, which is likely due to the reduction of gold oxide NPs,⁵¹ formed by oxidation of the Au support mesh during earlier cycles. The current measured at this peak increases tenfold by the 500th cycle (Figure 5.19 c), as more Au is oxidised, and thus more gold oxide reduced. Damage to the TEM grid was evident in TEM imaging (Figure 5.19 d), recorded after the 500 cycles, dipping the grid in water to rinse and then leaving to dry. A number of damage mechanisms are observed, including: i) hole formation, ii) mottling and iii) folding of the carbon film, and iv) Au NP deposition (shown on Figure 5.19 d with red squares). The evidence of Au deposition on the C film (Figure 5.19 d), supports the assignment of gold oxide reduction to the peak observed at ~ 0.7 V vs SCE in Figure 5.19 b and c.



Figure 5.19: CV response from electrochemical stability testing of commercial Au backed sp² bonded amorphous carbon TEM grid. Cycles 1 and 10 (a), 10, 20, and 100 (b), 100 and 500 (c) shown from the total 500 cycles, over a potential window of -0.2 V to +1.05 V vs. SCE, in 0.5 M H₂SO₄, at scan rate of 50 mVs⁻¹. A Pt coil was used as a counter electrode. Black arrows show scan direction. d) Low magnification TEM image of the carbon film after 500 cycles showing damage including i) hole formation, ii) mottling and iii) folding of the carbon film, and iv) Au NP deposition.

For some studies, it may be of interest for samples to undergo heating in air, with TEM imaging before and after. Thin amorphous carbon films are also likely to break under thermal stress and oxidise when heated in an oxygen containing environment.¹⁵ The BDD EC-TEM substrate was, however, observed to be stable when heated to elevated temperatures (100-400°C) in air (Figure 5.20 a). This was compared to C/Cu commercial TEM grids, where oxidation of the carbon film, resulting in visible damage, occurs at 100°C, with the film integrity deteriorating further with increasing temperature (Figure 5.20 b). This again shows the wider range of operating/experimental conditions accessible when using a BDD EC-TEM substrate.



Figure 5.20: Photographs of a) a BDD EC-TEM substrate i) before heating in air and ii) after heating in air to 100°C, then 200°C, then 300°C, and finally 400°C for 4 hours at each temperature, and b) an amorphous carbon (sp^2) coated copper backed commercial TEM grid i) before heating in air and ii-v) after heating in air for 4 hours to ii) 100°C, iii) 200°C, iv) 300°C, and v) 400°C. A fresh C/Cu grid was used for each annealing temperature due to induced damage in each heating experiment. The same BDD EC-TEM substrate was used throughout with annealing temperature increasing from lowest to highest.

BDD is stable under elevated temperatures and also is a very good conductor of heat. These properties lend BDD for use as a substrate for experiments that require *in-situ* heating. The thermally induced crystallisation of manganese oxide was used to demonstrate this. It is important to note that although electrochemical deposition will occur on both sides of the BDD EC-TEM substrate, any TEM images are recorded from a single face of the substrate.

Following electrodeposition and TEM imaging of amorphous MnO_2 (Figure 5.21 a and b i), the sample was heated *in-situ* (and thus under vacuum) in 50°C increments until crystallisation was observed (400°C). The sample was then left to cool to 30°C before recording images of the crystallised structure (Figure 5.21 a and b ii and iii). The crystallisation temperature observed of 400°C in vacuum is broadly in agreement with values reported previously for the thermally induced transformation of amorphous MnO_2 to crystalline $Mn_2O_3.^{52,53}$



Figure 5.21: a) TEM images and b) corresponding diffraction patterns of manganese oxide electrodeposited on a BDD substrate at i) 25°C before heating and ii,iii) at 30°C after heating to 400°C. Red circles in a) indicate the areas that diffraction patterns shown in b) were recorded over. Blue square in a)ii) indicates the region magnified in a)iii).

