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Investigation and Optimisation of Electrochemical Electron Paramagnetic Resonance Spectroscopy Experiments

by

Emily Braxton

A thesis submitted in partial fulfilment for the award of

Doctor of Philosophy in Analytical Science

Molecular Analytical Science Centre for Doctoral Training

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Abbreviations

4-hydroxy TEMPO  4-hydroxy-2,2,5,5-tetramethyl-1-piperidine-1-yloxy
BDD  Boron doped diamond
CE  Counter electrode
CV  Cyclic voltammogram
CW  Continuous wave
CVD  Chemical vapour deposition
DMPO  5,5-dimethyl-1-pyrroline N-oxide
DMSO  Dimethyl sulfoxide
EC  Electrochemical
EAOPs  Electrochemical advanced oxidative processes
EPR  Electron paramagnetic resonance spectroscopy
GC  Glassy carbon
HPHT  High pressure high temperature
HPLC  High performance liquid chromatograph
ID  Inner diameter
IHP  Inner Helmholtz plane
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LGR</td>
<td>Loop gap resonator</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammogram</td>
</tr>
<tr>
<td>MNP</td>
<td>2-methyl-2-nitrosopropane dimer</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer Helmholtz plane</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>POBN</td>
<td>α-(4-pyridyl N-oxide)-N-tert-butylnitroine</td>
</tr>
<tr>
<td>PBN</td>
<td>N-tert-butyl-α-phenylnitroine</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>RNO</td>
<td>p-Nitroso dimethylaniline</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>SRIM</td>
<td>Stopping range of ions in matter</td>
</tr>
<tr>
<td>TBAB</td>
<td>Tetrabutylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse electric</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse magnetic</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
</tbody>
</table>
# Glossary of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Hyperfine splitting factor</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>B / B</td>
<td>Applied magnetic field</td>
</tr>
<tr>
<td>B₁</td>
<td>Local magnetic field</td>
</tr>
<tr>
<td>Bₘ</td>
<td>Field modulation</td>
</tr>
<tr>
<td>Bᵣ</td>
<td>Effective magnetic field at the resonance condition</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>[C]</td>
<td>Concentration</td>
</tr>
<tr>
<td>e</td>
<td>Charge of an electron</td>
</tr>
<tr>
<td>E</td>
<td>Applied potential</td>
</tr>
<tr>
<td>E'</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>E⁰</td>
<td>Standard electrode potential</td>
</tr>
<tr>
<td>Eᵢ</td>
<td>Staircase increment</td>
</tr>
<tr>
<td>Eₚ</td>
<td>Peak potential</td>
</tr>
<tr>
<td>Eₛₕ</td>
<td>Pulse increment</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant (96485 C mol⁻¹)</td>
</tr>
</tbody>
</table>
Effective g-factor

$g_e$  Free-electron g-factor (2.00232)

$g_N$  Effective nuclear g-factor

$h$  Planck’s constant ($6.62607 \times 10^{-34}$ Js)

$\hbar$  Reduced Planck’s constant ($1.05457 \times 10^{-34}$ Js)

$i$  Current

$I$  Nuclear spin quantum number

$i_p$  Peak current

$IE$  Interaction energy

$L$  Inductance

$k$  Rate constant

$k_0$  Intrinsic rate of electron transfer

$k_B$  Boltzmann constant ($1.38065 \times 10^{-23}$ J K$^{-1}$)

$k_{ov}/k_{red}$  Rate constants for the potential dependent oxidative and reductive electron transfer reactions respectively

$MW_a$  Molecular weight of analyte

$MW_s$  Molecular weight of solvent

$m_e$  Mass of an electron

$m_I$  Magnetic quantum number

$m_p$  Mass of a proton
$m_s$  Electron spin angular momentum quantum number

$n$  number

$N_{+\frac{1}{2}}$  Number of spins in $m_s=+\frac{1}{2}$ state

$N_{-\frac{1}{2}}$  Number of spins in $m_s=-\frac{1}{2}$ state

$P$  Microwave power

$Q$  Quality factor

$Q_L$  Loaded quality factor

$Q_U$  Unloaded quality factor

$r$  Radius

$R$  Gas constant (8.3145 J mol$^{-1}$K$^{-1}$)

$R_S$  Solution resistance

$R_{UN}$  Uncompensated resistance

$RC$  Time constant

$S$  Electron spin quantum number

$S$  Spin angular momentum

$t$  Time

$t_g$  Gap thickness

$T$  Temperature

$V_a$  Molecular volume of analyte
\( V_s \)  
Sample volume

\( V_r \)  
Resonator volume

\( w \)  
Width of gap

\( Z \)  
Height of loop gap resonator

\( \alpha \)  
Transfer coefficient

\( \gamma \)  
Gyromagnetic ratio

\( \frac{\partial c}{\partial x} \)  
Concentration gradient

\( \Delta E \)  
Energy difference of two electron Zeeman levels

\( \Delta E_p \)  
Peak separation

\( \Delta \nu \)  
Width of resonance absorption at half height

\( \varepsilon \)  
Extinction coefficient

\( \varepsilon \)  
Dielectric constant

\( \eta \)  
Over potential

\( \eta_f \)  
Filling factor

\( \eta_s \)  
Dynamic viscosity of solvent

\( \mu_0 \)  
Permeability of free space

\( \mu_B \)  
Bohr magneton (9.27401 \( \times 10^{-24} \) J T\(^{-1}\))

\( \mu_I \)  
Magnetic dipole moment of nuclei

\( \mu_N \)  
Nuclear magneton (5.05078 \( \times 10^{-27} \) J T\(^{-1}\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_S )</td>
<td>Magnetic dipole moment of electron</td>
</tr>
<tr>
<td>( \mu_z )</td>
<td>z-component of magnetic dipole moment of an electron</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Frequency</td>
</tr>
<tr>
<td>( \nu_R )</td>
<td>Resonant frequency</td>
</tr>
<tr>
<td>( \nu_s )</td>
<td>Scan rate</td>
</tr>
<tr>
<td>( \rho_a )</td>
<td>Density of analyte</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Factor for solute-solvent interaction</td>
</tr>
</tbody>
</table>
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Declarations

This thesis has been submitted to the University of Warwick to support my application for the degree Doctor of Philosophy. It has been composed by myself and has not been previously submitted for any degree applications.

The work presented (including data generated and data analysis) was carried out by myself except in the cases outlined below:

- Collection and analysis of interferometry images in Chapter 4 Figure 4.3 was done by Joshua Tully.
- Analysis of EPR spectrum in Chapter 4 Figure 4.13 was aided by Ben Breeze.
- Experimental design and collection of etch profiles and rate data in Chapter 5 was performed by Joshua Tully.
- The methodology used to detect hydrogen peroxide in Chapter 5 Figure 5.7 was developed by Rachel Lai-Cheong.

Chapter 5 of this thesis has been published by the author:

Abstract

Electrochemically generated hydroxyl radicals (HO·) is thought to be the most prevalent and powerful species exploited in the areas of electrosynthesis and electrochemical advanced oxidative processes. The electrochemical generation of HO· requires an electrode material which only exhibits a very weak interaction with HO· such as boron doped diamond. HO· is directly generated through the electrochemical oxidation of water which is a high dielectric solvent; the use of high dielectric solvents in electron paramagnetic resonance spectroscopy can be problematic. Since free radicals are highly reactive and therefore have a short lifetime, the role of a spin trap is necessary for their detection. However, there are many intricacies when using a spin trap like 5,5-dimethyl-1-pyrroline N-oxide (DMPO) such as the artefactual generation of spin adducts due to inverted spin trapping and the Forrester-Hepburn mechanism. In this thesis, the optimal conditions of EPR spectrometer for the detection of spin trapped free radicals in aqueous media are investigated. Additionally, the generation of false positive spin adduct species from inverted spin trapping was thoroughly studied, as well as the consequences of electrochemical oxidation of DMPO. Finally, the optimised conditions and information learned about inverted spin trapping in electrochemical systems was applied to a real-life system. In this case, probing the mechanism behind non-contact electrochemical etching of sp² carbon to create diamond membranes.
Chapter 1: Introduction

This chapter intends to give a brief overview of the key fundamental concepts underpinning the results presented, as well as putting the results in context with the current scientific understanding in the literature. Topics covered include: an overview of dynamic electrochemistry\textsuperscript{1,2} and electron paramagnetic resonance spectroscopy (EPR) theory,\textsuperscript{3,4} followed by discussion of electrochemically generation of free radical species and how free radicals are subsequently detected.

1.1. Dynamic Electrochemistry Theory

During an electron transfer reaction between an electrode and a redox species, the electrode can act as a source (for reduction) or sink (for oxidation) of electrons. The simplest electrochemical (EC) reaction can be described as:

\[
0_{(aq)} + ne^{-} \overset{k_{\text{red}}}{\underset{k_{\text{ox}}}{\rightleftharpoons}} R_{(aq)} \tag{1.1}
\]

where \(O\) and \(R\) represent the oxidised and reduced form of an electroactive redox species respectively that are interconverted by electron transfer. \(k_{\text{ox}}\) and \(k_{\text{red}}\) are the rate constants for the potential dependent oxidative (backward) and reductive (forward) electron transfer reactions respectively and \(n\) is the number of electrons transferred. The equilibrium position of the reaction is related to the standard electrode potential \((E^0)\) under standard conditions of 1 atm, 298 K and unit activity. At \(E^0\), the reaction rate constant is denoted the intrinsic rate of electron transfer \((k^0)\). Under non-standard equilibrium conditions, the Nernst equation can be used to determine the relative activities of \(R\) and \(O\) \((a_R\) and \(a_O\) respectively) at the electrode surface (Equation 1.2).

\[
E' = E^0 - \frac{RT}{nF} \ln \left( \frac{a_R}{a_O} \right) \tag{1.2}
\]
Where $E'$ is the electrode potential in V, $R$ is the gas constant (8.3145 J mol$^{-1}$K$^{-1}$), $T$ is temperature in K and $F$ is the Faraday constant (96485 C mol$^{-1}$).

When the applied potential ($E$) equals $E^0$, $k^0$ for the forward reaction equals that of the back reaction and thus there is no overall current flow. Making the electrode potential more positive (for an oxidation) or more negative (for a reduction) compared to $E^0$ results in an exponential increase in the rate constants for the forward and back reactions described by the Butler-Volmer model (Equation 1.3 and 1.4 for $k_{\text{red}}$ and $k_{\text{ox}}$ respectively). \(^1\)

\[
\begin{align*}
    k_{\text{red}} &= k^0 \left( e^{\frac{-\alpha F \eta}{RT}} \right) \\
    k_{\text{ox}} &= k^0 \left( e^{\frac{(1-\alpha) F \eta}{RT}} \right)
\end{align*}
\tag{1.3, 1.4}
\]

Where $\alpha$ is the transfer coefficient and the deviation of $E$ from $E^0$ is termed overpotential ($\eta$) given in Equation 1.5 and “drives” the electron transfer reaction. Values of $\alpha$ tend to be around 0.5 for metal electrodes reflecting the transition state is roughly halfway between the reagents and products.

\[
\eta = E - E^0
\tag{1.5}
\]

The current ($i$) is also proportional to the flux ($j$) of electroactive species to the electrode surface (in mol cm$^{-2}$s$^{-1}$) described in Equation 1.6, where $A$ is the electrode area (cm$^2$).

\[
i = nAFj
\tag{1.6}
\]

The rate of the overall reaction is dependent on: (i) electron transfer at the electrode surface, (ii) surface reactions such as adsorption, desorption or precipitation, (iii) chemical reactions such as protonation or dimerisation and (iv) mass transport of the electroactive species from bulk to the electrode surface. These processes are depicted in Figure 1.1. In most cases, several steps make up the overall EC reaction however, the rate determining step is the slowest which typically either constitutes either the electron transfer or mass transport step.
These types of electron transfer reactions are heterogeneous, taking place between a solid electrode surface and the electroactive redox analyte in solution. The interface between the electrode and electrolyte solution acts as an electrical capacitor due to charge rearrangement at the surface of the electrode dependent on the applied potential. In particular, ions and dipolar molecules (such as water) in solution arrange themselves at the electrode surface to balance the charge at the electrode surface producing an electrical double layer, depicted in Figure 1.2.\(^1\)

\[\text{Figure 1.1: Illustration of possible pathways in an electrode reaction.}\]

\[\text{Figure 1.2: Illustration of electrical double layer.}^5\]
The double layer consists of several regions to compensate the charge on the electrode. Firstly, the Stern layer which is also referred to as the inner Helmholtz plane (IHP), where unsolvated ions and dipolar solvent molecules are adsorbed directly onto the electrode surface. The outer Helmholtz plane (OHP) is the distance of closest approach of solvated ions. Beyond the OHP is the diffuse layer, described by Gouy and Chapman, formed by the competing interactions of the attraction/repulsion forces from the electrode against Brownian motion which tends to disperse excess ions. The diffuse layer extends out into bulk solution where the ions have no net arrangement. The potential distribution across the electrode is largely dropped off between the electrode and the OHP and continues to gradually fall through the diffuse layer out to a characteristic value of the bulk solution. The electrical double layer screens the electrode charge to approaching ions and its size varies with concentration and type of supporting electrolyte used. 

Transport of species to the electrode surface can occur by three mechanisms: migration, convection and diffusion; diffusion is always present for a static experiment. Migration effects arise due to the electric field at the electrode/solution interface exerting electrostatic force on ions inducing movement of the ions to and from the electrode. In EC experiments, migration contributions are excluded by the addition of a high concentration of inert (i.e. non-electroactive) supporting electrolyte. This has an added benefit of increasing the solution conductivity and minimising solution resistance ($R_s$) effects between the working electrode (WE) and reference electrode (RE). If large currents flow and/or $R_s$ is significant, the measured potential can be reduced due to Ohmic drop, Equation 1.7.

$$E = iR_s$$

For convection transport routes, careful control of the experiment temperature will prevent natural thermal convection which can be unpredictable. However, application of external forces such as bubbling of gas through solution, stirring, flow conditions or rotation of the electrode will introduce forced convection effects. Forced convection can increase mass transport to the electrode surface; for channel flow electrodes and
rotating disk electrodes (RDE), a well-defined hydrodynamic behaviour is formed. However, bubbling of solution and stirring can produce ill-defined/erratic hydrodynamic behaviours.

For many stationary EC experiments, diffusion is the only mass transport contribution to be considered. In an EC experiment, the consumption of an electroactive species at the electrode surface creates a concentration gradient. New electroactive molecules will diffuse from high concentration in bulk solution to the low concentrations at electrode surface. Linear diffusion in one dimension to a planar surface is described by Fick’s first law, given in Equation 1.8.

\[ j = -D \frac{\partial c}{\partial x} \]  

(1.8)

where \( D \) is the diffusion coefficient and \( \frac{\partial c}{\partial x} \) is the concentration gradient.

1.1.1. Electrochemical set-up

In general, macro-scale EC experiments are performed using a three-electrode configuration consisting of a WE, RE and counter electrode (CE). A CE is utilised to avoid the current generated at the WE from passing through the RE. The same magnitude of current that flows through the WE flows through the CE but in the opposite direction driving the reverse reaction.\(^6\) The area of the CE is typically larger than the WE to prevent limitations on the current flowing through the CE. The applied potential is controlled between the WE and RE whilst, the current is measured between the WE and CE; the circuit configuration is shown in Figure 1.3.
Figure 1.3: Circuit diagram of potentiostat set-up for a three-electrode configuration.

The purpose of the RE in a three-electrode configuration is to hold a well-defined and stable constant potential throughout the duration of the experiment for the WE to be measured relative to this reference point. In REs, stable redox couples are employed where the aqueous components are present in high concentrations to create a good RE. The potential of a RE is governed by the Nernst Equation (Equation 1.2) therefore having a high concentration minimises any perturbations in the potential due to small concentration fluctuations. For these reasons concentrations of 1 M all the way up to saturated solutions are opted for. For example, the most common REs, such as saturated calomel electrode (SCE) or silver-silver chloride (Ag/AgCl) electrodes, exploit high to saturated chloride concentrations to maintain a constant potential. The use of a CE in a potentiostatic circuit eliminates current passing through the RE which would otherwise alter its potential perturbing the reference point.

A two-electrode set-up consisting of only the WE and RE can be utilised however, it is prone to current being passed through the RE especially when macro-electrodes are used generating large currents. Usually a two-electrode system is used for ultramicroelectrodes or dropping mercury electrodes where small currents are passed though, a two-electrode system can also be used to simplify an electrolysis reaction at high potentials. In this case, the potential of the WE will vary over time.
1.1.1.1. Electrode materials

WEs are commonly made from good conducting materials of known material and composition such as carbon-based electrode materials like glassy carbon (GC) and metal electrodes like Au and Pt. Diamond is an exceptional material with notable properties such as high mechanical stability, chemical resistance, high thermal conductivity among many more. Diamond has a wide band gap (5.47 eV at 300K) however, when sufficiently doped with boron (≥ 10^20 B atoms cm^-3) the resulting boron doped diamond (BDD) becomes a p-type semi-conductor. BDD as an electrode material is well-known for its renowned properties including: (i) wide solvent window, (ii) low background current, (iii) biocompatibility, (iv) reduced fouling and (v) reduced oxygen reduction reaction (ORR). A solvent window is defined as the potential range where no solvent oxidation and reduction reactions are happening. The wide potential range for BDD (>3 V in 0.10 M KNO\textsubscript{3} between the bounds of ± 0.4 mA cm\textsuperscript{-2}) arises from BDD being “electrocatalytically retarded” and lacking binding sites for efficient inner sphere electron transfer. Inner sphere electron transfer process requires absorption sites on the electrode surface to proceed. Water oxidation and reduction is easily facilitated by unfilled d-orbitals on noble metals (Au and Pt) and reactive quinone-like groups on GC reducing the operational potential range on these electrode materials. Cyclic voltammograms (CVs) showing solvent windows for 0.10 M KNO\textsubscript{3} on Au, Pt, GC and BDD at 0.1 V s\textsuperscript{-1} have been given in Figure 1.4. As can be seen in Figure 1.4a and Figure 1.4b, Pt and Au metal electrodes are effective ORR materials with multiple peaks present significantly reducing the potential range where no faradaic processes are occurring. In Figure 1.4c, a peak due to the oxidation of sp\textsuperscript{2} on the GC surface can be seen as well as peaks due to ORR but these are kinetically hindered than compared to Pt and Au. Finally in Figure 1.4d, BDD shows a wide solvent window with only the water oxidation/reduction processes occurring. This is beneficial as it provides a large potential range for analytical measurements to be recorded.
Figure 1.4: Aqueous based CVs for (a) 2 mm Au disk WE, (b) 2 mm Pt disk WE, (c) 3 mm GC disk WE and (d) 1 mm BDD disk WE in 0.10 M KNO₃ at 0.1 V s⁻¹.

Furthermore, BDD passes very small currents compared to metal electrodes (from Figure 1.4, ca. 2 mA for metal electrodes and ca. 0.06 mA for BDD) attributed to the low capacitance of the material, low density of states and a lack of binding sites. This permits BDD to achieve low detection limits for trace analysis compared to other electrode materials. The wide solvent window and low detection limits achievable make BDD an attractive electrode material in many applications.