5.3.2 Electrochemical etch method

A thin membrane, approximately 900 nm thick (as calculated by SRIM, see section 5.2.2.1 for further details), was removed from the bulk BDD via electrochemical etching of a graphitic damage layer, produced by ion implantation. This is particularly exciting as this is (1) the first time BDD membranes have been etched in this way (as opposed to intrinsic, undoped diamond) and (2) the first time polycrystalline diamond has been etched in this way (as opposed to single crystal). A photograph of the BDD membrane and support frame is shown in Figure 5.22 a, with the frame geometry shown in Figure 5.22 b. Some small areas of the BDD did not etch, however the majority of the membrane has been successfully lifted off of the membrane. A heterogeneous etch has been found to be typical of comparable single crystal intrinsic diamond membranes fabricated via this technique.²⁷ Some of the thinner edges, of the support frame have also snapped off; these features should be excluded in future experiments to provide a more robust support frame.



Figure 5.22: a) Photograph of a BDD membrane, fabricated by electrochemical etching of an ion implanted graphitic layer, attached to a BDD support frame. b) Geometry of BDD support frame.

The BDD membrane was also imaged with FE-SEM (Figure 5.23). The BDD surface had a high level of salt contamination (Figure 5.23 a), though the grain structure of the polycrystalline BDD beneath was observable at higher magnification (Figure 5.23 b). These salt deposits are most likely residual K_2SO_4 from the etch solution. In an attempt to remove the salt, the membrane was left in water to soak for two weeks.



Figure 5.23: FE-SEM images taken at 5 kV of the BDD membrane after elecrochemical etching.

Figure 5.24 shows FE-SEM images of the BDD membrane after soaking. The vast majority of the salt crystals have now been removed, with the polycrystalline grain structure clearly visible, even at lower magnification. The BDD surface has clearly been retained during the electrochemical etch and lift off processes. To avoid the need for this additional soaking step, future work



Figure 5.24: FE-SEM images taken at 5 kV of the BDD membrane after elecrochemical etching and soaking in water for two weeks.

will investigate using salt-free electrolytes for electrochemical etching, such as sulphuric acid.

Though this data is a very promising first step towards the production of BDD EC-TEM substrates via electrochemical etching, the membrane produced is too thick (ca. 900 nm) to allow electron beam transparency, and thus TEM imaging. Two strategies are proposed to achieve the required thinness (ca. < 100 nm): (1) adopting an additional reactive ion etching (RIE) step to thin the membrane further, or (2) tuning the depth of ion implantation to lift off a thinner membrane initially.

RIE, used commonly in microfabrication, uses a plasma under vacuum to etch surfaces with a high degree of directional control.⁵⁵ RIE has drawn interest for patterning BDD films, including oxygen plasma etching to create microelectrode arrays to enhance electrocatalytic activity,⁵⁶ and SF₆ plasma etching to drastically increase electrode surface area to make electric double-layer capacitors.⁵⁷ Due to the polycrystalline nature of the BDD material, varying etch rates on different grains must be considered.⁵⁸

Alternatively, and undoubtedly the simpler route, the ion implantation step could be optimised to produce a damage layer much nearer to this surface, resulting in the lift-off of a BDD membrane that is thin enough to be electron beam transparent. This was not pursued initially due to concerns over the robust of a thinner membrane i.e., for a preliminary, proof of concept experiment, a thicker membrane was more likely to be lifted off successfully. Table 5.4 shows a selection of SRIM simulated implant depths for different elements and energies. The lower energy helium energies could produce BDD membranes that are thin enough to be electron beam transparent without the need for an additional RIE step. The homogeneity of the etch (and thus thickness of the membrane) should also be considered for both possible fabrication routes; it may be the case that one of these two approaches produces a smoother membrane with a more even thickness, which is desirable for TEM imaging. For these reasons, both options will be explored in the future, and the BDD membranes fabricated via each route compared.

Table 5.4: Table to show various ion implantation conditions that have been used to prepare ion implanted BDD samples for future electrochemical etch experiments.

Energy of ion implantation	Element	SRIM calculated implant depth (nm)
2 MeV	Carbon	900
1 MeV	Helium	500
35 KeV	Helium	100
25 KeV	Helium	60

5.4 Conclusion

Utilising BDD as an alternative support material for TEM imaging offers a number of advantages over traditional amorphous sp² bonded carbon films, including; enhanced chemical, electrochemical, and temperature stability, mechanical robustness allowing repeated IL-TEM imaging, and delivering dual functionality as both TEM support and electrode, with no concern for introducing metal contamination.