1.1.2. Voltammetric scan techniques

1.1.2.1. Cyclic and linear sweep voltammetry

Potential sweep voltammetric techniques are the most widely used due to their simplicity. For these techniques, the potential is applied “linearly” through the application of a digital staircase in one direction only (linear sweep voltammetry, LSV) or in both directions (cyclic voltammetry, CV). Typically, the sweep starts at a potential
where only non-faradic reactions are taking place and scans either anodically and/or cathodically to result in a faradaic oxidation or reduction electron transfer event. The waveform for a CV experiment where a reduction reaction takes place followed by an oxidation reaction is given in Figure 1.5a. The CV current response for this reduction followed by oxidation of a reversible redox couple is provided in Figure 1.5b under conditions of diffusion-limited linear diffusion.

![Figure 1.5](image_url)

**Figure 1.5**: (a) Waveform of a CV experiment and (b) the voltammogram obtained for a reversible electron transfer reaction. $E^\text{ox}_{p}$ and $E^\text{red}_{p}$ represent the peak potential for the oxidation and reduction reaction respectively. $i^\text{ox}_{p}$ and $i^\text{red}_{p}$ represent the peak current for the oxidation and reduction reaction respectively. Finally, $\Delta E_p$ represents the difference in peak potentials.

In Figure 1.5b, as the scan can be seen to commence, the potential is driven negatively which increases the potential dependent rate constant for reduction of the redox species resulting in an exponential increase in the current recorded in accordance with Butler-Volmer (Equation 1.3 and 1.4). Under linear diffusion conditions, where the diffusional flux of O into the surface is unable to sustain a constant diffusion gradient, the current peaks ($i_p$) and then falls with increasing negative potential. The potential is then swept in the other direction on the reverse scan for the oxidation of electroactive species (R) at the electrode surface. The peak potential ($E^{\text{ox}}_p$ and $E^{\text{red}}_p$) and the peak current ($i^{\text{ox}}_p$ and $i^{\text{red}}_p$) are dependent on the reversibility of the redox couple O and R. The Nicholson Shain model predicts a peak separation ($\Delta E_p$) of $57/n$ mV at 298 K for a reversible electron transfer reaction.\textsuperscript{15,16}
The $i_p$ for a reversible system under diffusion-controlled conditions is calculated using the Randles Sevcik equation:\(^1\)

$$|i_p| = 0.4663AF[C]\left(\frac{nFv_sD}{RT}\right)^{\frac{1}{2}} \quad (1.9)$$

where $[C]$ is the bulk concentration in mol cm$^{-3}$ and $v_s$ is the scan rate in V s$^{-1}$.

Alternatively for an irreversible diffusion-controlled electron transfer reaction, the $i_p$ is described by Equation 1.10.

$$|i_p| = 2.99 \times 10^5 \alpha^{\frac{1}{2}} n^{\frac{3}{2}} AD^{\frac{1}{2}} v_s^{\frac{1}{2}} [C] \quad (1.10)$$

1.1.2.1. Chronoamperometry

Chronoamperometry utilises potential step waveforms where the potential is stepped between two values. Under typical conditions, the potential is stepped from an initial potential ($E_1$) where only non-faradic processes occur to a final potential ($E_2$), often where O to R (or R to O) is taking place at a diffusion-controlled rate, shown in Figure 1.6a. Under these conditions, as shown in Figure 1.6b, initially a large current flows which falls with time due to the evolving concentration gradient.

![Figure 1.6](image)

**Figure 1.6:** (a) Waveform for potential step for an EC oxidation reaction. (b) Current response from a stationary chronoamperometry experiment.

The current-time profile is described by the Cottrell equation (Equation 1.11) where $t$ is time.
In this thesis, when chronoamperometric techniques were exploited, the solution was stirred to minimise the size of this diffusion layer and thus the current drop off. Note, the decay of the non-faradic response is significantly faster than the faradaic decay and described by the following expression:\(^\text{(1.11)}\)

\[
|i| = \frac{nFAD^2[C]}{\pi^2t^2}
\]

where \(E_{SW}\) is the pulse amplitude, \(E_i\) is the staircase increment, \(R_{UN}\) is the uncompensated resistance and \(RC\) represents the time constant (relating to the uncompensated resistance and capacitance).

\[
i = \frac{2E_{SW} - E_i}{R_{UN}} e^{-t/RC} \quad \text{(1.12)}
\]

1.2. Electron Paramagnetic Resonance Spectroscopy

EPR spectroscopy is an analytical technique capable of selective, specific and sensitive measurement of unpaired electron species belonging to the larger category of paramagnetic species. Consequently, EPR can be utilised to unearth information about paramagnetic centres, their surrounding environment and the dynamic processes they are involved in.\(^3,18,19\) EPR spectroscopy can be exploited in a range of areas from studying simple inorganic and organic free radicals in liquid (and/or solid phase) to larger and more complex systems such as organometallic compounds or magnetic materials.\(^20\) In industry, EPR can often be found in areas such as: the food industry (to examine the result of sterilisation by irradiation),\(^21-23\) the pharmaceutical industry (to assess stability)\(^24,25\) and the polymeric material industry (investigating radical polymerisation and degradation).\(^26-28\) Additionally, EPR spectroscopy has been to applied other fields such as geology and archaeology (as a dating tool),\(^29\) biology (to investigate lipid interactions and organisation),\(^30,31\) catalysis,\(^32,33\) semiconductors\(^34-36\) and to study defects in solid state materials.\(^37,38\)

The underlying principles and physics for EPR are very similar to those encountered in nuclear magnetic resonance (NMR) spectroscopy, with both relying on the interaction
of electromagnetic radiation with inherent magnetic dipole moments of the sample being analysed. In NMR, the magnetic dipole moment arises from the nuclei (in the cases where the nuclear spin quantum number (I) is a non-zero spin) while in EPR it is unpaired electrons which give rise to the magnetic dipole moment. Unlike NMR, there are very few systems which meet the criteria required for EPR detection. Nonetheless, this can be advantageous in complex systems as background signals are minimised.

Nearly all modern NMR spectrometers are operated in a pulsed fashion where radio wave electromagnetic radiation is pulsed into the sample while the magnetic field is held constant. While in EPR, continuous wave (CW) is still the most prevalent operation mode where the low power microwave (MW) electromagnetic radiation irradiates the sample whilst the applied magnetic field is swept. The following information covers the fundamental theory of CW-EPR and the instrumentation which facilitates the recording of EPR spectra.

1.2.1. Theory

Electrons possess an intrinsic property called spin which is characterised by the spin angular momentum (S). This property is a vector with a magnitude:

$$|S| = \sqrt{S(S+1)}$$  \hspace{1cm} (1.13)

where S is the electron spin quantum number. The allowed orientations of S along the z-direction are given by the electron spin angular momentum quantum numbers (m_s) which range from +S to -S in 2S + 1 integral steps, Equation 1.14.

$$m_s = -S, -S + 1, \ldots, +S - 1, +S$$  \hspace{1cm} (1.14)

For the case of an electron S= ½ therefore, only two spin states are possible (m_s= +½ “spin-up” and m_s= -½ “spin-down”). In the absence of an applied magnetic field, these two spin states are degenerate (equal in energy). Resultantly, the electron has the same probability of being present in either state.
1.2.1.1. Spin magnetic moment

In classical terms, the electron has a mass \(m_e\) and charge \(e\) rotating around an axis with spin angular momentum creating a current. This circulating current produces a magnetic dipole moment of an electron \(\mu_s\) which is proportional to the gyromagnetic ratio \(\gamma\):

\[
\mu_s = -\gamma S\hbar = -g_e \frac{e \hbar}{2m_e} S
\]  \hspace{1cm} (1.15)

where \(\hbar\) is reduced Planck’s constant \((1.05457 \times 10^{-34} \text{ Js})\) and \(g_e\) is the free-electron g-factor \((2.00232)\).

For a free-electron, Equation 1.15 is more commonly expressed as:

\[
\mu_s = -g_e \mu_B S
\]  \hspace{1cm} (1.16)

where \(\mu_B\) is Bohr magneton \((\mu_B = e\hbar/(2m_e) = 9.27401 \times 10^{-24} \text{ J T}^{-1})\).\(^{39}\)

The \(z\)-component of the magnetic dipole moment of an electron \((\mu_z)\), along the applied magnetic field \((B)\) direction, relates to \(m_s\) giving two distinct magnetic dipole moments in Equation 1.17.

\[
\mu_z = -g_e \mu_B m_s
\]  \hspace{1cm} (1.17)

1.2.1.2. The influence of magnetic and microwave fields

The interaction of the magnetic dipole moment with the applied magnetic field is referred to as the Zeeman effect. Applying an external magnetic field in the \(z\)-direction results in a net magnetisation in the sample parallel to the \(z\)-direction whereas, the components in the \(x\)- and \(y\)-directions are averaged out. When an external magnetic field is applied, the degeneracy of the two \(m_s\) spin states is lost. The interaction energy \((\text{IE})\) is a scalar product of the magnetic dipole moment and \(B\):

\[
\text{IE} = -\mu_s B
\]  \hspace{1cm} (1.18)

Assuming that \(B\) is orientated along the \(z\)-axis then the equation becomes:
\[ \text{IE} = g_e \mu_B m_s B \quad (1.19) \]

where \( B \) is the magnitude of the vector \( B \).

In the z-direction, the two values of the magnetic dipole moment give rise to two different energy states referred to as the electron Zeeman levels. Each alignment has a specific energy due to the Zeeman effect. In the lowest energy level state \( (m_s = -\frac{1}{2}) \) the electron magnetic dipole moment is aligned parallel to the applied magnetic field. On the other hand, in the highest energy level state \( (m_s = +\frac{1}{2}) \) the electron magnetic dipole moment is aligned anti-parallel to the external magnetic field.

When an external magnetic field is applied, the difference in energy \( (\Delta E) \) between the electron Zeeman levels is given by:

\[ \Delta E = g_e \mu_B \Delta m_s \quad (1.20) \]

where \( \Delta m_s \) has values of \( \pm 1 \) to converse angular momentum.

\( \Delta E \) is also the energy required to promote an electron spin transition between the two spin states. In EPR spectroscopy, this energy comes from absorbing or emitting a photon of energy such that the resonance condition is met:

\[ \Delta E = h \nu \quad (1.21) \]

where \( h \) is Planck’s constant \((6.62607 \times 10^{-34} \text{ Js})\) and \( \nu \) is the frequency in Hz.

In CW-EPR, the resonance condition is achieved by applying a fixed MW frequency and sweeping the magnetic field. Figure 1.7 illustrates the absorption that occurs when the magnetic dipole moment and MW radiation interact as a function of the magnetic field during an EPR experiment.
Figure 1.7: The Zeeman effect for an electron with increasing B. At the resonance condition, the energy difference matches the excitation energy resulting in an electron spin transition thus an EPR signal. This signal can be plotted as either an absorption (dashed) or first derivative (solid).

However, this resonance condition can only be detected if there is significant difference in population between the two spin states. The relative populations of these states are given by the Maxwell-Boltzmann distribution:

\[
\frac{N_{+\frac{1}{2}}}{N_{-\frac{1}{2}}} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{g_e \mu_B B}{k_B T}\right)
\]  

(1.22)

where \( N_{+\frac{1}{2}} \) and \( N_{-\frac{1}{2}} \) is the number of spins in \( m_s = +\frac{1}{2} \) and \( m_s = -\frac{1}{2} \) state respectively, \( k_B \) is the Boltzmann constant (1.38065 x 10\(^{-23}\) J K\(^{-1}\)), and \( T \) is temperature in K.

Maxwell-Boltzmann statistics dictates that there are slightly more electrons present in the lower energy spin state than compared to the higher energy spin state. Absorption of MW energy promotes transitions from lower energy spin state to higher energy spin states leading to an equalisation in the population difference. When the population of the two spin states becomes equal, the system is said to be saturated. Under these circumstances, no further transitions can be induced by absorption of MW energy resulting in a drop off in EPR signal. Electron spin centres can interact with
each other as well as the surrounding lattice ensuing relaxation mechanisms which restore the system to the Maxwell-Boltzmann distribution after transitions have occurred from MW adsorption.

1.2.1.3. g-factor

The presence of additional local magnetic fields (more commonly referred to a $B_1$) at the electron due to interaction of nuclei magnetic moments causes the electron to experience a different effective magnetic field than the field being applied. This is expressed as an effective g-factor ($g$) which depends on:

$$g = \frac{hv}{\mu_B B_r}$$  \hspace{1cm} (1.23)

where $B_r$ is the effective magnetic field at the resonance condition.

This parameter is unique to each individual radical as it depends on the electron’s surroundings and the type of atom the unpaired electron resides on. The g factor in EPR is the analogue for chemical shift in NMR. Moreover, the value of g (along with the hyperfine coupling, discussed in Section 1.2.1.4.) can be used to distinguish the type of radical being quantified. For example, a free electron in a vacuum has a g value of 2.00232 whereas, an electron close to a metal centre can have a g of up to 9 or 10.40

Local enhancements in the magnetic dipole moment may also come from orbital angular momentum. This effect arises due to mixing of ground and excited states which causes the orbital angular momentum and electron spin to couple, referred to as spin-orbital coupling. This can lead to large deviations in g. Spin-orbital coupling arises from orbital motion and is thus orientation dependent (anisotropic). This is an important factor for single crystals, powdered solids and solutions of high viscosity. On the other hand, in low viscosity solutions used in this thesis, these effects are averaged out through rapid molecular tumbling.
1.2.1.4. Hyperfine coupling

Interactions between the nuclear spin and the applied external magnetic field is called Nuclear Zeeman splitting. In the same manner as $\mu_z$, Equation 1.17, the magnetic dipole moment of nuclear spin ($\mu_i$) can be expressed as:

$$\mu_i = g_N \mu_N m_i$$  \hspace{1cm} (1.24)

where $g_N$ is the effective nuclear g-factor, $\mu_N$ is the nuclear magneton ($\mu_N = e\hbar/(2m_p) = 5.05078 \times 10^{-27}$ J T$^{-1}$), $m_p$ is the mass of a proton and $m_i$ is magnetic quantum number.

Additionally, it is possible for nuclear spins which possess a magnetic moment to interact with the electron spin system producing an interaction called the electron nuclear hyperfine interaction or more commonly hyperfine interaction. The magnetic moment of the nuclei induces local fluctuations in the applied magnetic field that the electron experiences referred to as $B_1$. This hyperfine interaction along with nuclear Zeeman splitting causes perturbations in IE which can raise or lower the energy level of the spin state. Consequently, a greater or less quantity of $B$ is necessary to promote an EPR transition therefore, line-splitting occurs due to the different effective magnetic field that the electron encounters which is depicted in Figure 1.8.

![Figure 1.8](image)

**Figure 1.8**: The effect of hyperfine interactions where the local magnetic field reduces or enhances the external applied magnetic field resulting in splitting of the EPR lines by the hyperfine splitting factor (a).

The magnitude of the hyperfine interaction is defined as a hyperfine splitting factor (a). The splitting observed in the EPR spectrum is characteristic of the number (n) and
type of nuclei present (with the number of peaks being equal to $2nI + 1$) in the paramagnetic species and therefore can be used to identify the radical species. Similarly, to the $g$-factor, hyperfine interactions exhibit anisotropic effects in solids or solution with high viscosity but for low viscosity solutions this effect is averaged out by molecular tumbling. Throughout this thesis, low viscosity solutions have been used thus only isotropic effects need to be considered for this study.\(^{41}\)

**1.2.2. The spectrometer**

There are four main components to the instrumentation of the EPR spectrometer including the magnets, MW bridge, resonator and the control and data acquisition console. This is shown in Figure 1.9, each component is discussed in further detail in sub sections following.

![Figure 1.9](image)

**Figure 1.9:** Schematic representation of main components for an EPR spectrometer. The MW bridge consists of (a) Gunn diode, (b) variable attenuator, (c) circulator, (d) variable attenuator, (e) phase shifter, and (f) diode.

**1.2.2.1. The magnets**

The magnet assembly consists of the magnets, a power supply and field sensor called the Hall probe. The magnets are either made from iron core electromagnets or superconducting magnets are employed for fields < 2 T. The magnets are controlled by a variable power supply which creates the magnetic field.
Chapter 1: Introduction

The magnet set-up is designed to give a homogeneous magnetic field over the volume of the sample, a linear sweep over the magnetic range of interest and high stability at static field. To ensure these conditions are kept constant for precise measurements and reproducibility, a Hall probe is positioned inside of the magnet. This maintains the field at the requested value by correcting the current applied through a feedback loop.

1.2.2.2. Magnetic field modulation

Phase-sensitive detection is used in CW-EPR to enhance sensitivity by diminishing background noise. The optimum signal enhancement is achieved by controlling the field modulation and modulation amplitude. An additional oscillating magnetic field (called the field modulation; \(B_m\)) is applied parallel to the external magnetic field at a typical frequency of 100 kHz using modulation coils placed either side of the resonator. This oscillating magnetic field causes the detector output to also oscillate at 100 kHz. The peak-to-peak amplitude is proportional to the gradient of the absorption profile leading to a first derivative profile being recorded, this is illustrated in Figure 1.10.

![Figure 1.10: The effect of applying a 100 kHz field modulation; absorption profile (left) and first derivative profile (right) after phase-sensitive detection.](image)

Phase-sensitive detection will only detect signals at the same modulation (i.e. 100 kHz) as that applied and of the reference arm (discussed in Section 1.2.2.3). This filters noise generated at lower frequencies increasing the signal-to-noise ratio. To circumvent distortion effects, \(B_m\) should be kept to a tenth of the narrowest EPR
linewidth. Above this threshold, an increase in signal size can be gained but at the
detriment of precise line shape and eventually causing a decrease in signal magnitude.

1.2.2.3. Microwave bridge

EPR spectroscopy can be performed over a large range of MW frequencies however,
MW energy can only be generated in small frequencies windows called bands. Band
frequencies and their corresponding field strength are given in

Table 1.1. X-band is used the most predominately in EPR as it is ideally suited for the
detection of organic and free inorganic molecules in solution.

<table>
<thead>
<tr>
<th>Band</th>
<th>Typical Frequency (GHz)</th>
<th>Resonant field for $g_e$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1</td>
<td>0.039</td>
</tr>
<tr>
<td>S</td>
<td>3</td>
<td>0.107</td>
</tr>
<tr>
<td>X</td>
<td>9</td>
<td>0.338</td>
</tr>
<tr>
<td>K</td>
<td>24</td>
<td>0.856</td>
</tr>
<tr>
<td>Q</td>
<td>35</td>
<td>1.248</td>
</tr>
<tr>
<td>W</td>
<td>94</td>
<td>3.360</td>
</tr>
</tbody>
</table>

The main components of the MW bridge are shown in Figure 1.9. MWs are generated
by a Gunn diode or klystron (Figure 1.9a) and then are split down two separate paths:
the sample arm and the reference arm. For optimum sensitivity, the MW detector
should be operated in the linear regime thus the reference arm provides bias MW
power to the detector to maintain it in the linear region.

Along the sample path, the MWs initially pass through a variable attenuator (Figure
1.9b) to accurately adjust the MW power required. The MW energy then passes
through a circulator (Figure 1.9c) which directs the incident MWs into the resonator
through a waveguide or co-axial cable. The circulator also directs the reflected power (from absorption of MWs in the sample) towards the detector (Figure 1.9f). The reference arm also has a variable attenuator (Figure 1.9d) to bring the MW detector into the desired range. Once in the range of interest, the MWs pass the phase shifter (Figure 1.9e) which matches the phase of the reference and reflected signal for detection. This process facilitates the phase-sensitive detection.

1.2.2.4. The resonator

The resonator is designed to enhance sensitivity by amplifying the MW energy density surrounding the sample to induce EPR transitions. Different types of resonators are available such as cavities, dielectric and loop gap resonators (LGR); all resonators have different strengths and weaknesses so are purposely picked for the experiment being carried out. The design of the resonator has been engineered such that the sample sits in the maximum magnetic field whilst also being in the minimum electric field (Figure 1.11). This ensures power loss due to the absorption of the electric field by electric dipole moments in the sample is minimal which is vitally important in high dielectric loss solvents.

A condition referred to as critical coupling is reached between the resonator and MW bridge to ensure no MW energy is reflected to the detector in the absence of
transitions minimising baseline noise. Critical coupling is achieved using an iris screw which is positioned in a hole located at the top of the resonator. The iris screw can be used to alter the amount of MW energy that can enter or leave the resonator. Critical coupling is an important criterion to meet to allow easier detection of small changes in reflected power once the baseline has been set to zero.

In actuality, the resonator does not perfectly store all MW energy, and some energy is lost through generation of electric currents, which in turn generates heat in the resonator walls. The efficiency of the resonator is often characterised by the quality factor (Q) which is defined by:

\[ Q = \frac{2\pi (\text{MW energy stored in the resonator})}{\text{MW energy dissipated from the resonator}} = \frac{\nu_R}{\Delta\nu} \]  

(1.25)

where \(\nu_R\) is the resonant frequency and \(\Delta\nu\) is the width of the resonance absorption at half height.

With no sample present in the resonator, the unloaded quality factor (\(Q_U\)) depends on the fundamental properties of the resonator such as the geometry, operating frequency and material it is constructed from. When a sample is loaded into the resonator, the loaded quality factor (\(Q_L\)) depends on the resonator properties as well as the properties of the sample. In samples with high dielectric solvents, \(Q_L\) is often drastically different to \(Q_U\).  

In addition to \(Q_U\), the EPR signal of the sample being measured is proportional to:

\[ \text{EPR Signal} \propto Q_L \eta_f P^{\frac{1}{2}} \]  

(1.26)

where \(\eta_f\) is the filling factor and \(P\) is MW power. The proportionality constant is different for different resonators.

The filling factor is the amount the sample intercepts the MW magnetic field and can be expressed as a ratio between the sample volume (\(V_s\)) and resonator volume (\(V_r\)) as followed:
\[ \eta_f = \frac{\int_S \mathbf{B}^2 dV_S}{\int_r \mathbf{B}^2 dV_r} \]  

(1.27)

The \( \eta_f \) in a cavity resonator is generally small due to the large internal volumes however, LGRs are fabricated with smaller sample spaces to maximise the \( \eta_f \).\textsuperscript{18,43,44} Therefore, an appropriate selection of resonator design is crucial to maximising \( Q_L \) and \( \eta_f \) to boost the signal intensity recorded.

Solvents with high dielectric constants are often referred to as “lossy” samples where the sample absorbs MW energy reducing the overall \( Q \). If the sample loss is too great, it is not possible to critically couple the resonator.

### 1.2.2.4.1. Cavity resonators

A cavity resonator consists of a metallic chamber whose dimensions are related to the wavelength of applied MWs. Cavities are often classified by the modes which they operate in; they can operate in either transverse electric (TE) or transverse magnetic (TM) modes. The superscript that follows the mode then denotes the number of half waves supported in each dimension. The \( Q_L \) for the cavity resonators is typically very high making them very sensitive but large hollow design means they exhibit a relatively low filling factor \( (\eta_f = 0.01) \) drastically reducing sensitivity.

### 1.2.2.4.2. Loop gap resonators

The simplest design of LGR consists of a single loop and a gap which act as an inductor and capacitor respectively and was first applied to EPR spectroscopy by Wood, Hyde and Francisz.\textsuperscript{45} Due to their design, LGRs can be modelled as RLC circuit; an electric circuit containing a resistor, an inductor and a capacitor. In the LGR, the resonance frequency for \( n \) gaps is given by:

\[ \nu_{res} = \frac{1}{2\pi\sqrt{LC}} \]  

(1.28)

and L and C are defined as:
\[ L = \frac{\mu_0 \pi r^2}{Z} \quad \text{and} \quad C = \frac{\varepsilon w Z}{t_g n} \]  

where \( L \) is the inductance, \( C \) is the capacitance, \( \mu_0 \) is the permeability of free space, \( r \) is radius of loop, \( Z \) is the height of the LGR, \( \varepsilon \) is the dielectric constant, \( w \) is the width of the gap, \( t_g \) is the gap thickness and \( n \) is the number of identical gaps.\(^{46}\)

By increasing the number of gaps, the capacitance of the resonator is reduced and thus a larger inductance can be held. This means that larger sample volumes can be used while keeping the resonator frequency high allowing larger \( \eta_f \) to be accommodated. Incorporation of multiple loops and gaps allows the frequency to be tailored. For example, a 5-loop-4-gap LGR (also referred to as a rising sun) has a resonance frequency of around 9.6 GHz. Due to the custom design, LGRs are connected to the MW bridge using a co-axial cable. In this setup there is no iris to achieve critical coupling, so coupling is reached through fine tuning the positions of the resonator relative to the MW aerial.

LGRs are also ideal for systems which have a high dielectric constant. Their design means that the electric field is confined within the gaps while the sample sits in the loop. This minimises any interaction between the MW electric field and the high dielectric constant sample diminishing any detrimental heating effects. One disadvantage is that the critically coupled value for a LGR resonator is lower than for a cavity resonator however, the impact of this on reducing sensitivity is partially offset by higher \( \eta_f \) for an LGR.

### 1.2.3. Experimental considerations

#### 1.2.3.1. Types of sample holders

The majority of EPR spectroscopy experiments are performed using standard quartz EPR tubes (shown in Figure 1.12a) however, when “lossy” samples are being measured these can be problematic. This is because the standard quartz EPR tube introduces a large volume of sample into the centre of the EPR resonator; this can then interact with the electric field absorbing MW energy. Since the signal is proportional to the
amount of sample place into the EPR spectrometer (Equation 1.26), this means larger sample volumes will increase the amount of signal. Yet with larger volumes of high dielectric solvent presented in the EPR could lead to greater MW absorption! Over the years, different sample holders have also been engineered overcome the problems when working with high dielectric solvents.

Flat cells are designed for liquids prone to high dielectric loss such as water; the flat cell design is shown in Figure 1.12b. The technology works by confining the sample to a 0.3 mm pathlength with a large surface area to give rise to sufficient EPR intensity. When the flat cell is correctly aligned in the resonator, the thin pathlength lies along the nodal plane where the MW electric field is zero, but the MW magnetic field is still at a maximum. This permits a larger sample volume to be present within the EPR resonator without the sample interacting negatively with the MW electric field improving the sensitivity of the experiment.

Similarly, Bruker’s AquaX star-bore tubing design (shown in Figure 1.12c) breaks up the volume of sample present into smaller sections, so smaller volumes of the high dielectric sample are exposed to the MW electric field and the overall interaction is minismised. The Bruker AquaX cell was shown to give a 8.7-fold signal increase compared to a single bore cell for aqueous samples.
Figure 1.12: Diagrams depicting the following sample holders: a) quartz EPR tube b) Bruker ER160FC WG-812 aqueous flat cell and c) Bruker AquaX star-bore tubing. The commercially available range for the inner diameter (given as d in the diagram above) of the quartz EPR tubes is 1 mm to 4 mm.

1.2.3.2. Microwave power saturation

As discussed before, it is possible for the spin states to reach a saturated regime when too much MW power is applied. Applying too high of a MW power promotes a vast number of transitions which diminishes the population difference between electron Zeeman states as there is insufficient time for relaxation to occur. This leads to the EPR intensity being lower than expected for the given MW power as well as distortion in the line shape of the spectra.

Resultantly, for quantification applications, it is important to operate the EPR spectrometer in the linear region of the MW power. This linear region varies between different resonators, sample concentrations and types of samples. The linear region is easily identified by starting at low MW power and ramping up to higher powers in four-fold steps (increase in attenuation of +6 dB). With each four-fold step in MW
power, the EPR intensity should increase by a factor of 2 without saturation effects. When the change in EPR intensity is no longer a factor of 2 the saturated regime has been reached.

### 1.2.4. Spin Trapping

The method adopted for EPR detection of paramagnetic species is dictated by the reactivity and stability of the radical. Solution state free radicals tend to be very reactive thus the use of a diamagnetic spin trap is often necessary. This is due to not being able to produce a high enough steady state concentration of free radicals to overcome the sensitivity barrier for direct EPR detection due to short free radical lifetimes. Secondly, if the free radical being detected has a short relaxation time, its linewidth may be too broad to be observable. This is the case for both the HO\(^{\cdot}\) and singlet oxygen\(^{,49}\), which are also extremely short lived entities.

In the general case, the radical (R\(^{\cdot}\)) will react with the spin trap (ST) to form a more persistent paramagnetic species referred to as a spin adduct, Equation 1.30.

\[
\text{ST} + \text{R}^{\cdot} \rightarrow \text{ST-R}^{\cdot}
\]  

(Equation 1.30)

EPR spin traps usually have either a nitroso or nitrone (Figure 1.13) functionality. Nitroso spin traps are highly selective but predominately used to detect carbon-based radicals. Since the reaction of a nitroso spin traps with oxygen based free radicals results in unstable spin adducts\(^,49,50\) On the other hand, nitrone spin traps can react with carbon, hydrogen, oxygen, nitrogen and halide radicals producing stable spin adduct species. This makes nitrone spin traps more versatile for a wider diversity of free radicals\(^.51\) Furthermore, nitrone spin traps which possess a \(\beta\)-hydrogen allow for identification of small free radicals through the splitting parameter that arises from the \(\beta\)-hydrogen.
Figure 1.13: Structure of nitrone and nitroso functional groups used in EPR spin traps.

The use of both nitrone and nitroso based spin traps will result in the formation of a nitroxide spin adduct through covalent bonding of the original radical. The nitroxide is relatively stable (half-life typically around 20 min) due to mesomeric stabilisation of the unpaired electron (Figure 1.14).

Figure 1.14: Mesomeric structures of nitroxide functional group stabilising the unpaired electrode on either the nitrogen atom (left) and oxygen atom (right).

1.3. Electrochemical Generation of Free Radical Species

In the EC arena, EC generation of paramagnetic species via oxidation or reduction of a diamagnetic species is common. Industrially, this phenomenon is being used most significantly for efficient, environmentally friendly and cost effective applications in electrosynthesis and electrochemical advanced oxidative processes (EAOPs). Both are very popular and growing areas of research. Electrosynthesis and EAOPs can occur by via either direct electron transfer of species in solution or indirectly via the EC formation of a highly reactive oxidising species. Such species mainly consist of reactive oxygen species (such as ozone, singlet oxygen, HO•), as well as other reactive free radicals. The most common method for EC radical production is via the oxidation of a redox species; typical reactions are detailed in Section 1.3.1 and Section 1.3.2 below.
1.3.1. Direct electrochemical production of free radicals

Chlorides, bromides, sulfates, phosphates, carbonates and nitrates are easily oxidised on a wide range of electrode materials to produce chlorine (Cl\(^-\), Equation 1.31), bromide (Br\(^-\), Equation 1.32), sulfate (SO\(_4^{2-}\), Equation 1.33), phosphate (PO\(_4^{3-}\), Equation 1.34), carbonate (CO\(_3^{2-}\), Equation 1.35) and nitrate (NO\(_3^-\), Equation 1.36) radicals.

\[
\begin{align*}
\text{Cl}^-_{(aq)} & \rightarrow \text{Cl}^\cdot_{(aq)} + e^- & E^0 = +2.43 \text{ V vs SHE}^61 (1.31) \\
\text{Br}^-_{(aq)} & \rightarrow \text{Br}^\cdot_{(aq)} + e^- & E^0 = +1.96 \text{ V vs SHE}^61 (1.32) \\
\text{SO}_4^{2-}_{(aq)} & \rightarrow \text{SO}_4^\cdot^-_{(aq)} + e^- & E^0 = +2.44 \text{ V vs SHE}^61 (1.33) \\
\text{H}_2\text{PO}_4^{3-}_{(aq)} & \rightarrow \text{H}_2\text{PO}_4^\cdot^-_{(aq)} + e^- & E^0 = +2.75 \text{ V vs SHE}^61 (1.34) \\
\text{CO}_3^{2-}_{(aq)} & \rightarrow \text{CO}_3^\cdot^-_{(aq)} + e^- & E^0 = +1.57 \text{ V vs SHE}^61 (1.35) \\
\text{NO}_3^-_{(aq)} & \rightarrow \text{NO}_3^\cdot^-_{(aq)} + e^- & E^0 = +2.47 \text{ V vs SHE}^61 (1.36)
\end{align*}
\]

Electrode materials such as BDD and PbO\(_2\) are thought to promote the oxidation of these electrolytes (Equation 1.31-1.36) and even acetic acid.\(^62\) These free radicals are available to react in solution or recombine to form stable oxidising species such as peroxosulfate (S\(_2\)O\(_8^{2-}\)), peroxophosphate (P\(_2\)O\(_8^{4-}\)), peroxocarbonate (C\(_2\)O\(_6^{2-}\)), and chlorine (Cl\(_2\)). Cl\(_2\) will further disproportionate in solution depending on the pH, remaining as Cl\(_2\) or forming either hypochlorous acid (HClO) or hypochlorite (OCl\(^-\)).\(^63\)

1.3.2. Electrochemical oxidation of water to form hydroxyl radicals

The most favourable thermodynamic route for the oxidation of water results in the production of oxygen and protons, via the loss of 4 electrons, Equation 1.37. In reality the actual mechanism is more complex involving a series of different steps and the adsorbed HO\(^-\) radical as an intermediate.\(^64,65\)

\[
2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_2_{(g)} + 4\text{H}^+_{(aq)} + 4e^- \tag{1.37}
\]
However, dependent on the chemical properties of the electrode and strength of adsorption of the HO·, water can also undergo oxidation via 1 or 2 electron transfer pathways producing HO· and H2O2 respectively (Equation 1.38 and Equation 1.39). For the 1 electron route, electrode surfaces which minimise HO· adsorption, such as BDD and TiO2 are preferred. For the 2 electron route, electrode materials such as WO3 and SnO2 promote this reaction pathway. Such understanding has come from both density functional theory calculations theoretical and experimental studies.66,67

\[
\text{H}_2\text{O}(l) \rightarrow \text{HO}^\cdot (aq) + \text{H}^+ (aq) + e^- \quad E^0 = +2.73 \text{ V vs SHE}^{61} \quad (1.38)
\]

\[
2\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}_2(aq) + 2\text{H}^+ (aq) + 2e^- \quad E^0 = +1.76 \text{ V vs SHE}^{66} \quad (1.39)
\]

Back in the 1990’s, Comninellis and co-workers helped pave the way for this understanding by defining two extreme classifications of electrodes towards water oxidation: “active” and “non-active” electrodes.68,69 For both electrode types, water is first oxidised to form adsorbed HO· on the surface shown in Equation 1.40 where M designates an active site on an electrode surface.

\[
\text{M}(s) + \text{H}_2\text{O}(l) \rightarrow \text{M(HO}^\cdot)(s) + \text{H}^+ (aq) + e^- \quad (1.40)
\]

In the case of “active” electrodes, a strong interaction between the surface and the HO· is present. This strong interaction results in the absorbed HO· interacting with the electrode surface leading to an oxygen transition forming a higher order oxide (MO), Equation 1.41.

\[
\text{M(HO}^\cdot)(s) \rightarrow \text{MO}(s) + \text{H}^+ (aq) + e^- \quad (1.41)
\]

For a “non-active” electrode, there is a very weak interaction between the electrode surface and HO· allowing the HO· to react in solution; TiO2 and BDD are examples of a “non-active” electrode. Therefore, to study the EC generation of HO· a “non-active” electrode is necessitated. Thus, BDD is an attractive option due to its capacity to generate HO· and exemplary EC benefits such as wide solvent windows and low background current which are ideal for analytical measurements.
In the case of “non-active” electrodes, once formed HO\(^-\) can combine with another HO\(^-\) to form H\(_2\)O\(_2\) (Equation 1.42). HO\(^-\) can then attack H\(_2\)O\(_2\) to form the hydroperoxyl radical (HO\(_2\)^\(-\)), Equation 1.43.

\[
\text{HO}^- (aq) + \text{HO}^- (aq) \rightarrow \text{H}_2\text{O}_2 (aq) \tag{1.42}
\]

\[
\text{HO}^- (aq) + \text{H}_2\text{O}_2 (aq) \rightarrow \text{HO}_2^- (aq) + \text{H}_2\text{O} (aq) \tag{1.43}
\]

In solution, HO\(^-\) is also a sufficiently strong enough oxidising agent to oxidise species to their radical counterpart, like chloride (Equation 1.44), sulfate (Equation 1.45), phosphate (Equation 1.46) and carbonate (Equation 1.47).

\[
\text{Cl}^- (aq) + \text{HO}^- (aq) \rightarrow \text{HOCl}^- (aq) \tag{1.44}
\]

\[
\text{HSO}_4^- (aq) + \text{HO}^- (aq) \rightarrow \text{SO}_4^2^- (aq) + \text{H}_2\text{O} (l) \tag{1.45}
\]

\[
\text{HPO}_4^{2-} (aq) + \text{HO}^- (aq) \rightarrow \text{PO}_4^{3-} (aq) + \text{H}_2\text{O} (l) \tag{1.46}
\]

\[
\text{CO}_3^{2-} (aq) + \text{HO}^- (aq) \rightarrow \text{CO}_3^- (aq) + \text{HO}^- (aq) \tag{1.47}
\]

Note, this is not an exhaustive list of species which HO\(^-\) can oxidise. As well as oxidising inorganic species (Equations 1.44-1.47), HO\(^-\) can oxidise organic species. A more common class of organic molecules are the aliphatic organic molecules (RH). Oxidation by HO\(^-\) proceeds by an initial hydrogen abstraction, Equation 1.48.

\[
\text{RH} + \text{HO}^- \rightarrow \text{R}^- + \text{H}_2\text{O} \tag{1.48}
\]

This initiates a radical oxidation chain reaction where the organic radical form will react with molecular oxygen to form a peroxy-radical (ROO\(^-'\)), Equation 1.49.

\[
\text{R}^- + \text{O}_2 \rightarrow \text{ROO}' \tag{1.49}
\]

The ROO\(^-'\) radical can abstract a hydrogen from another aliphatic organic molecule regenerating a new organic free radical, Equation 1.50. This free radical go through the cycle again (Equations 1.48 to 1.50).

\[
\text{ROO}' + \text{R}-\text{H} \rightarrow \text{ROOH} + \text{R}^- \tag{1.50}
\]
The carboxyl acid manufactured during Equation 1.50 reaction can be unstable and often further degrades to form carbon dioxide and water. HO\textsuperscript{−} can also react with aromatic organic molecules (ArH) by an addition to an unsaturated bond, (Equation 1.51).

\[
\text{ArH} + \text{HO}^\cdot \rightarrow \text{ArH(OH)}^\cdot
\]  

(1.51)

Much like the aliphatic case, the resultant radical can react with molecular oxygen to form a peroxy-radical, Equation 1.52. This peroxy-radical will abstract a hydrogen from a nearby organic molecule, recreating a radical to undergo subsequent reactions, Equation 1.53.

\[
\text{ArH(OH)}^\cdot + \text{O}_2 \rightarrow [\text{ArH(OH)OO}]^\cdot
\]  

(1.52)

\[
[\text{ArH(OH)OO}]^\cdot + \text{R-H} \rightarrow \text{ArH(OH)} + \text{O}_2 + \text{R}^\cdot
\]  

(1.53)

1.4. Free Radical Generation using Non-Electrochemical Techniques

The application of strong oxidising environments can also generate free radicals via non-EC means. These include photo irradiation, ultrasonic irradiation, ionising irradiation and solution/surface driven chemical oxidation, described in more detail below.