A novel fabrication route for the production of BDD EC-TEM substrates has now been developed, ion milling a thin disc of CVD grown BDD to electron beam transparency by creating a hole in the middle of the disk. The edge of the ion-milled hole is thin enough to be electron beam transparent, and also consists of many micro and nanoscale irregular features that can be used to aid location finding. The mechanical robustness of BDD makes it an ideal material for repeat measurements, as amorphous carbon films are more fragile can be torn easily.

In addition, for the first time, BDD membranes have been produced via electrochemical etching of a graphitic damage layer, produced by ion implantation. This will allow production of BDD EC-TEM substrates with significantly increased areas of electron beam transparent, less prone to snapping due to the support frame. Although this technique is very much in its infancy, the preliminary data is promising and the possibility of future optimisation promising.

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6 Conclusions and future outlooks

BDD electrodes have found use in a diverse range of fields in recent years, mainly due to their superior material properties over competing electrode materials, including superior hardness, chemical stability, low capacitance, and a wide electrochemical solvent window, as discussed in chapter 1. Despite having already found widespread use, new electrochemical application areas are still being developed for BDD. Currently, the majority of applications utilise CVD grown BDD in freestanding wafer or thin film format. The work presented in this thesis demonstrates the possibilities achievable by moving away from this typical BDD format and using alternative growth procedures. For some applications a pure BDD surface is not ideal, as it is electrocatalytically inert. We also show how, by using laser micromachining, sp² bonded carbon can also be intentionally integrated into the BDD surface in a very robust format. We highlight the advantages of this material by considering the electrochemical generation of dissolved ozone from water.

In chapter 3, a novel HPHT synthesis route was developed for the fabrication of BDD MPs. This demonstrates an alternative production method to CVD growth of electrochemically-viable BDD particles. HPHT growth offers of the possibility of large scale, cost-effective production, not attainable with CVD. The use of a Fe–Ni carbide forming catalyst aided in enabling lower temperatures and pressures than previously reported, ~5.5 GPa and 1200 °C, whilst AlB₂ functioned as both a source of B and N sequester. Freestanding BDD electrodes were then fabricated by HPHT compaction of these MPs, which can be treated akin to freestanding CVD BDD wafers, followed by laser cutting into the desired electrode geometry. These electrodes demonstrated a high surface area and low material resistance with a sub-microscopic porous electrode structure as demonstrated by SECCM and standard double layer capacitance measurements. Future work will look to vary the HPHT compaction conditions with a view to both increasing and decreasing the BDD porosity beyond what was achieved in this thesis. Mechanical ball milling of BDD was also utilised in chapter 3 for the top-down production of smaller highly doped BDD NPs from a feedstock of small pieces of CVD BDD wafer. Tempered steel was chosen as the preferred material of the milling balls and chamber due to the small size and spherical morphology of the BDD NPs produced. Large particles and agglomerates were present in the milled samples, but these were easily removed, though centrifuging and filtering steps, to give a narrow size distribution of 100.4 ± 6.3 nm. The effect of milling parameters, including the weight ratio of balls to BDD, rotation speed (rpm), volume of water added, and total milling time should next be optimised to achieve the best possible yield and size of NPs. Electrochemical characterisation and testing of milled NPs will also be a key step in proving the promise of this material in powder based electrochemical applications.

Future work in this area will look to combine the HPHT BDD MPs with milling procedures, as an alternative feedstock to CVD BDD, as a means to producing high volumes of BDD NPs. Again, the scalability and possibility of reduced cost through adoption of HPHT BDD growth will be considerably beneficial. Packaging of both HPHT BDD MPs, and milled BDD NPs (from CVD or HPHT BDD feedstock) should also be investigated further.

Although BDD is generally chosen as an electrode material of choice due to its material properties that result from the sp³ bonded carbon, for some applications intentionally introducing sp² bonded carbon can be adventitious. Laser micromachining followed by an oxidative acid treatment was found, in chapter 4, to provide a fast and cost-effective method to incorporate sp^2 bonded carbon onto the surface of a BDD electrode. Importantly the sp² bonded carbon formed via this procedure was both mechanically and electrochemically robust, and was therefore suitable for use in applications that BDD traditionally also finds use. TEM/STEM/EELS studies established that during laser micromachining an unstable sp² bonded carbon layer ~100's nm thick, results from laser micromachining. However, oxidative acid treatment, transforms the surface into a ~5 nm thick layer of DSC. This DSC layer is incredibly robust and survived further oxidative acid treatments. It is also postulated that the DSC layer also survives 20 hrs of continuous EOP run time as no reduction in performance is observed. Further TEM/EELS studies are necessary to confirm this hypothesis.