1) **Photo-irradiation**: Free radicals can be produced by the application of ultraviolet (UV) light either directly via photolysis of water\textsuperscript{70–73} or via photoactivation of a catalyst (referred to as photocatalysis).\textsuperscript{74–78} For example, HO\textsuperscript{−} can be produced from H\textsubscript{2}O\textsubscript{2} at ca. 310 nm, Equation 1.54.

\[
\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{HO}^\cdot(\text{aq})
\]  

(1.54)

2) **Ultrasonic irradiation**: the use of ultrasonic irradiation can be used to generate free radicals either directly or through the activation of a catalysts (referred to as sonocatalysis).\textsuperscript{72,79–81} Direct ultrasonic irradiation applied to water can produce HO\textsuperscript{−} via Equation 1.55, where )) indicates the application of ultrasonic irradiation.
Ultrasonic irradiation applied to a catalyst, like TiO$_2$, promotes the catalyst to its excited state moving electrons from the valence band to the conductance band. This creates electron-hole pairs which can react with solution components at the surface to produce free radical species.\textsuperscript{79}

3) Ionising irradiation: the use of gamma ($\gamma$) irradiation and heavy ions can be used to produce free radicals in solution referred to as radiolysis.\textsuperscript{82–84} For example, application of $\gamma$ rays to water leads to the formation of HO$^-$ (Equation 1.56).

$$ \text{H}_2\text{O}(l) \overset{\gamma}{\rightarrow} \text{H}_2\text{O}^+(aq) + e^- \rightarrow \text{HO}^-(aq) + \text{H}^+(aq) \quad (1.56) $$

4) Solution/surface driven chemical oxidation: the Weiss mechanism\textsuperscript{85} describes how active sites on a metal surface can catalyse the decomposition of H$_2$O$_2$ by electron transfer to produce HO$^-$, Equation 1.57:

$$ M_{x(s)} + \text{H}_2\text{O}_2(aq) \rightarrow M_{x+1(s)} + \text{HO}^-(aq) + \text{OH}^-(aq) \quad (1.57) $$

where $M_x$ and $M_{x+1}$ denotes active sites on the metal surface. A similar reaction can happen in solution called the Haber-Weiss reaction or more often referred to as Fenton chemistry. In this case, Fe$^{2+}$ (or less frequently Cu$^{2+}$) converts H$_2$O$_2$ into HO$^-$, Equation 1.58.\textsuperscript{73,86–88}

$$ \text{Fe}^{2+}(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{HO}^-(aq) + \text{OH}^-(aq) \quad (1.58) $$

Fenton chemistry can be further combined with electrochemistry (referred to as electro-Fenton)\textsuperscript{57,89} and photo irradiation (referred to as photo-Fenton)\textsuperscript{90} to promote the reaction.

1.5. Free Radical Detection

HO$^-$ is highly reactive and possess one of the strongest oxidation potentials ($E^0$) of electrochemically generated free radical species. As previously described in Section
1.3.2, HO\(^-\) can react directly when produced or react with other solution components, oxidising them to make free radical species. For this reason, the HO\(^-\) is the most popularly investigated free radical species therefore, this thesis will focus on the detection of HO\(^-\) radicals.

Direct detection of HO\(^-\) has been postulated to be facilitated through ultraviolet-visible (UV-Vis) spectroscopy with a low absorption coefficient (\(\epsilon = 540 \text{ L mol}^{-1} \text{ cm}^{-1}\)) at 230 nm,\(^{91}\) in-situ EPR spectroscopy and even electrochemistry using differential pulse voltammetry.\(^{92}\) However, due to the extremely high reactivity and short lifetimes of HO\(^-\) (lifetime of HO\(^-\) in water is ca. \(\mu\)s)\(^{93}\) only a low steady state concentration is built up. Furthermore, as stated previously, in EPR spectroscopy the fast relaxation time of HO\(^-\) gives rise to a broad linewidth which is often difficult to observe.\(^{49}\) Due to these complexities direct detection is extremely challenging and requires instrumentation adaption to achieve high signal-to-noise ratios and good resolution. Therefore, ubiquitously free radical detection is simplified using probes and scavengers to indirectly confirm the presence of these species. These methods comprise of HO\(^-\) reacting selectively with a compound for subsequent measurement of either the consumption of the reagent or the accumulation of the product. Key examples of each category of probe types have been detailed below, a more exhaustive summary has been provided by Fernández-Castro and co-workers.\(^{94}\)

Absorbance probing methods monitor the decrease in the absorbance of the probe or the increase in absorbance from the product (made via reaction of probe and HO\(^-\)). Absorbance probing methods can either be measured with a UV-Vis spectrometer or coupled to a high performance liquid chromatograph (HPLC). The most successful absorbance probe is dimethyl sulfoxide (DMSO) which reacts with HO\(^-\) to form formaldehyde (HCHO, Equation 1.59-1.61) which can be quantified with absorbance methods.\(^{95-97}\)

\[
\text{DMSO}_{(aq)} + \text{HO}^-_{(aq)} \rightarrow \text{Methanesulfinic acid}_{(aq)} + \text{CH}_3\cdot_{(aq)} \hspace{1cm} (1.59)
\]

\[
\text{CH}_3\cdot_{(aq)} + \text{HO}^-_{(aq)} \rightarrow \text{CH}_3\text{OO}^-_{(aq)} \hspace{1cm} (1.60)
\]
\[
\text{CH}_3\text{OO}^{'(aq)} \rightarrow \text{HCHO}^{(aq)} + \text{CH}_3\text{OH}^{(aq)} + \text{O}_2(g)
\] (1.61)

The instability of the formaldehyde produced can lead to the underestimation of HO' concentration. Another popular probe is salicylic acid which undergoes a hydroxylation reaction with HO' to form 2,3-dihydroxybenzoic acid;\(^{98–103}\) reaction scheme presented in Figure 1.15.

![Figure 1.15: Scheme for the reaction between salicylic acid and HO'].(chain)

Although, the products are detectable by absorbance, fluorescence and EC methods, UV-Vis is the most frequently opted for. Salicylic acid has been shown to undergo hydroxylation reaction under EC conditions without the presence of HO'.\(^{102,103}\) An example of a probe where the absorbance decreases over time is p-Nitroso dimethylaniline (RNO).\(^{104–106}\) In this case, the ca. \(\mu\)M concentration of RNO in solution is monitored over time at 440 nm as HO' are generated. The HO' formed react with RNO depleting the absorbance over time however, some disadvantages are that this type of probe does not distinguish between different free radicals formed and RNO is highly susceptible to oxidation. A further wide range of probes been used as absorbance probes, such as benzoic acid and their derivatives.\(^94\)

Fluorescence probes methods consist of a probe reacting with HO' to produce a fluorescence product. The accumulation of this fluorescent product is monitored by excitation of the product resulting in the emission of fluorescence which is recorded. Like absorbance probes, fluorescence probes can either be measured with a spectrometer or coupled to HPLC fitted fluorescence detector. Frequently for the detection of HO', terephthalic acid (or sodium terephthalate)\(^{96,107–109}\) and coumarin\(^{99,110,111}\) are used as fluorescence probes; reactions depicted in Figure 1.16.
Chapter 1: Introduction

Figure 1.16: Reaction scheme for the fluorescence probes terephthalic acid and coumarin reaction with HO⁻.

Both reactions can have poor yields when reacting with HO⁻ creating other hydroxy isomers instead of the fluorescent product. Furthermore, the reaction of terephthalic acid and HO⁻ is dependent on solution pH and has poor solubility in aqueous solutions. In the case of chemiluminescent probes an excitation is also measured however, in this case the excitation is formed from the chemical reaction between the probe and HO⁻. Examples of these probes include: indoxyl-β-glucuronide, tris(2,2'-bipyridine) ruthenium (III) (Ru(bpy)₃²⁺), and phthalhydrazide. Chemiluminescence probes can be highly unstable, for example, Ru(bpy)₃²⁺ must be generated in solution just prior to use.

As discussed in Section 1.2.4, spin traps can be used in EPR spectroscopy to measure free radical species. The most frequently used EPR spin probe for HO⁻ is 5,5-dimethyl-1-pyrroline N-oxide (DMPO), reaction for the spin trapping of HO⁻ with DMPO is illustrated in Figure 1.17. The spin adduct product from this reaction (DMPO-OH⁻) is relatively unstable with a half-life of only 20 min, so measurements need to be made shortly after the trapping event.

Figure 1.17: Spin trapping reaction of DMPO with HO⁻.
Finally, as previously discussed HO• can recombine to form H₂O₂ (Equation 1.37) and as such many studies have looked at measuring H₂O₂ to confirm the presence of HO•. However, this method is not suitable when EC generation HO• as H₂O₂ can be produced on an electrode surface at lower potential than HO• via a 2 electron oxidation, Equation 1.39.

1.6. Aims and Objectives

The first two results chapters of this thesis are primarily concerned with the use of EC-EPR for the EC generation and subsequent detection of HO•. The focus is on HO• given its importance in electrosynthesis and EAOPs. Chapter 3 investigates the best EPR configuration (spectrometer set-up and sample holder used) to achieve low limits of EC generated HO• detection (ca. 100 nM to 10 μM). The configuration was also investigated to achieve a quick scan time in the aqueous environments which are prone to dielectric loss but also is necessary to electrochemically generate HO•. Being able to work at such low levels is essential to detect small concentrations differences in the number of paramagnetic species produced by the EC methods. Finally in Chapter 3, factors which effect the stability of DMPO-OH• were investigated such as CE separation, deoxygenation and the Forrester-Hepburn mechanism.

EC production of HO• necessitates the application of very high oxidising potentials to oxidise water on BDD. BDD is used as it only has a weak interaction with the HO• allowing them to react in solution. EPR spin trapping is the ‘go-to’ method for confirmation of the existence of electrochemically generated HO•. However, the impact of the high oxidising potential on oxidation of the spin trap itself, and implications for quantification of the HO• radical concentration accurately has been relatively ignored. In Chapter 4 we investigate the implication of spin trap EC oxidation in more detail on the use of EPR as a technique for identification of EC generated HO radicals.

Finally, taking the knowledge gained from Chapter 3 and Chapter 4, Chapter 5 focuses on the application of best EC-EPR practices for the identification and quantification of free radicals in an EC fabrication application, the production of sub-micrometre thick
diamond membranes. Here the aim is to use EPR to identify the electrochemically generated radical pathways associated with the non-contact electrochemically etching of thin graphite layers in single crystal diamond in high conductivity aqueous electrolyte solutions.

1.7. References


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Chapter 2 : Experimental

In this chapter, experimental information regarding procedures common throughout the entire thesis have been detailed. Further specific experimental information is provided within each results chapter.

2.1. Reagents and Materials

All solutions were prepared using deionised water of ≥18.2 MΩ cm resistivity at 25 °C (Milli-Q, Millipore Corp.). All chemicals were used as received from the supplier. Stock 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was stored in a freezer at -18 °C and hydrogen peroxide was stored in a fridge at 4 °C prior to use. Chemicals were weighed using an analytical balance (A200S, Sartorius); a tabulation of all chemicals and materials used can be found in Table 2.1.

Table 2.1: Full list of chemicals and materials and their details used as part of this thesis.

<table>
<thead>
<tr>
<th>Chemical/Material</th>
<th>Supplier</th>
<th>Other information</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-hydroxy-2,2,5,5-tetramethyl-1-piperidine-1-yloxy (4-hydroxy TEMPO)</td>
<td>Alfa Aesar</td>
<td>98+%</td>
</tr>
<tr>
<td>Alumina MicroPolish Suspension</td>
<td>Buehler</td>
<td>0.05 μm</td>
</tr>
<tr>
<td>Ammonium iron (II) sulfate hexahydrate</td>
<td>Sigma Aldrich</td>
<td>≥99.0%</td>
</tr>
<tr>
<td>Araldite Rapid Epoxy Adhesive</td>
<td>Araldite</td>
<td>-</td>
</tr>
<tr>
<td>Boric acid</td>
<td>Sigma Aldrich</td>
<td>99.97%</td>
</tr>
<tr>
<td>5,5-dimethyl-1-pyrroline N-oxide (DMPO)</td>
<td>Enzo Life Sciences</td>
<td>&lt;98%</td>
</tr>
<tr>
<td>Material</td>
<td>Supplier</td>
<td>Purity/Details</td>
</tr>
<tr>
<td>------------------------------------------------------------</td>
<td>---------------------------</td>
<td>----------------------------------------------------</td>
</tr>
<tr>
<td>Ethanol</td>
<td>VWR Chemical</td>
<td>99.9% absolute</td>
</tr>
<tr>
<td>Hexammineruthenium (III) chloride</td>
<td>Strem chemicals</td>
<td>99%</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>Fisher Scientific</td>
<td>30 % v/v uninhibited</td>
</tr>
<tr>
<td>Loktite 460</td>
<td>Henkel</td>
<td>-</td>
</tr>
<tr>
<td>2-methyl-2-nitrosopropane dimer (MNP)</td>
<td>Sigma Aldrich</td>
<td>-</td>
</tr>
<tr>
<td>N-tert-butyl-α-phenylnitrone (PBN)</td>
<td>Sigma Aldrich</td>
<td>&gt;99.5 %</td>
</tr>
<tr>
<td>Perchloric acid</td>
<td>Sigma Aldrich</td>
<td>99.999% trace metal basis</td>
</tr>
<tr>
<td>α-(4-pyridyl N-oxide)-N-tert-butyl nitronitrone (POBN)</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>RS Components</td>
<td>-</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>Sigma Aldrich</td>
<td>≥99%</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>Sigma Aldrich</td>
<td>≥99.0%</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>Honeywell</td>
<td>&gt;99.0%</td>
</tr>
<tr>
<td></td>
<td>Sigma Aldrich</td>
<td>99.97%</td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td>Acros Organics</td>
<td>Pure</td>
</tr>
<tr>
<td></td>
<td>Sigma Aldrich</td>
<td>Analysis Grade</td>
</tr>
<tr>
<td>Silver epoxy</td>
<td>Chemtronics</td>
<td>-</td>
</tr>
<tr>
<td>Sodium phosphate dibasic heptahydrate</td>
<td>Sigma Aldrich</td>
<td>&lt;98.0%</td>
</tr>
</tbody>
</table>
2.2. Acid Cleaning Protocol

To fully clean and oxygen-terminate the diamond and boron doped diamond (BDD) samples, an acid cleaning protocol was employed which is well described in the literature. Diamond and BDD samples were placed in boiling concentrated H$_2$SO$_4$ (analytical reagent grade <95%, Fisher Scientific) saturated with KNO$_3$ (reagent grade <99.0 %, Honeywell) for 30 min and then taken out and rinsed with deionised water. The diamond and BDD samples were then placed in boiling concentrated H$_2$SO$_4$ for a further 30 min and then finally removed and rinsed with deionised water.

2.3. Electrochemical Set-up

For the majority of electrochemical (EC) experiments in this thesis, a three-electrode set-up was utilised employing either a CHI1140B, CHI760E or CHI1150A potentiostat (CH Instruments Inc.). Except for Chapter 5, where a two-electrode configuration was used by applying a potential between two electrodes using a variable DC power supply (EA-PS 9750-04, Elektro-Automatik GmbH).

2.3.1. Electrodes

Throughout this thesis the following working electrodes (WE) were used: 7 by 1 cm BDD WE, 1 mm BDD WE, 3 mm disk glassy carbon (GC) WE (IJ Cambria Scientific Ltd), 2 mm Pt disk WE (IJ Cambria Scientific Ltd) and Pt wire (0.75 mm in diameter and 2 cm in length) electrodes. For aqueous based experiments, a saturated calomel
electrode (SCE, IJ Cambria Scientific Ltd) reference electrode (RE) was used. Alternatively for non-aqueous experiments, a leak free Ag/AgCl (LF-1.6, Alvatek) was used as a RE. Finally, when a three-electrode configuration was employed a Pt coil was used as a counter electrode (CE).

2.3.2. Boron doped diamond electrode fabrication

For BDD electrode studies, the BDD was grown using microwave chemical vapour deposition (CVD),\(^1\) by Element Six, containing a small amount of sp\(^2\) bonded carbon (Electrochemical Processing Grade).\(^1\) This CVD BDD contained a boron dopant density of \(> 10^{20}\) B atoms cm\(^{-3}\), i.e. above the metallic threshold.\(^2\) The BDD was used in one of two electrode formats, as shown in Figure 2.1, either a 7 by 1 cm BDD WE (which when placed in solution has both faces accessible to solution) or a 1 mm disk BDD WE sealed in a glass capillary.

![Figure 2.1: Illustration of (a) 7 by 1 cm BDD WE and (b) 1 mm disk BDD WE sealed in glass capillary.](image)

From a 460 μm thick BDD wafer, where the growth surface had been mechanically polished to nanometre roughness a 1 mm diameter cylinder was laser-cut using a 355 nm Nd:YAG 34 ns laser micromachiner (E-355H-ATHI-O system, Oxford Lasers). For these studies, a rectangle of 7 cm by 1 cm was laser cut from a 700 μm thick
freestanding wafer of BDD, containing both growth and nucleation faces. The surface roughness for the growth face was 7 μm and for nucleation face was 150 nm on the 7 by 1 cm BDD WE, measured using white light interferometry.

To clean and fully oxygen-terminate the surface, BDD electrodes were acid cleaned after being laser-cut or laser-roughened, see Section 2.2, to clean and remove loose laser induced debris.\(^3\)

To ensure a good ohmic contact, the top 0.5 by 1 cm rectangle was laser roughed prior to sputtering to aid adhesion followed by an acid clean, Section 2.2. Ohmic contacts\(^4\) were formed via sputtering (Moorfields MiniLab 060 sputterer/evaporator) Ti/Au (10:400 nm) onto the top 0.5 by 1.0 cm area of the nucleation face of the rectangular electrode or the backside of the polished cylinder and then the electrodes were annealed at 400 °C for 5 hr. For the rectangle electrode, a wire was attached with silver epoxy (Chemtronics, CircuitWorks) and then the contact-wire connection was coated in non-conductive epoxy (Araldite Rapid Epoxy Adhesive, Araldite) to protect it from solution. The 1 mm BDD cylinder was sealed in a glass capillary (O.D. 2 mm; I.D. 1.16 mm, Harvard Apparatus Ltd.) using a process previously outlined.\(^1\)

2.4. Electron Paramagnetic Resonance Spectroscopy

All electron paramagnetic resonance (EPR) spectroscopy was performed on a continuous wave (CW) X-band spectrometer (Bruker EMX, Bruker). Experimental configuration and parameters are listed in each chapter. Fitting and simulation of the EPR spectra was performed using the MATLAB package EasySpin (Version 5.2.25).\(^5\)

2.5. References


Chapter 3: Optimisation of EPR Configuration for Detection of Electrochemical Radicals

3.1. Overview

As highlighted in Chapter 1 Section 1.3, the hydroxyl radical (HO') is attributed to being the most prevalent species exploited in electrosynthesis and electrochemical advanced oxidative processes (EAOPs). The electrochemical (EC) generation of HO' necessitates the use of a “non-active” electrode like boron doped diamond (BDD) in an aqueous media based on Equation 3.1.

\[ \text{H}_2\text{O}_{(l)} \rightarrow \text{HO'}_{(aq)} + \text{H}^+_{(aq)} + \text{e}^- \tag{3.1} \]

Since HO' is directly electrochemically generated from water, which is a high dielectric solvent, the use of water cannot be avoided when investigating the EC generation of HO'. Thus, the optimisation of spectrometer configuration to operate in water is required for EC detection of HO'. High-dielectric solvents (also called “lossy” samples), such as water, can be problematic in electron paramagnetic resonance (EPR) spectroscopy as water is prone to unwanted absorption of microwave (MW) energy. The absorbance of MW energy in aqueous solutions gives rise to dielectric heating. This absorption of MW decreases the quality factor (Q, Equation 1.25) and if too much water is present, it is not possible to critically couple to the resonator ultimately rendering EPR detection unfeasible in large volumes of water. Nevertheless, the use of different resonators and sample holder designs can be utilised to minimise these detrimental MW absorption effects whilst maximising resolution on detection described in Chapter 1 Section 1.2.2.4 and Section 1.2.3.1. Therefore, it is of paramount important to this study to fully optimise the EPR configuration to overcome the effects of using water as the dielectric solvent in EC-EPR studies.
HO\textsuperscript{−} are highly reactive and short-lived species (lifetime in water: \( \mu s \))\textsuperscript{11} therefore, to measure HO\textsuperscript{−} in EPR, spin trap reagents are utilised to make a more persistent radical.\textsuperscript{12–14} The most popular spin trap for the detection of HO\textsuperscript{−} is 5,5-dimethyl-1-pyrroline N-oxide (DMPO).\textsuperscript{12,15–19} DMPO has a \( \beta \)-hydrogen allowing differentiation between small free radicals and a nitroxide group to react with HO\textsuperscript{−} to produce a stable spin adduct (DMPO-OH\textsuperscript{−}). The reaction for the spin trapping of HO\textsuperscript{−} with DMPO is shown in Figure 3.1. The \( \beta \)-hydrogen assists discrimination between small free radicals as the \( \beta \)-hydrogen will cause hyperfine splitting based on the incoming free radical.

![Figure 3.1: Spin trapping reaction for DMPO with HO\textsuperscript{−}.
](image)

Despite being more persistent than HO\textsuperscript{−}, DMPO-OH\textsuperscript{−} is still unstable with a half-life of 20 min\textsuperscript{20} although, the degradation mechanism is still unknown/not reported. Therefore, a good alternative when trying to optimise EPR configurations is to use the stable (lifetime of days in solution) 4-hydroxy-2,2,5,5-tetramethyl-1-piperidine-1-yloxy (4-hydroxy TEMPO). This is beneficial as time constraints for measurements are eliminated. Furthermore, the EC formation of HO\textsuperscript{−} produces low concentrations of HO\textsuperscript{−} very close to the electrode surface which strains the limit of the detection. Thus, an alternative option when investigating how to optimise the EPR for HO\textsuperscript{−} detection is to instead generate high concentrations of HO\textsuperscript{−} via Fenton Chemistry,\textsuperscript{21–24} Equation 3.2.

\[
\text{Fe}^{2+}_{(aq)} + \text{H}_2\text{O}_2_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{HO}^\cdot_{(aq)} + \text{OH}^−_{(aq)}
\] (3.2)

The final factor to examine is whether there are any other non-EC mechanisms at play which can also result in the production of DMPO-OH\textsuperscript{−}. For example, DMPO is exposed to water prior to and throughout the duration of the EC experiment. The Forrester-Hepburn mechanism\textsuperscript{25–27} (given in Equation 3.3 for DMPO) describes the nucleophilic attack of a nucleophile (NuH) on DMPO, followed by electron abstraction facilitated by an appropriate oxidising agent (such as oxygen in solution) or a redox event.
Chapter 3: Optimisation of EPR configuration for detection of electrochemical radicals

\[
\text{DMPO} + \text{NuH} \rightarrow [\text{H-DMPO-Nu}] \rightarrow \text{DMPO-Nu}^- + \text{H}^+ - \text{e}^- \quad (3.3)
\]

The most abundant nucleophile, albeit a very weak nucleophile, in aqueous environments is water. Water can react with DMPO to produce H-DMPO-OH which when undergoing an electron abstraction will form DMPO-OH\(^-\) (Equation 3.4).

\[
\text{DMPO} + \text{H}_2\text{O} \rightarrow [\text{H-DMPO-OH}] \rightarrow \text{DMPO-OH}^- + \text{H}^+ - \text{e}^- \quad (3.4)
\]

Dependent on the timescale of this reaction, Equation 3.4 means DMPO-OH\(^-\) could be present via chemical pathways in solution rather than EC generation, leading to false interpretation of results. Furthermore, the Forrester-Hepburn mechanism is further accelerated by the presence of chelating metal impurities such as Fe (III), \(^{28,29}\) Cu(II), \(^{29}\) Ti (V), \(^{30}\) Au(III) \(^{31}\) and Tl(III) \(^{32}\). These metals can bind to the spin trap promoting easier nucleophilic attack of the spin trap.

In this chapter, the optimal resonator and sample holder for working with the high dielectric solvent water is investigated in detail. The best EPR parameters are determined for the EC generation of HO\(^-\) to detect transient spin adduct species which quickly decay whilst finding a balance with achieving a low limit of detection and good ease of use. Factors that could potentially affect the stability of DMPO-OH\(^-\) are investigated such as the products produced at the counter electrode (CE) and the presence of oxygen in solution. Finally, the susceptibility of DMPO to the Forrester-Hepburn mechanism in water is examined.

3.2. Experimental

3.2.1. Reagents and solutions

All solutions were prepared using deionised water of \(\geq18.2\) MQ cm resistivity at 25 °C (Milli-Q, Millipore Corp.). All chemicals were used as received from the supplier. 5,5-dimethyl-1-pyrroline N-oxide (DMPO, <98%, Enzo Life Sciences Ltd) was stored in a freezer at -18 °C and hydrogen peroxide (H\(_2\)O\(_2\), 30% v/v uninhibited, Fisher Scientific) was stored in a fridge at 4 °C prior to use. Solutions of the stable radical species, 4-hydroxy-2,2,5,5-tetramethyl-1-piperidine-1-yloxy (4-hydroxy TEMPO, 98+, Alfa
Aesar) were made up at 100 nM, 1 μM, 10 μM and 100 μM in deionised water. For EC experiments, solutions of 10 mM DMPO in 0.10 M perchloric acid (HClO₄, 70 %, 99.999% trace metals basis, Sigma Aldrich) were made. The Fenton chemistry reaction was studied from a solution of 10 mM Fe²⁺ (ammonium iron (II) sulfate hexahydrate, ≥ 99.0%, Sigma Aldrich), 10 mM DMPO, 1 M H₂O₂ in a 0.10 M phosphate buffer pH 4.

The phosphate buffer was prepared from sodium phosphate dibasic heptahydrate (Na₂HPO₄.7H₂O, <98.0%, Sigma Aldrich) and sodium phosphate monobasic (NaH₂PO₄.H₂O, ≥98%, Millipore) then pH check using a pH meter (SevenEasy, Mettler Toledo).

3.2.2. Electron paramagnetic resonance spectroscopy setup

EPR spectroscopy was performed on a continuous wave (CW) X-band spectrometer (Bruker EMX, Bruker). Samples for measurement were placed in either (1) a 1 mm inner diameter (ID) quartz EPR tube (Wilmad® quartz (CFQ) EPR tubes, Sigma-Aldrich), (2) an aqueous flat cell (ER 160FC WG-812, Wilmad®) or (3) an extruded star-bore tubing (AquaX, Bruker) all discussed previously in Chapter 1 Section 1.2.3.1. EPR experimental parameters are listed before each spectrum. Fitting and simulation of the EPR spectra was performed using the MATLAB package EasySpin (Version 5.2.25).³³

3.2.2.1. EPR resonators

Three resonators have been used for this work: two cavity resonators and one loop gap resonator (LGR). The two cavity resonators are in either: transverse electric (TE) mode or in transverse magnetic (TM) mode. For convenience, the names of the two cavity resonators in this study have been simplified based on the last two letters of the resonator code. Information about these resonators is given below in Table 3.1.
Table 3.1: List and details of resonators used in this study.

<table>
<thead>
<tr>
<th>Name in study</th>
<th>Resonator</th>
<th>Description</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>hs</td>
<td>ER 4109HS</td>
<td>Bruker cylindrical cavity</td>
<td>TE011</td>
</tr>
<tr>
<td>tm</td>
<td>ER 4103TM</td>
<td>Bruker cylindrical cavity</td>
<td>TM110</td>
</tr>
<tr>
<td>LGR</td>
<td>5-loop-4-gap</td>
<td>Custom LGR</td>
<td>-</td>
</tr>
</tbody>
</table>

For this research, a home built 5-loop-4-gap resonator (often referred to as a rising sun)\textsuperscript{34,35} has been used discussed in \textbf{Chapter 1 Section 1.2.2.4.2}, the design of which has been shown below in \textbf{Figure 3.2}. The LGR was built for in-house use by Tadaeusz Oles (Jagiellonian University, Krakow).

![Design of 5-loop-4-gap LGR.](image)

\textbf{3.2.3. Electrode fabrication}

Full details on electrode fabrication are described in \textbf{Chapter 2 Section 2.3.2}. In brief, a rectangle (7 cm by 1 cm) was cut from a 700 μm thick freestanding wafer of boron doped diamond (BDD, Element Six, Electrochemical Processing Grade) using a laser micromachiner (E-355H-ATHI-O system, Oxford Lasers). The electrode was cleaned and fully oxygen-terminated using an acid wash, described in \textbf{Chapter 2 Section 2.2}. To ensure a good ohmic contact, Ti/Au (10:400 nm) was sputtered onto the top 0.5 by 1.0 cm of the rectangular electrode and then annealed at 400 °C for 5 hr. A wire was attached with silver epoxy (Chemtronics, CircuitWorks) and the contact-wire
connection coated in non-conductive epoxy (Araldite Rapid Epoxy Adhesive, Araldite) to protect it from solution.

3.2.4. Electrochemical set-up

A three-electrode set-up was utilised for all EC processes carried out employing a potentiostat (CH1140B, CH Instruments Inc.) and a three-electrode configuration consisting of the 7 cm by 1 cm BDD working electrode (WE), a saturated calomel electrode (SCE, IJ Cambria Scientific Ltd) reference electrode (RE) and a Pt coil CE. All EC-EPR experiments were performed with a magnetic flea stirring the solution on a magnetic stirrer plate (RCT basis, IKA). To separate out the products made at the CE, a two compartment cell was used, as shown in Figure 3.3, where the CE is isolated behind a porous frit (pore size ca. 10 μm) made by the Scientific Glassblowing Service (University of Southampton, UK).

![Figure 3.3: Image of two-compartment cell used in this study.](image)

3.3. Results and Discussion

3.3.1. Comparison of sensitivity for hs, tm and LGR EPR resonators

Three different EPR resonators have been investigated for their use in aqueous based media; these are the hs, tm and LGR. The hs resonator is a cylindrical cavity offering a high unloaded quality factor ($Q_U$) allowing extremely sensitive detection of radical species. However, the performance of the hs resonator is severely diminished when water is introduced. The tm resonator also has a cylindrical cavity but functions at a
lower $Q_U$. Nonetheless, the tm cavity has been specifically designed for performance with high-dielectric solvent and is therefore less impeded by the introduction of aqueous samples. The LGR design consists of a series of loops and gaps which confine the MW electric field within its gaps, allowing the water to occupy a larger volume in the central loop without experiencing MW absorption effects. Although, the LGR has a lower $Q_U$ (partially due to more joins in cables) than both cylindrical cavities, this loss in sensitivity is overcome by a larger filling factor ($\eta_f$) than compared to both cylindrical cavities. The $\eta_f$ for a 10 mm of “non-lossy” sample in a 3 mm ID EPR tube is 0.01 for the hs cavity and closer to 0.5 for the LGR.\textsuperscript{34} All three resonators have both advantages and disadvantages therefore, careful selection is required for each specific application.

For all three resonators, solutions of 100 nM, 1 µM, 10 µM and 100 µM 4-hydroxy TEMPO in deionised water were tested in the same 1 mm ID quartz tube, shown in Figure \textbf{3.4}. 4-hydroxy TEMPO is a commercially available stable nitrooxide radical similar in size and structure of the spin adducts of interest thus, provides a good comparison when investigating which resonator provides the best sensitivity. The number of peaks in the splitting pattern is given by $2nI + 1$ where $n$ is the number of nuclei, and $I$ is the nuclear spin quantum number. The 4-hydroxy TEMPO radical will give three signals (from $2nI +1$, for one $^{14}$N with $I=1$) in equal proportion (1:1:1 ratio) in the EPR spectrum.\textsuperscript{37} For measurements using the tm and hs resonators, the following spectrometer parameters were used: a non-saturating MW power of 15.8 mW; sweep width, 10 mT; time constant, 20.48 ms; conversion time, 40.96 ms; and a modulation amplitude, 0.03 mT. All spectra reported are an average of 16 scans. All conditions but one condition are the same for the LGR which used a sweep width of 25 mT.
Figure 3.4: 4-hydroxy TEMPO solutions at (i) 100 nM, (ii) 1 μM, (iii) 10 μM and (iv) 100 μM in deionised water collected using (a) hs resonator, (b) tm resonator, or (c) LGR in 1 mm ID quartz tube. For measurements using the tm and hs resonators, the following spectrometer parameters were used: a non-saturating MW power of 15.8 mW; sweep width, 10 mT; time constant, 20.48 ms; conversion time, 40.96 ms; and a modulation amplitude, 0.03 mT. All spectra reported are an average of 16 scans. All conditions but one condition are the same for the LGR which used a sweep width of 25 mT.
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From the spectra shown in Figure 3.4, it can be observed that all three resonators can measure the 1, 10, and 100 μM solutions of 4-hydroxy TEMPO. For the hs resonator, Figure 3.4ai, some evidence for the 100 nM 4-hydroxy TEMPO can be seen but the signal is not greater than the noise to make a definitive identification. For the tm resonator in Figure 3.4bi, the 100 nM solution is not visible at all on the other hand, in the case of the LGR in Figure 3.4ci, the signal can be seen in large excess above the noise. In some spectra presented, a peak due to D’ signature from the quartz tube at 352 mT in the hs and tm resonators and at 347.5 mT in the LGR is also observed. The signature is dependent on the orientation of the quartz tube inside of the resonator as the defect is fixed in a set position in the quartz tube. Moreover, the magnitude of this signal will vary dependent on the orientation of the quartz tube in the resonator. From the data in Figure 3.4, it can be concluded that the LGR provides the best resolution for aqueous based detection of stable radical species. The hs resonator also displayed a better signal-to-noise ratio than the tm resonator. However, when the LGR was used to try and detect electrochemically generated DMPO-OH’, no signal could be observed whereas ample signal could be seen with the hs resonator. This is surprising given the better signal-to-noise of the LGR for the 4-hydroxy TEMPO samples. Although the LGR used in this study can boast a much larger $\eta_f$ when used in conjugation with a 3 mm ID tube of “non-lossy” sample, the use of the high dielectric solvent water necessitates using smaller 1 mm ID tubes to minimise MW absorption which reduces the large $\eta_f$ for the LGR. Therefore, if the sample volume can be increased in the hs resonator, a larger $\eta_f$ can be achieved than the $\eta_f$ for the LGR. The effective height of the active resonator area is much larger in the hs resonator than compared to the LGR (due to resonator size) therefore, more sample can be introduced into the hs resonator increasing the $\eta_f$. Thus, for the low concentration samples produced by electrochemistry in this thesis, the hs resonator was deemed the optimal resonator for detection. In the future, the use of a LGR designed for 1 mm ID tubes could be used to increase the resolution by having the full $\eta_f$ benefit.
3.3.2. Comparison of sensitivity for different sample holders

Three different sample holders have been explored to determine which provides the best sensitivity for aqueous based media; these are: the traditional 1 mm ID quartz tube, extruded star-bore tubing,\textsuperscript{39} and the flat cell.\textsuperscript{39} Quartz tubes with an ID greater than 1 mm were also explored however, too much MW absorption meant the resonator could not be critically coupled preventing their use. To provide a fair comparison between the different sample holders, the same resonator was used to provide a consistent baseline. Despite the LGR previously demonstrating the best sensitivity, it could not be utilised in this study due as the internal chamber of the LGR is not large enough to accommodate the flat cell. Therefore, as the hs cavity provided a slight improvement over the tm cavity and could accommodate all three sample holders, it was used to compare the three sample holders.

Solutions of 100 nM, 1 µM, 10 µM, and 100 µM 4-hydroxy TEMPO in water were tested in either a: 1 mm ID quartz tube, star-bore tubing or flat cell - shown in Figure 3.5. Data for the 1 mm ID quartz tube is a repeat of Figure 3.4a. The following spectrometer parameters were used: a non-saturating MW power of 15.8 mW; sweep width, 10 mT; time constant, 20.48 ms; conversion time, 40.96 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 16 scans. For the flat cell, all conditions used were the same except a sweep width of 25 mT.
Figure 3.5: 4-hydroxy TEMPO solutions at (i) 100 nM, (ii) 1 μM, (iii) 10 μM and (iv) 100 μM in deionised water collected using (a) 1 mm ID quartz tube, (b) starbore tubing or (c) flat cell in the hs resonator. Note: data for 1 mm ID quartz tube is a repeat of Figure 3.4ai, ii, iii and iv. The following spectrometer parameters were used: a non-saturating MW power of 15.8 mW; sweep width, 10 mT; time constant, 20.48 ms; conversion time, 40.96 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 16 scans. All conditions but one conditions are the same for the flat cell which used a sweep width of 25 mT.
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For all three sample holders, shown in **Figure 3.5**, clear signatures for the 1, 10 and 100 μM 4-hydroxy TEMPO are displayed. In **Figure 3.5a**i, the 100 nM 4-hydroxy TEMPO solution is barely detectable as discussed before. The star-bore tubing, shown in **Figure 3.5b**i, showed a very small improvement in sensitivity over the 1 mm ID quartz tube. The greatest improvement in sensitivity comes from the flat cell (**Figure 3.5c**i) where the 100 nM 4-hydroxy TEMPO is clearly detectable above the noise. This comparison identifies the flat cell (with the hs cavity) as the optimal sample holder to use for detection of stable radicals in aqueous media.