The impact of sp² bonded carbon on the EOP was then investigated. In chapter 4, BDD electrodes containing CVD grown BDD EOP cells were fabricated with a range of sp² bonded carbon surface contents from minimal (where only sp² bonded carbon created from diamond growth is present) to 80%. This was achieved by laser micromachining slots through the BDD electrodes, which were then acid cleaned, resulting in the formation of a DSC layer at the slot edges. Different slot dimensions and patterns were utilised to achieve varying sp² bonded carbon contents. The maximum ozone output (at 0.6 A) was found to increase notably with an increase in sp² bonded carbon, from 0.88 mg L⁻¹ cm² A⁻¹ for 5% sp² bonded carbon to 4.00 (80% sp²) mg L⁻¹ cm² A⁻¹ for 80% sp² bonded carbon. The peak current efficiency achieved doubled from 17.8% for the 5% electrode to 36% for the 70% electrode. 60% sp² bonded carbon was identified as a key threshold to exceed for maximum efficiency, as between 60% and 80% the peak current efficiency was relatively constant.

This was postulated to be due to the stronger bonding of hydroxyl (·OH) and oxygen (·O) radicals (essential in the EOP mechanism) to a sp² bonded carbon surface versus a BDD surface. Future work will look to use computational modelling to gain further mechanistic insight into the EOP process and role of sp² carbon versus sp³ bonded carbon surfaces. With the knowledge gained on EOP production using CVD grown BDD electrodes, EOP electrodes were also fabricated from freestanding compacted HPHT BDD MP electrodes. The HPHT MP electrodes were shown to be robust enough to survive the laser micromachining process. Both the CVD and HPHT MP electrodes (the same design was used for comparison studies) produced dissolved ozone continuously for 20 hours of generation with no loss of performance. Only a slight reduction in ozone output and efficiency was observed when compared to CVD BDD electrodes, with room for future optimisation, by improving MP compaction to reduce porosity and resistivity.

A particularly exciting application area of which BDD is just beginning to find use is that of the carbon support in TEM imaging of nanostructures and nanoparticles. Using BDD EC-TEM substrates instead of sp² bonded carbon films provides enhanced stability (chemical, electrochemical, and temperature) and mechanical robustness allowing repeated IL-TEM imaging. In chapter 5, two novel BDD EC-TEM substrate fabrication routes were developed. Firstly, PIPS ion milling was used to create discs of BDD with a small hole in the middle, around which the BDD is thin enough to be electron beam transparent. Irregular features around the hole coastline can be used to aid location finding for IL-TEM experiments. Typically, an Au/Ti contact was used to connect the BDD EC-TEM substrate for electrochemical experiments, but concern for metal contamination can be removed entirely by using a conductive C based ink contact.

The second methodology presented consists of 1) sub-surface ion implantation to create a damaged BDD layer, 2) annealing to convert this layer to graphitic sp² bonded carbon, followed by 3) an electrochemical etch which preferentially etches the graphitic layer, allowing lift-off of a BDD membrane adhered to a thin BDD support frame. The preliminary data presented in chapter 5 is a fundamental first step in the development of this novel fabrication technique, and further work will continue to optimise fabrication and demonstrate the suitability of lift-off BDD membranes as EC-TEM substrates. This will focus on three main aspects; 1) moving to a salt-free electrolyte (e.g., sulphuric acid) to avoid salt residue, 2) introducing a post-etch RIE step to thin the membrane down to electron beam transparency, and 3) optimising the ion implantation to create a damage layer nearer the surface to lift-off thinner BDD membranes in the initial electrochemical etch. In comparison to the PIPS milling method, production of BDD EC-TEM substrates via this route has the potential to significantly increase the size of the electron beam transparent area per substrate. Membranes are also much less prone to snapping due to the support frame and nature of fabrication and are more akin to the standard sp² bonded amorphous carbon TEM grids commonly in use.

In general, the work presented in this thesis demonstrates that possible uses for BDD in electrochemistry have not been exhausted. The importance of the properties, and presence, of $sp^2 vs sp^3$ bonded carbon is evident, and by understanding and exploiting the interplay between these two classes of carbon based materials opens up new possibilities for advancing research.