The flat cell and star-bore tubing sample holders did provide slight improvement over the 1 mm ID quartz tube in terms of signal-to-noise ratio. Practically filling the star-bore tubing and flat cell without air bubbles (which reduces the η and thus the EPR signal) manually and positioning the star-bore tubing or flat cell in the EPR spectrometer in a quick time frame for measurement is problematic. In future work, the development of a flow cell could alleviate problems with manual sample filling. Therefore, as minimal improvement in signal-to-noise was seen for the flat cell and star-bore tubing over the 1 mm ID quartz tube, the ease of use of the 1 mm ID quartz has favoured its use. Going forward all samples will be analysed in a 1 mm ID quartz tube.

3.3.3. Optimisation of detection of electrochemically generated DMPO-OH⁻

To electrochemically generate DMPO-OH⁻ in aqueous solution for EPR detection, a solution of 10 mM DMPO in 0.10 M HClO₄ was held at a constant potential of +2.10 V vs SCE for 600 sec in a one-compartment cell stirred at 600 rpm. In this set-up the CE is placed in the same solution as the WE and CE. Further information on the intricacies of EC generation and spin trapping in relation to EPR detection of DMPO-OH⁻, are described in detail in **Chapter 4**.

Aliquots taken 0, 300 and 600 sec were measured using EPR spectroscopy with the optimal configuration determined as the hs resonator and 1 mm ID quartz tube, shown in **Figure 3.6**. For this work HClO₄ was used as the supporting electrolyte due to its high stability at this oxidising potential, preventing the production of other
radical or highly oxidising electrolyte components. For example, in the case of the electrolyte H₂SO₄, HO⁻ attack can produce sulfate radicals and peroxodisulfate anions;⁴⁰,⁴¹ also discussed in more detail in Chapter 5. In addition, highly acidic conditions were selected as it is postulated that acidic conditions enhance HO⁻ production.⁴² The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.

Figure 3.6: EPR spectra collected at (a) 0, (b) 300 and (c) 600 sec during the electrolysis of a 10 mM DMPO solution in 0.10 M HClO₄ at a constant potential of +2.10 V vs SCE using a 7 by 1 cm rectangle BDD electrode. The following spectrometer parameters were used: a non-saturating MW power of 12.72 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.
The resultant EPR spectra for the DMPO-OH$^-$ is expected to have four peaks in a ratio of 1:2:2:1 due to the nearby nuclei which are $^{14}$N ($I=1$) and $^1$H ($I=\frac{1}{2}$) giving rise to the 1:2:2:1 splitting pattern observed. In Figure 3.6, this signal can just about be detected at 300 and 600 sec however, the signal quickly decayed away preventing subsequent measurements. Note, due to this decay the scan time for these measurements was dramatically decreased from 10 min per scan to 30 sec but even on the faster time frame the signal decay is noticeable.

### 3.3.4. Stability of DMPO-OH$^-$ spin adduct

In the EC cell used for Figure 3.6, the CE is present in the same solution as the RE and WE in order to complete the circuit by allowing the opposite current to flow at the CE to that of the WE. So as an oxidative reaction occurs at the WE, the CE increases in reductive potential until it can pass the appropriate sized reductive current. To do this there must be a reductive redox reaction occurring at the CE to balance the system. Equation 3.5 to 3.8 shows some of the possible reductive reactions occurring at the CE.

\[
\begin{align*}
2\text{H}_2\text{O}_\text{l} + 2\text{e}^- &\rightarrow \text{H}_2\text{g} + 2\text{OH}^-_{\text{aq}} \\
\text{O}_2_{\text{aq}} + 4\text{H}^+_{\text{aq}} + 4\text{e}^- &\rightarrow 2\text{H}_2\text{O}_\text{l} \\
\text{O}_2_{\text{aq}} + 2\text{H}^+_{\text{aq}} + 2\text{e}^- &\rightarrow \text{H}_2\text{O}_2_{\text{aq}} \\
2\text{H}^+_{\text{aq}} + 2\text{e}^- &\rightarrow \text{H}_2\text{g}
\end{align*}
\]

These opposing reactions at the CE cause unwanted by-products to be produced which could have detrimental effects on the generation of HO$.^-$ Firstly, these by-products species (such as H$_2$, OH$^-$ and H$_2$O$_2$) could react with HO$^-$ reducing the number of radicals to react with DMPO. Secondly, the production of hydroxide ions (and removal of H$^+$) would shift the pH in the system which may in turn reduce the efficiency of the production of HO$^-$. Finally, the presence of some of these by-products, such as H$_2$O$_2$, can reduce the lifetime of DMPO-OH$.^-$. One of the main deactivation routes is reaction of the DMPO-OH$.^-$ with H$_2$O$_2$. H$_2$O$_2$ can be formed from: (i) HO$^-$ reacting with HO$^-$ (Chapter 1 Equation 1.42), (ii) the 2 electron water oxidation process (Chapter 1 Equation 1.39) and (iii) the 2 electron oxygen reduction reaction (ORR;
Equation 3.7). The presence of H$_2$O$_2$ dramatically reduces the lifetime of the DMPO-OH$^\cdot$ spin adduct$^{43}$ which could potentially account for the decay in the signal.

In order to segregate these by-products produced at the CE, a two-compartment electrolysis cell was used, shown in Figure 3.3. The experiment (from Figure 3.6) was repeated using a two-compartment electrolysis cell, with the solution stirred at 800 rpm. In this cell, the RE and WE were separated from the CE by a porous frit (pore size ca. 10 µm). A solution of 10 mM DMPO in 0.10 M HClO$_4$ was held at a constant potential of +2.10 V vs SCE for 600 sec. Samples were measured by EPR spectroscopy at 0, 300 and 600 sec as before, shown in Figure 3.7. The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.
Figure 3.7: EPR spectra collected at (a) 0, (b) 300 and (c) 600 sec during the electrolysis of a 10 mM DMPO solution in 0.10 M HClO₄ at a constant potential of +2.10 V vs SCE using a 7 by 1 cm rectangle BDD electrode in a two-compartment cell. The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.

By comparing Figure 3.6 and Figure 3.7, a very slight improvement in signal can be seen for DMPO-OH˙ at 300 and 600 sec in the two-compartment cell than compared to the one compartment cell. Therefore, this study demonstrated that the segregation of the unwanted by-products at the CE has made a minimal improvement and increased the amount of DMPO-OH˙ detected. Nafion™ membrane is a cation exchange membrane which selectively allows protons to flow from one compartment to the next. This type of membrane would better shield the WE, compared to the current porous frit used, from the negatively charged species being produced at the
CE which would also reduce pH fluctuations. Although minimising pH fluctuations could also be achieved by the use a pH buffer, this would introduce more solution components which can react with HO\(^{-}\) discussed in Chapter 1 Section 1.3.2. This could be detrimental in two ways by: (i) reducing the concentration of HO\(^{-}\) present for spin trapping and/or (ii) potentially giving rise to different radical species which would complicate analysis. In future work, an electrolysis cell fitted with a Nafion\textsuperscript{TM} membrane may further benefit the production of DMPO-OH\(^{-}\) spin adduct.

To investigate the role of oxygen on HO\(^{-}\) generation, the two-compartment cell experiment was repeated but this time with the solution being thoroughly deoxygenated throughout the experiment. The system was purged in both compartments using a flow of nitrogen gas prior to and during generation. A solution of 10 mM DMPO in 0.10 M HClO\(_4\) was held at a constant potential of +2.10 V vs SCE for 600 sec and stirred at 800 rpm. Samples were measured by EPR spectroscopy at 0, 300 and 600 sec as before, shown in Figure 3.8. The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.
Figure 3.8: EPR spectra collected at (a) 0, (b) 300 and (c) 600 sec during the electrolysis of a 10 mM DMPO solution in 0.10 M HClO₄ at a constant potential of +2.10 V vs SCE using a 7 by 1 cm rectangle BDD electrode in a two-compartment cell under deoxygenated conditions. The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.

When comparing Figure 3.7 to Figure 3.8, it is possible to see the signal-to-noise ratio has been again improved by deoxygenating the solution. This could be due to any or a combination of the following: (i) a higher electrode efficiency for producing HO⁻ due to solution agitation helping to remove bubbles from the electrode surface (which blocks the surface and reduce the active electrode area). (ii) Deoxygenating of the solution could increase the stability of the DMPO-OH⁻ spin adduct produced. When oxygen is present, singlet oxygen can be produced and oxidised DMPO and DMPO-OH⁻.45 (iii) The removal of paramagnetic oxygen dissolved in solution. Paramagnetic
oxygen can lead to peak broadening within the EPR spectrum.\textsuperscript{46} The removal of oxygen would sharpen the peaks improving the signal-to-noise ratio. In EAOPs, deoxygenated conditions are not commonly employed, therefore despite the benefit seen from deoxygenating (i.e. line sharpening), oxygenated conditions have been kept to replicate the systems commonly being investigated.

To assess whether the DMPO-OH\textsuperscript{\cdot} lifetime was influenced by the EC environment, a comparison experiment involved generating the HO\textsuperscript{\cdot} radicals by chemical means, rather than electrochemically, via Fenton Chemistry.\textsuperscript{21–24} Fenton chemistry requires a source of Fe\textsuperscript{2+} in solution and H\textsubscript{2}O\textsubscript{2} (Equation 3.2). Controlling the solution pH in a Fenton reaction is important, the reaction mixture needs to be kept in the pH range of <5 with the greatest catalytical efficiency in the pH range of 3 to 4.\textsuperscript{47} If the pH is too high, the Fe\textsuperscript{2+} precipitates out as Fe(OH)\textsubscript{3} which then catalytically decomposes the H\textsubscript{2}O\textsubscript{2} to O\textsubscript{2}.\textsuperscript{47} Thus, it is important to buffer the reaction mixture to maintain the pH in the ideal region throughout the experiment with the large amount of hydroxide ions formed from the reaction (Equation 3.2).

The HO\textsuperscript{\cdot} radicals were generated chemically using a solution of 10 mM Fe\textsuperscript{2+}, 1 M H\textsubscript{2}O\textsubscript{2} and 10 mM DMPO made up in a phosphate buffer pH 4. The system was stirred at 800 rpm. Samples were taken and tested at time points of 0 (before the addition of H\textsubscript{2}O\textsubscript{2}), 15, 30 and 65 min, after the addition of the H\textsubscript{2}O\textsubscript{2} and EPR spectra recorded, shown in Figure 3.9. The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.
Figure 3.9: EPR spectra collected at (a) 0, (b) 15, (c) 30 and (d) 65 min after the generation of HO· using Fenton chemistry from a solution of 10 mM ammonium iron (II) sulfate, 1 M H₂O₂ and 10 mM DMPO made up in a phosphate buffer pH 4 had begun. The following spectrometer parameters were used: a non-saturating MW power of 19.97 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.

In Figure 3.9 at 15 min, a large amount of DMPO-OH· spin adduct can be observed, well above the baseline (Figure 3.9a) from the Fenton chemistry reaction. However, at longer times of 30 and 65 min, the EPR signal for DMPO-OH· can be seen to decrease due to the decay of DMPO-OH·. This demonstrates DMPO-OH· is unstable regardless of the way it is created which is not surprising given its half-life of 20 min. In this system, the data reinforces the point that detection needs to take place within a quick timeframe of the generation of HO· therefore, there is play off between long
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generation times to make sufficient concentration to be measured and relatively quick measurement times to detect the DMPO-OH\(^-\) before it decays.

When the samples for the EC generation of HO\(^-\) are taken, they are withdrawn by a syringe and placed in the quartz tube where the sample no longer experiences any EC potentials which means the production of new HO\(^-\) ends and only previously made HO\(^-\) remain in solution. As such the EC generation of HO\(^-\) reaction is ceased. On the other hand, when the aliquots of the HO\(^-\) made via Fenton chemistry are taken they still contain Fe\(^{3+}\) and H\(_2\)O\(_2\) which can still react via the catalysis reaction and continually produce new HO\(^-\). This catalysis reaction will continue until all H\(_2\)O\(_2\) present has been consumed. In this way, the EC generated HO\(^-\) reaction can be considered as quenched whereas, the Fenton reaction continues. This makes it difficult to numerically compare the timescale of EPR experiment and the rates of decay for DMPO-OH\(^-\) via both approaches.

3.3.5. Hydrolysis of DMPO over time via the Forrester-Hepburn mechanism

The Forrester-Hepburn\(^{25-27}\) (in general for DMPO in Equation 3.3 and with water as a nucleophile in Equation 3.4) depicts the nucleophilic attack of the spin trap followed by subsequent electron abstraction. In an aqueous system, the most abundant nucleophile is water thus DMPO-OH\(^-\) could be made without the presence of HO\(^-\). This could lead to misinterpretation of results, false positive detection and under/over-estimation of HO\(^-\) quantification in aqueous solution. It is well documented that nitrone based spin traps, like DMPO, are prone to hydrolysis over prolonged time periods. To determine how long it takes for the Forrester-Hepburn mechanism to take place with DMPO in aqueous environments, EPR spectra were recorded every ca. 3 min over time for a solution containing 7.5 mM DMPO in deionised water shown in Figure 3.10. For comparison in Figure 3.10a, a spectrum for DMPO-OH\(^-\) was generated at +1.90 V vs SCE for 5 min in 30 mM DMPO in 0.10 M HClO\(_4\). The following spectrometer parameters were used: a non-saturating MW power of 19.92 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.04 mT. All spectra reported are an average of 9 scans.
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Figure 3.10: (a) EPR spectrum collected at 5 min after electrolysis of 30 mM DMPO solution in 0.10 M HClO$_4$ at a constant potential of +1.90 V vs SCE using a 7 by 1 cm rectangle BDD electrode. (b) The intensity recorded at 350.3 mT as a function of time. The following spectrometer parameters were used: a non-saturating MW power of 19.92 mW; sweep width, 10 mT; time constant, 10.24 ms; conversion time, 20.48 ms; and a modulation amplitude, 0.04 mT. All spectra reported are an average of 9 scans.

In Figure 3.10a, a typical EPR spectrum is shown for DMPO-OH$^\cdot$. Based on this spectrum, to monitor if DMPO-OH$^\cdot$ is made over a 40 hrs time window due to the Forrester-Hepburn mechanism, the intensity at 350.3 mT (the position of the second peak) was plotted over time shown in Figure 3.10b. Over the 40 hrs tested no DMPO-OH$^\cdot$ was observed due to the hydrolysis of DMPO with the intensity fluctuating due to...
spectrometer drifting both positively and negatively. This demonstrates that water is an extremely weak nucleophile not capable of attacking DMPO in the 40 hrs tested. Therefore, under these conditions the Forrester-Hepburn mechanism does not need to be considered.

3.4. Conclusions

The optimal resonator and sample holder (taking into consideration best resolution and ease of use) for working with the high dielectric solvent water was determined to be the hs resonator and 1 mm ID quartz tube. Although, future work developing a flow system would improve the ease of use associated with the flat cell and star-bore tubing which could allow enhancement in resolution. The EC generation of DMPO-OH\(^{-}\) showed its short lifetime and resultantly, the EPR parameters were modified to assist measurements in a quick time frame by reducing the time per scan from 10 min to 30 sec. Both isolating the CE behind a glass frit and deoxygenating the solution showed beneficial effects for the detection of DMPO-OH\(^{-}\). In the future, further improvements could be seen by using a two-compartment cell with the CE isolated behind a Nafion\textsuperscript{TM} membrane to prevent pH fluctuations. However, neither of these adaptions were used going forward due to the small increase in signal seen. Under the conditions used in this thesis, primarily acidic aqueous environments, the generation of the artefactual DMPO-OH\(^{-}\) due to Forrester-Hepburn mechanism can be ignored.

3.5. References


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Chapter 4 : Pitfalls in Electrochemical Electron Paramagnetic Resonance Analysis- Electrochemical Oxidation of the Spin Trap DMPO

4.1. Overview

Free radicals are often highly reactive species, and electrochemical (EC) oxidation/reduction of a target species is a powerful approach for their formation for a wide range of applications including electrochemical advanced oxidation processes (EAOPs)\textsuperscript{1–3} and electrosynthesis.\textsuperscript{4–9} A particularly popular free radical is HO’, which can be generated via the EC oxidation of water, shown in Equation 4.1, at high anodic potentials $E^0 = +2.49 \text{ V vs SCE}^{10}$ for $\text{H}_4^+ = 1 \text{ mol dm}^-3$ (pH -0.081).

$$\text{H}_2\text{O}(l) \rightarrow \text{HO}’_{(aq)} + \text{H}^+_{(aq)} + e^-$$  \hspace{1cm} (4.1)

To promote freely available HO’ “non-active” electrodes are required, such as boron doped diamond (BDD),\textsuperscript{11} which disfavour adsorption of HO’ on their surface. HO’ is considered the predominant species responsible for the degradation of the environmental pollutants in EAOPs.\textsuperscript{1,3}

The most popular techniques for free radical detection are electron paramagnetic resonance (EPR) spectroscopy\textsuperscript{12–14} and fluorescence spectroscopy.\textsuperscript{15–17} Typically, EPR is the favoured method due to the low achievable limits of detection as well as accurate identification of different free radical species through distinctive splitting patterns. However, due to the extremely short lifetimes of many free radicals, particularly in aqueous solutions, EPR and fluorescence spectroscopy often necessitates the use of spin trap reagent to convert the free radical into a more persistent species. This is especially true for HO’ detection in water which has a lifetime of $\mu$s.\textsuperscript{18}
In EPR spin trap chemistry, the free radical (R˙) reacts with the spin trap (ST) to form a longer-lived paramagnetic ST-R˙ called the spin adduct (Equation 4.2).

$$\text{ST} + \text{R}^\cdot \rightarrow \text{ST}-\text{R}^\cdot$$  \hspace{1cm} (4.2)

ST-R˙ thus provides indirect evidence for the detection of the free radical of interest. However, it is important to note, there are other possible pathways which also result in the formation of ST-R˙, but don’t require R˙ as the starting species. These include inverted spin trapping,$^{19-22}$ as shown in Equation 4.3. This is where the spin trap loses an electron (by EC, photochemical, ionisation or redox effects) making it susceptible to attack by a nucleophile (NuH) and formation of ST-Nu˙.

$$\text{ST} - \text{e}^- \rightarrow \text{ST}^+ + \text{NuH} \rightarrow \text{ST-Nu}^\cdot + \text{H}^+$$  \hspace{1cm} (4.3)

In Chapter 3 Section 3.3.5, the other mechanism considered was the Forrester-Hepburn mechanism$^{23-25}$ (Equation 4.4) which describes nucleophilic attack of NuH on the spin trap, followed by electron abstraction by an appropriate oxidising agent or redox event.

$$\text{ST} + \text{NuH} \rightarrow [\text{H-ST-Nu}] \rightarrow \text{ST-Nu}^\cdot - \text{H}^+ - \text{e}^-$$  \hspace{1cm} (4.4)

Equations 4.3 and 4.4 are especially problematic when considering the spin trap detection of HO˙ in an aqueous system, via formation of the hydroxyl spin adduct (ST-OH˙). This is because the most abundant nucleophile is water (albeit weak), meaning there is the possibility for forming ST-OH˙ via either EC oxidation of the ST (Equation 4.3) or direct attack of ST by water (Equation 4.4).

However, whilst Equations 4.3 and 4.4 are well reported in the spin trapping of HO˙ in biological literature$^{24,26,27}$ and for fluorescence detection of HO˙,$^{28}$ detailed studies are lacking for electrochemically generated and EPR spin trapped HO˙ free radicals in aqueous systems. This is somewhat surprising, especially as EPR is the ‘go-to’ method for confirmation of the existence of electrochemically generated HO˙.$^{12-14,29-31}$ As the oxidation potential for HO˙ is so high (Equation 4.1), and potentials in EAOPs being even higher, concerns must be raised over the EC oxidation of the spin trap itself...
(Equation 4.3), and the role of water as a nucleophile (Equation 4.3 and 4.4) which is always present in excess.

In other non-EC disciplines, the role of inverted spin trapping (Equation 4.3) has been tackled by the addition of free radical scavengers such as ethanol, dimethyl sulfoxide (DMSO) or ethyl acetate.\textsuperscript{32–34} If the spin adduct is formed as a result of spin trapping free radicals in solution (i.e. Equation 4.2) then the addition of a free radical scavenger would mop up free radicals leading to a significant reduction in spin adduct concentration. Furthermore, if the radical scavenger contains an α-hydrogen, it is possible for the free radical to abstract the α-hydrogen and produce a radical with a different distinctive spin adduct for identification, than compared to the spin adduct formed by Equations 4.3 and 4.4. Nonetheless, these methods fail to consider the implications of placing an organic molecule in a strong EC oxidising environment.

EPR spin traps usually have either a nitroso or nitrone functionality which generates a nitroxide free radical spin adduct when the free radical is trapped.\textsuperscript{35} Inclusion of such functional groups will however, make the spin trap prone to EC oxidation as they are known to be more easily oxidised than water.\textsuperscript{19,36} A popular spin trap for electrochemically generated HO˙ detection is 5,5-dimethyl-1-pyrroline N-oxide (DMPO).\textsuperscript{12–14,29,31,37} The nitrone based DMPO adducts possess a β-hydrogen enabling the discrimination of small radical species through the splitting parameter that arises from the β-hydrogen making DMPO an ideal choice of spin trap.\textsuperscript{38}

Even though the first report of the EC oxidation of DMPO was published in the 1980s\textsuperscript{36} using a Pt electrode in a non-aqueous solvent, the potential issues of using this spin trap for HO˙ radical detection has still not been widely acknowledged in the EC-EPR community. In this investigation, 16 spin traps were tested and DMPO exhibited the most positive oxidative potential.\textsuperscript{36} Since then, to our knowledge, only one other study has investigated the EC oxidation of DMPO, this time in aqueous media, reporting a peak oxidative potential +1.48 V vs SCE.\textsuperscript{39} However, no EC-EPR data was shown at potentials where only DMPO oxidation occurs to examine whether DMPO EC oxidation itself could lead to a false positive in the identification of HO˙ using EPR.
In this chapter, a comprehensive investigation of the EC oxidation of DMPO in aqueous solution is given as well as a discussion of the products formed. The implications of DMPO oxidation on successful HO˙ detection (formed via EC means) in EPR spectroscopy is also explored. The effect of adding a radical scavenger (ethanol) in an EC-EPR experiment is also investigated as to whether this can provide further evidence of HO˙ formation. Finally, EC characterisation of other common EPR spin traps is performed.

4.2. Experimental

4.2.1. Reagents and solution preparation

Solutions were prepared using deionised water of ≥18.2 MΩ cm resistivity at 25 °C (Milli-Q, Millipore Corp.). All chemicals were used as received from the supplier. Stock DMPO (<98%, Enzo Life Sciences Ltd) was stored in a freezer at -18 °C prior to use and prepared at a range of concentrations (1 – 10 mM) in 0.10 M HClO₄ (70 %, 99.999% trace metals basis, Sigma Aldrich) unless otherwise stated. To maintain a DMPO to electrolyte ratio of ≥ 1:10 in order to minimise migration and ohmic drop, DMPO solutions at 15, 20 and 30 mM were prepared in 0.15 M, 0.20 M, and 0.30 M HClO₄ respectively. A solution of hexammineruthenium (III) chloride (Ru(NH₃)₆³⁺; 99%, Strem chemicals) was prepared at 1 mM in 0.10 M KNO₃ (≥99.0%, Sigma Aldrich). To calculate the spin adduct concentrations, the stable radical 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine 1-oxyl (4-hydroxy TEMPO; 98+%, Alfa Aesar) was prepared at concentrations over a range of 500 nM to 100 μM in deionised water, to produce a calibration curve. Solutions of 10 mM N-tert-butyl-α-phenylnitrone (PBN; >99.5%, Sigma Aldrich), α-(4-pyridyl N-oxide)-N-tert-butylnitrone (POBN; 99%, Sigma Aldrich) and 2-methyl-2-nitrosopropane dimer (MNP; Sigma Aldrich) were also prepared in 0.10 M HClO₄. EC-EPR experiments, using ethanol as a radical scavenger were performed in an aqueous solution containing 5 M ethanol (99.9% absolute, VWR Chemicals) in 0.10 M HClO₄. Finally, a solution of 0.10 M tetrabutylammonium tetrafluoroborate (TBAB; 99%, Sigma Aldrich) in ethanol was prepared.
4.2.2. Electrode fabrication

Full details on electrode properties are fabrication are described in Chapter 2, Section 2.3.2. In brief, a rectangle (7 cm by 1 cm) was cut from a 700 μm thick freestanding wafer of BDD, containing both growth and nucleation faces (Electrochemical Processing Grade) using a 355 nm Nd:YAG 34 ns laser micromachiner (E-355H-ATHI-O system, Oxford Lasers). From a 460 μm thick BDD wafer (also Electrochemical Processing Grade), where the growth surface had been mechanically polished to nanometre roughness, a 1 mm diameter cylinder was also laser-cut. The electrodes were cleaned and fully oxygen-terminated using an acid clean, described in Chapter 2 Section 2.2. To ensure a good ohmic contact, the top 0.5 by 1 cm rectangle was laser roughed prior to sputtering to aid adhesion. Ohmic contacts were formed via sputtering (Moorfields MiniLab 060 sputterer/evaporator) Ti/Au (10:400 nm) onto the top 0.5 by 1.0 cm area of the nucleation face of the rectangular electrode and the backside of the polished cylinder and then annealed at 400 °C for 5 hr. For the rectangle electrode, a wire was attached with silver epoxy (Chemtronics, CircuitWorks) and the contact-wire connection coated in non-conductive epoxy (Araldite Rapid Epoxy Adhesive, Araldite) to protect it from solution. The cylinder was sealed in a glass capillary (O.D. 2mm; I.D. 1.16 mm, Harvard Apparatus Ltd.) using a process previously outlined.42

4.2.3. Electrochemical set-up

A three-electrode set-up was utilised for all EC experiments employing either a CHI1140B, CHI760E or CHI1150A potentiostat (CH Instruments Inc.). The three-electrode configuration consisted of: either the 7 cm by 1 cm BDD working electrode (WE), a 1 mm disc BDD WE, a 2 mm disc Pt WE (IJ Cambria Scientific Ltd) or a 3 mm disc glassy carbon (GC) WE (IJ Cambria Scientific Ltd). As reference electrodes (RE), a saturated calomel electrode (SCE, IJ Cambria Scientific Ltd) for aqueous experiments and a leak free Ag/AgCl reference (LF-1.6, Alvatek) for non-aqueous experiments were used and a Pt coil as a counter electrode (CE). To ensure a clean EC surface prior to each EC characterisation measurement, all WE’s were polished using alumina paste
(MicroPolish Suspension 0.05 µm, Buehler) on a polishing pad (MicroCloth PSA, Buehler), followed by polishing on a wetted polishing pad before a final rinse with deionised water.

All EC-EPR experiments were performed with a magnetic flea stirring the solution on a magnetic stirrer plate (RCT basis, IKA) to increase mass transport to the electrode thus reducing the current drop off, discussed in Chapter 1 Section 1.1.2. To thoroughly clean the electrode, prior to each EC-EPR measurement, the 7 by 1 cm BDD WE underwent a cathodic pre-treatment of -2.00 V vs SCE for 60 sec in 0.10 M HClO₄ (vide infra). For the EC-EPR experiments with ethanol, the same cathodic pre-treatment was performed but instead a solution of 5 M ethanol in 0.10 M HClO₄ was employed. For comparison to other data presented, non-aqueous experiments performed using a leak free Ag/AgCl RE have been converted into potentials vs SCE.

4.2.4. Interferometry

White-light interferometry images were collected using a 5× objective on a ContourGT profilimiter (Bruker) and processed in Gwyddion (Version 2.5.2).

4.2.5. Electron paramagnetic resonance spectroscopy

Based on the results gained in Chapter 3, EPR spectroscopy was performed on continuous wave (CW) an X-band spectrometer (Bruker EMX, Bruker) fitted with a cylindrical cavity resonator (4119HS/0207, Bruker). Aliquots of solution for measurement were placed in a 1 mm inner diameter (ID) quartz EPR tube (Wilma® quartz (CFQ) EPR tubes, Sigma-Aldrich). For all measurements, the following optimised spectrometer parameters were used: a non-saturating microwave (MW) power of 10 mW; central magnetic field, 352 mT; sweep width, 10 mT and a modulation amplitude, 0.04 mT. All spectra reported are an average of 16 scans to increase signal to noise by roughly a factor of 4. Fitting and simulation of the EPR spectra was performed using the MATLAB package EasySpin (Version 5.2.25).
4.3. Results and Discussion

To explore the EC characteristics of DMPO in aqueous solution, cyclic voltammograms (CVs) were first recorded in a solution of 0.10 M HClO$_4$ (black line) and 10 mM DMPO in 0.10 M HClO$_4$ (red line) at a 1 mm diameter disk BDD electrode at 0.1 V s$^{-1}$ as shown in Figure 4.1a. Note, all scans in Figure 4.1 commence at 0.00 V vs SCE and then proceed first in the anodic direction up to +2.50 V vs SCE. For this work, high analyte concentrations have been chosen as these are the concentrations opted for in EC-EPR experiments to ensure excess spin trapping agents to free radicals produced.$^{12,13,29}$ HClO$_4$ was used as the supporting electrolyte due to its high stability and resilience to HO$^\cdot$ attack previously discussed in literature. This is in contrast to electrolytes such as H$_2$SO$_4$ where HO$^\cdot$ attack can produce sulfate (SO$_4^{2-}$) free radicals and peroxodisulfate anions (discussed in more detail in Chapter 5).$^{44,45}$ In addition, the pH of 0.10 M HClO$_4$ solution used was 2. Acidic conditions were chosen as it is thought acidic conditions enhance HO$^\cdot$ production.$^{46}$ Moreover, the generation of HO$^\cdot$ from water oxidation results in the production of H$^+$, hence excess acid helps to minimize local fluctuations in pH.
In the anodic region in **Figure 4.1a**, an oxidative current peak ($E_p = +1.90$ V vs SCE) can be seen on the BDD electrode in the DMPO solution which is not visible on the CV for 0.10 M HClO$_4$ only. The current then starts to increase rapidly starting at +2.35 V vs SCE due to the oxidation of water. The peak current is attributed to the EC oxidation of DMPO. No peak is observed on the reverse scan before the EC reduction of protons in solution (pH= 2) at -1.78 V vs SCE. This signifies the EC oxidation of DMPO is an irreversible process and DMPO itself does not undergo an EC reduction within the potential range tested.
To determine the EC characteristics of DMPO on different electrode materials further CVs were collected in 10 mM DMPO in 0.10 M HClO₄ on a 2 mm Pt disk electrode and a 3 mm GC disk electrode at 0.1 V s⁻¹, shown in Figure 4.2.

![Figure 4.2](image_url)

**Figure 4.2**: CVs for the EC response of 0.10 M HClO₄ only (black) and 10 mM DMPO in 0.10 M HClO₄ (red) on (a) 2 mm disk Pt and (b) 3 mm GC disk WE at 0.1 V s⁻¹.

The DMPO EC oxidative signature can also be seen on both Pt and GC electrodes, at +1.65 V vs SCE and +1.70 V vs SCE, respectively, that are not present in the electrolyte only CV. They are both attributed to EC oxidation of DMPO. The oxidative potentials are slightly less positive than for BDD, suggesting that electrode material has a small influence on the electron transfer kinetics of DMPO oxidation.

To examine the oxidative response in more detail, Figure 4.1b shows ten consecutive CVs recorded for 30 mM DMPO in 0.30 M HClO₄ at 0.1 V s⁻¹ on a 1 mm disk BDD electrode. A clear diminution in the peak current response is seen, even after just one scan, where the peak current has dropped by 88.6 %. The current drop is most likely due to the products of DMPO oxidation dimerising and then forming polymerisation products on the electrode surface. Such behaviour is also commonly observed with the EC oxidation of catecholamines.⁴⁷ The presence of a thin “fouling” film on the surface of the electrode was experimentally verified by performing a scratch test on the BDD electrode surface after electrolysis of 10 mM DMPO (at +1.70 V and +2.50 V vs SCE) on the 7 by 1 cm BDD WE in 0.10 M HClO₄ for 10 min. The resultant topography was measured by interferometry, in Figure 4.3. These potentials were chosen as +1.70
Chapter 4: Electrochemical Oxidation of DMPO

V vs SCE lies in the region of where only DMPO oxidation is occurring whilst +2.50 V vs SCE is in the region where DMPO oxidation and generation of HO⁻ is thought to occur for a pH 2 solution (E= +2.34 V vs SCE for pH 2 solution as used herein).

(a)(i) +1.70 V

(a)(ii) +2.50 V

(b)(i) +1.70 V

(b)(ii) +2.50 V

Figure 4.3: Interferometry images of electrode surface after electrolysis and scratch. (a) Interferometry images of scratches on BDD surface after 10 min electrolysis of 10 mM DMPO in 0.10 M HClO₄ at (i) +1.70 V vs SCE and (ii) +2.50 V vs SCE. (b) Topographies of scratches on BDD surface after 10 min electrolysis of 10 mM DMPO in 0.10 M HClO₄ at (i) +1.70 V vs SCE and (ii) +2.50 V vs SCE.

From these images and depth profiles, a clear difference in surface height, around the areas that have been scratched with tweezers, after the DMPO electrolysis is visible. The underlying BDD also has the advantage that the surface is mechanically resistant to the scratch probe used so will not deform. The height difference is assumed to be due to removal of DMPO fouling products which form a thin film on the electrode.
surface by the scratch of the tweezers. The film was determined to be a maximum of 0.5 μm thick at +1.70 V vs SCE from the cross-sectional interferometric data (although it is possible light may not be able to penetrate all the way down to the underlying BDD electrode). When applying a higher oxidation potential, i.e. +2.50 V vs SCE also for 10 min, interferometry revealed the film had grown in thickness to a maximum of 1.25 μm. The data in Figure 4.3 thus verifies the presence of a fouling film due to the EC oxidation of DMPO and reveals the film continues to grow at potentials where HO' are produced. The \( x,y \) resolution of the interferometer was not sufficient to ascertain whether the film was entirely uniform and free from nano sized pinholes.

Furthermore, the impact of the film on the electron transfer at the BDD/film interface was also assessed by running \( \text{Ru(NH}_3)_6^{3+/2+} \) CVs after the application of different applied potentials from +0.90 V to +2.50 V vs SCE in increments of +0.20 V in 10 mM DMPO for a period of 5 min, Figure 4.4. \( \text{Ru(NH}_3)_6^{3+/2+} \) is thought to be an outer-sphere redox species on BDD.\(^{48}\)
Figure 4.4: CVs of 1 mM Ru(NH$_3$)$_6^{3+/2+}$ in 0.10 M KNO$_3$ on a 1 mm BDD electrode at 0.1 V s$^{-1}$. The CVs were recorded after a 5 min electrolysis in 10 mM DMPO in 0.10 M HClO$_4$ at (a) +0.90, (b) +1.10, (c) +1.30, (d) +1.50, (e) +1.70, (f) +1.90, (h) +2.30, (i) +2.50, (j) +2.70 and (k) +2.90 V vs SCE.

As can be seen in Figure 4.4, as the electrode potential is made successively more positive up to +1.90 V vs SCE, the CV shape changes from peak-shaped (where linear
diffusion dominates) to a steady state response. This steady state response is indicative of isolated nano/microelectrode behaviour. Above +2.30 V vs SCE, the CV returns to more of peak shaped. DMPO oxidation commences at +1.40 V vs SCE as shown in Figure 4.1. This suggests after DMPO oxidation commences a film which partially blocks the surface forms, creating “microelectrodes” through pinholes in the film, which become sufficiently isolated (at +1.90 V vs SCE) such that the diffusion profile changes to one reflective of isolated pin-hole behaviour.  

Interestingly, at potentials greater than +2.30 V vs SCE, the peak-shaped response of the CV is recovered with similar currents returning to those at potentials where DMPO oxidation initially begins. This may indicate at the higher potentials the film has been partially/or fully cleaned off the electrode surface and linear diffusion resumes. Water oxidation occurs at higher potentials producing bubbles at the electrode surface which can provide a cleaning mechanism to remove the oxidised film. Note, this experiment has the caveat of being performed on a 1 mm disk electrode (small surface area, ca. nm roughness), the 7 by 1 cm electrode (which has a larger surface area and significantly larger surface roughness) might facilitate the formation and adhesion of film. Therefore, for all further experiments a cleaning step was deemed necessary to ensure a clean BDD electrode surface between consecutive EC oxidation measurements, given the high DMPO concentrations used in these experiments. For the EC only measurements using the 1 mm BDD electrode (Figure 4.1), the electrode was cleaned using an alumina polishing pad (see Section 4.2.3. for more details) between voltammograms.

Not all redox couples interact in the same way with an electrode surface and/or film and it is interesting to compare Ru(NH$_3$)$_6^{3+}$ behaviour against that of DMPO, in the presence of the film. CVs were thus run for 10 mM DMPO in 0.10 M HClO$_4$ pre (black) and post (red) electrolysis, here the electrode was held at a potential of +1.90 V vs SCE for a period of 5 min, in the DMPO solution, Figure 4.5. This potential was chosen as it showed the most change in the CV wave shape for Ru(NH$_3$)$_6^{3+}$ (Figure 4.4) and was the peak potential extracted from Figure 4.1.
Figure 4.5: LSVs of 10 mM DMPO in 0.10 M HClO₄ on a 1 mm BDD WE at 0.1 V s⁻¹ before (black) and after (red) an DMPO electrolysis for 5 min at +1.90 V vs SCE.

In Figure 4.5, after the formation of the film, the peak due to DMPO oxidation can be seen to disappear as the current has dropped in magnitude. The decrease in magnitude in the region of the peak (0.038 μA to 0.016 μA), is greater than that observed for Ru(NH₃)₆³⁺ (1.85 μA to -0.05 μA). This suggests the EC oxidation of DMPO in the presence of the film is more strongly impacted than the reduction of Ru(NH₃)₆³⁺.

This could be due to DMPO requiring surface adsorption sites on the electrode surface whilst Ru(NH₃)₆³⁺₂⁺ is an outer sphere process so may be able to exploit any pinholes in the oxidised film. However, unlike Ru(NH₃)₆³⁺ reduction, during the scan, oxidation of DMPO will also be contributing further to formation of the film.

To explore the concentration dependence on DMPO oxidation, LSVs were recorded on the 1 mm disk BDD electrode, at 0.5 V s⁻¹, over the DMPO concentration range, 1 - 30 mM, shown in Figure 4.1c. The higher scan rate was adopted to try and minimise any fouling effects over the lifetime of an individual scan. As the concentration increases the peak current increases in a linear fashion over the range 1 - 15 mM in a reproducible manner. At the higher concentrations (> 15 mM) the peak currents
deviate slightly away from the linear progression, most likely due to unavoidable fouling effects on the electrode surface during the scan, exacerbated by the increased concentration.

To understand the relationship between scan rate and current response, LSVs were recorded over the scan rate range, 0.01 - 1 V s\(^{-1}\), in a solution containing 1 mM DMPO in 0.10 M HClO\(_4\) solution (Figure 4.1d). A lower concentration was implemented to try and minimise any fouling effects over the lifetime of an individual scan. The LSVs show four interesting features, the first is the characteristic current, recorded at \(E_p = +1.90\) V vs SCE. The inset in Figure 4.1d shows that this current scales linearly with the square root of scan rate which is indicative of a diffusion-controlled irreversible electron transfer process.\(^{50}\) The second is the LSVs do not show a well-defined peak, the LSVs are more plateau like. Third at the slowest scan rates, a second oxidation peak for DMPO can be observed at \(E_p = +2.44\) V vs SCE, as shown in Figure 4.6.

![Figure 4.6: LSV of 1 mM DMPO in 0.10 M HClO\(_4\) on a 1 mm BDD disk electrodes at 0.01 V s\(^{-1}\).](image)

The diffusion coefficient (D) for DMPO in 0.10 M HClO\(_4\) has been estimated for the purpose of calculating the expected current, using the Wilke-Chang Model,\(^{51}\) shown below in Equation 4.5. This method of D value approximation (in cm\(^2\) s\(^{-1}\)) was assumed
to be the most appropriate due to the similar sizes of DMPO to water solvent molecules.

\[
D = 7.4 \times 10^{-8} \left( \frac{(\varphi MW_s)^{0.1}}{\eta_s V_a}\right) \quad (4.5)
\]

Where \( \varphi \) is the factor for solute-solvent interaction (assumed to be 2.6 for water)\(^{52} \), \( MW_s \) is the molecular weight of the solvent (for water, 18 g mol\(^{-1} \)), \( T \) is the absolute temperature (298 K), \( \eta_s \) is the dynamic viscosity of the solvent (0.89 mPa.s at 25 °C of water)\(^{53} \) and \( V_a \) is the molar volume of the analyte. The molar volume of the analyte (cm\(^3\) mol\(^{-1} \)) can be determined by Equation 4.6 given below.

\[
V_a = \frac{MW_a}{\rho_a} \quad (4.6)
\]

Where \( MW_a \) is the molecular weight of the analyte (DMPO, 113.16 g mol\(^{-1} \)) and \( \rho_a \) is the density of the analyte (1.015 g cm\(^{-3} \)). The molar volume of DMPO was calculated to be 111.49 cm\(^3\) mol\(^{-1} \) and therefore, the diffusion coefficient of DMPO was estimated to be 9.86 \( \times \) 10\(^{-6} \) cm\(^2\) s\(^{-1} \).

Assuming that DMPO is a 1 electron oxidation process (vide infra) and a \( D \) for DMPO is 9.86 \( \times \) 10\(^{-6} \) cm\(^2\) s\(^{-1} \) estimated by Wilke-Chang model,\(^{51} \) the peak current (\( i_p \)) observed are much larger than expected when using the diffusion-controlled irreversible electron transfer equation,\(^{50} \) Equation 4.7.

\[
|i_p| = 2.99 \times 10^5 \alpha^n A D^{\frac{1}{2}} v^{\frac{1}{2}} [C] \quad (4.7)
\]

Where \( n \) is the number of electrons transferred, \( \alpha \) is the transfer coefficient (assumed to be 0.5), \( A \) is the area in cm\(^2\), \( v \) is the scan rate in V s\(^{-1} \) and \([C]\) is the concentration in mol cm\(^{-2} \). For example, Equation 4.7 predicts a peak current of 1.67 \( \times \) 10\(^{-5} \) A for a solution of 10 mM DMPO recorded at 0.1 V s\(^{-1} \) on a 1 mm BDD WE, however, instead a current of 4.60 \( \times \) 10\(^{-5} \) A is observed at +1.90 V vs SCE. Conversely from the data in the inset to Figure 4.1d for the peak current vs \( v^{\frac{1}{2}} \) at 1 mM, a \( D \) value of 2.96 \( \times \) 10\(^{-4} \) cm\(^2\) s\(^{-1} \) for DMPO is calculated using Equation 4.7. This is substantially higher than the theoretical value and unrealistic; the fastest diffusing species (H\(^+\)) in aqueous solution
only has a D of $7.0 \times 10^{-5}$ cm$^2$ s$^{-1}$. Note, in the only other related study by Pei and co-workers, LSVs were recorded for DMPO oxidation at a fixed rotation rate using a rotating disk electrode (RDE) made of titanium suboxide at various scan rates. A peak current response was observed (unusual for RDE studies) which varied with scan rate, also not unexpected in RDE studies. Incorrect use of the Randles Sevcik equation (reversible electron transfer, planar diffusion only) under these conditions, resulted in a D value of $7.91 \times 10^{-9}$ cm$^2$ s$^{-1}$ (unfeasibly small) being calculated for DMPO.  

To explain the higher than expected currents in the LSV response, it is speculated that once DMPO has been oxidised to DMPO$^+$ or DMPO-OH$^-$ (formed by fast reaction of the DMPO$^+$ with water) it can also undergo further electron loss. Possible electron loss oxidation pathways for DMPO and its oxidation products are listed in Figure 4.7. As shown, the EC oxidation of DMPO produces DMPO$^+$ which rapidly reacts with the water to form the DMPO-OH$^-$ spin adduct. DMPO-OH$^-$ can then undergo a further 1 electron oxidation to form the tautomers: 1-hydroxy-5,5-dimethyl-1-pyrrolid-2-one (HDMPN) and 2-hydroxy-5,5-dimethyl-1-pyrroline-N-oxide (HDMPO). Both tautomers are diamagnetic species so would not be observed via EPR. Each tautomer can undergo a further 1 electron oxidation to form either the stable paramagnetic species: 5,5-dimethyl-2-oxopyrroline-N-oxyl (DMPO-X$^-$) or 2-dihydroxy-5,5-dimethyl-1-pyrrolidinyloxy (HDMPO-OH$^-$). It has been previously reported that these DMPO oxidation products (DMPO-OH$^-$, HDMPN, HDMPO, DMPO-X$^-$ and HDMPO-OH$^-$) can be oxidised at lower potentials than DMPO. Hence, for the current passed, the effective number of electrons transferred is actually greater than 1 due to more than one electron transfer process occurring.
Figure 4.7: Reaction pathways for the EC oxidation of DMPO and its oxidative products.

For effective use in the EC-EPR spin trapping of HO⁻, DMPO-OH⁻ should ideally be formed only by Equation 4.2 and not via the false positive routes shown in Equation 4.3 and 4.4. In Chapter 3 Section 3.3.5., the role of water as a nucleophile capable of attacking DMPO to form the DMPO-OH⁻ spin adduct (via Forrester-Hepburn mechanism, Equation 4.4) was investigated. Over the 40 hrs monitored, no DMPO-OH⁻ signal was detected indicating water is an extremely weak nucleophile not capable of attacking DMPO on the timescales of EC-EPR experiments. Hence this data shows that in this system the complications from the Forrester-Hepburn mechanism (Equation 4.4) can be easily ignored.
However, given the data in Figure 4.1, which shows that DMPO can be electrochemically oxidised in water at potentials much lower than the thermodynamic electrode potential for HO· production (E= +2.34 V vs SCE for pH 2 solution) the impact of inverted spin trapping (Equation 4.3) must be explored in further detail. Understanding gained here also applies to the use of DMPO for the detection of other electrochemically generated free radicals. For example, the generation of chlorine (Cl·) and SO₄· free radicals from “inert” electrolytes Cl⁻ and SO₄²⁻ respectively, processes with an E⁰= +2.19 V vs SCE.¹⁰ This is of relevance as if a stronger nucleophile than water (such as Cl⁻) is present this will also preferentially attack the electrochemically oxidised DMPO⁺.

During the long generation times used in EC-EPR experiments and the indication of fouling events presented in Figure 4.1b, Figure 4.3, Figure 4.4 and Figure 4.5, electrode fouling cannot be ignored (*vide infra*). To overcome the fouling effects of DMPO oxidation, different cleaning steps were investigated. Four cleaning treatments were investigated: (i) rinsing, (ii) polishing, (iii) an applied cathodic potential (-2.00 V vs SCE for 60 sec) and (iv) an applied anodic treatment (+2.00 V vs SCE for 60 sec). Figure 4.8 shows CVs recorded in 10 mM DMPO in 0.10 M HClO₄ on a 7 by 1 cm BDD electrode at 0.1 V s⁻¹ before electrolysis (black), after a 5 min electrolysis +1.90 V vs SCE (red) and after one of the four cleaning steps (blue).
Figure 4.8: CVs of 10 mM DMPO in 0.10 M HClO$_4$ recorded on a 7 by 1 cm BDD electrode at 0.1 V s$^{-1}$ before electrolysis (black), after a 5 min electrolysis +1.90 V vs SCE (red), and after a cleaning step (blue). Four cleaning methods were looked at: (a) rinsing the electrode with deionised water (b) polishing with alumina slurry (c) a cathodic treatment at -2.00 V vs SCE for 60 sec in 0.10 M HClO$_4$, and (d) an anodic treatment at +2.00 V vs SCE for 60 sec in 0.10 M HClO$_4$.

From Figure 4.8a, the rinsing of the electrode after electrolysis did not sufficiently remove the film formed to return the CV back to the original DMPO peak magnitude. In Figure 4.8b, the size of the DMPO peak returned to a greater peak current than the original upon alumina polishing after electrolysis. However, this alumina polishing the electrode appeared to have a detrimental effect of the peak shape making it more difficult to be observed. Alumina polishing is known to impact the oxidation state of the BDD surface,$^{55}$ suggesting as found in Figure 4.8, that DMPO oxidation is sensitive to the surface chemistry. In both Figure 4.8c and Figure 4.8d, the peak current was recovered upon the application of potential (-2.00 V vs SCE and +2.00 V vs SCE respectively) to the electrode after electrolysis. Both potentials were chosen to evoke
water oxidation and reduction mechanisms to mechanically clean the surface with bubbles. Though in the case of the cathodic applied potential, the DMPO peak magnitude became higher than the before electrolysis demonstrating an amplification benefit in addition to cleaning. Therefore, to ensure a clean electrode at the start of each new applied potential experiment, the electrode was electrochemically cleaned by applying a cathodic pre-treatment (-2.00 V vs SCE for 60 sec in 0.10 M HClO₄).

Figure 4.9 shows the EPR detection of DMPO-OH⁻ as a function of applied electrode potential (vs SCE), starting from +0.90 V, increasing in steps of 0.20 V up to +2.90 V vs SCE. The solution contained 10 mM DMPO in 0.10 M HClO₄, which is a typical DMPO concentration in EC-EPR detection studies of HO⁻,¹²,¹³,²⁹ with the DMPO in large excess than compared to the concentration of electrogenerated radical. For these measurements the larger 7 by 1 cm rectangular BDD electrode was dipped into solution to an immersion depth of 5 cm (with both electrode surfaces active) for a generation time of 5 min. Such an electrode provides a larger surface area, coupled with a suitably long generation time, to maximise the concentration of any product formed. For each potential investigated an aliquot of solution was removed for placement in the EPR and the spectrum recorded. Note for each potential a fresh DMPO solution is made up just prior to measurement to ensure no reactions of the type described in Equation 4.4 occur.
Figure 4.9: (a) EPR spectra for 5 min electrolysis of 10 mM DMPO in 0.10 M HClO$_4$ at a constant potential of +0.90 V, +1.10 V, +1.30 V, +1.50 V, +1.70 V, +1.90 V, +2.10 V, +2.30 V, +2.50 V, +2.70 V and +2.90 V vs SCE respectively using a 7 by 1 cm rectangle BDD electrode. (b) Plot of double integrated intensity (black) and concentration (red) of DMPO-OH$^-$ extracted from EPR spectra vs the applied potential.

In the potential range +0.90 to +1.30 V vs SCE the only signature is that attributed to the D' signature at 352 mT, arising from the EPR quartz tube; this is present in all spectra. However, starting from a potential of +1.50 V vs SCE and present at all more positive potentials, the EPR spectra in Figure 4.9 show a distinct 1:2:2:1 pattern, which is characteristic of the spin adduct DMPO-OH$^-$.

To confirm this identification, the spectra were fitted and the extracted hyperfine coupling values of $a_N = a_H = 1.5$ mT are in agreement with those expected for DMPO-OH$^-$. Intriguingly, DMPO-OH$^-$ is visible at all potentials beyond the point where current due to EC oxidation of DMPO begins being passed. At pH 2 used in this study, the thermodynamic potential for HO$^-$ production from water oxidation is +2.34 V vs SCE, with currents starting to pass at potentials slightly less positive of $E^0$. It is important to note the $E^0$ reported for HO$^-$ is a prediction based on a Ti/TiOH couple which has a dependence on ionic strength. Therefore, this value should be taken as a guide and any kinetic limitations in electron transfer would shift the potential even more positive. However, even so, it cannot account for the observation of DMPO-OH$^-$ at potentials in the range +1.50 V to +2.30 V vs SCE. Therefore below +2.34 V vs SCE DMPO-OH$^-$ must be produced via alternative means.
It is further interesting to analyse how the DMPO-OH\(^{-}\) concentration changes as a function of applied potential, as shown in Figure 4.9b. The concentration of DMPO-OH\(^{-}\) has been determined by fitting of the four peaks due to DMPO-OH\(^{-}\) and then doubly integrating to get estimate the area under the peaks. This double integrated intensity was converted into a concentration of DMPO-OH\(^{-}\) using a 4-hydroxy TEMPO calibration. The DMPO-OH\(^{-}\) concentration rises as the potential increases from +1.30 to +1.90 V vs SCE and then falls with small rises over the potential range +2.10 to +2.90 V vs SCE.

Given the EC data in Figure 4.1, the mechanism shown in Scheme 4.10 is postulated for the EC oxidation of DMPO, i.e. the 1 electron EC oxidation of DMPO followed by subsequent rapid attack of the nucleophile water. The number of electrons transferred during the EC oxidation must be odd due to the generation of a paramagnetic species (Figure 4.9) with one electron transferred being the most feasible.

![Figure 4.10: Schematic for proposed mechanism for the EC oxidation of DMPO.](image)

To further verify that the EPR DMPO-OH\(^{-}\) signals below +2.34 V vs SCE were due to DMPO EC oxidation, EPR measurements were carried out on DMPO solutions (in 0.10 M HClO\(_4\)) of varying DMPO concentration, as shown in Figure 4.11. Prior to EPR analysis the DMPO was electrochemically oxidised by holding the potential at +1.90 V vs SCE for 5 min. As can be seen Figure 4.11a, the characteristic DMPO-OH\(^{-}\) (1:2:2:1) splitting pattern becomes evident for DMPO concentrations \(\geq 5\) mM, with the signal intensity growing in magnitude as the concentration of DMPO increases. Note, the signal for DMPO-OH\(^{-}\) obtained in 5 mM DMPO is on the threshold of the limit of detection (roughly 500 nM DMPO-OH\(^{-}\) for this set-up) and concentrations below this
would not be detected. Figure 4.11b shows a plot of the intensities and resulting DMPO-OH\(^{\cdot}\) concentrations.

![Figure 4.11](image)

**Figure 4.11**: (a) EPR spectra for 5 min electrolysis of 1, 2.5, 5, 7.5, 10, 15, 20 and 30 mM DMPO in 0.10 M HClO\(_4\) at a constant potential of +1.90 V vs SCE using a 7 by 1 cm rectangle BDD electrode. (b) Plot of double integrated intensity (black) and concentration (red) of DMPO-OH\(^{\cdot}\) extracted from EPR spectra vs the DMPO concentration.

In Figure 4.9, the highest concentration of DMPO-OH\(^{\cdot}\) detected was approximately 1 μM at +1.90 V vs SCE. Given the concentration of DMPO-OH\(^{\cdot}\) produced, the concentration of unconverted DMPO is in huge excess (4 orders of magnitude) compared to the concentration of DMPO-OH\(^{\cdot}\). Hence at a fixed potential, if HO\(^{\cdot}\) were being produced via water oxidation (Equation 4.1), then changing the DMPO concentration from 1-30 mM would not be expected to change the amount of spin adduct produced due to the huge excess of DMPO. From Figure 4.11b, the DMPO-OH\(^{\cdot}\) concentration increases in an almost linear fashion with increasing DMPO concentration, further supporting the hypothesis that EC oxidation of DMPO is the source of the DMPO-OH\(^{\cdot}\) species at this potential.

Given the data presented in Figures 4.9 and 4.11, there are two issues to consider further. The first is why does the EPR signal for DMPO-OH\(^{\cdot}\) decrease as the potential is increased, as seen in Figure 4.9? We postulate is due to fouling effects and/or the consumption (via EC oxidation) of DMPO-OH\(^{\cdot}\) (as suggested by Figure 4.7). The concentration of DMPO-OH\(^{\cdot}\) rises to a maximum of 906 nM at +1.90 V vs SCE and then falls by almost a half when moving more positive to +2.30 V vs SCE. The concentration
drops further to 394 nM at the highest potential (+2.90 V vs SCE) investigated. To explore what happens when the potential was increased even further than +2.90 V vs SCE, Figure 4.12 shows the extra data points (in red) for EPR detection of DMPO-OH$^-$ as a function of applied electrode potential, starting from +3.00 V vs SCE in steps of 0.5 V up to +5.00 V vs SCE. The solution contained 10 mM DMPO in 0.10 M HClO$_4$ and a pre-treatment of an applied cathodic potential (-2.00 V vs SCE for 60 sec in 0.10 M HClO$_4$).

Figure 4.12: (a) EPR spectra for 5 min electrolysis of 10 mM DMPO in 0.10 M HClO$_4$ at a constant potential of +3.00 V, +3.50 V, +4.00 V, +4.50 V and +5.00 V vs SCE respectively using a 7 by 1 cm rectangle BDD electrode. (b) Double integrated intensity of DMPO-OH$^-$ as a function of potential. Potentials of +0.90 V to +2.90 V vs SCE are repeat points from Figure 4.9. New data points at +3.00, +3.50, +4.00, +4.50 and +5.00 V vs SCE are highlighted in red.

Beyond +2.90 V vs SCE and up to a maximum of +5.00 V vs SCE, the signal for DMPO-OH$^-$ continues to drop off overall. This is interesting, as although the potential dependent rate constant for HO$^-$ production is increasing with increasingly positive potential, the decrease in DMPO-OH$^-$ signal suggests other factors are still dominating, as previously discussed. These include the formation of a fouling layer, which is exacerbated at the higher potentials, as highlighted in Figure 4.1b, Figure 4.3 and
Figure 4.4. Additionally, as the potential increases the overpotential for further oxidation pathways taking place, Figure 4.7, which remove the paramagnetic species DMPO-OH\(^{-}\) from solution also increases. Interestingly, no other paramagnetic products (DMPO-X\(^{-}\) and HDMPO-OH\(^{-}\)) were detected even at these higher potentials in Figure 4.12.

The second more important issue is, for electrode potentials where production of HO\(^{-}\) should be possible from the oxidation of water, how much of the DMPO-OH\(^{-}\) EPR signal is from direct water oxidation (Equation 4.1) and how much from EC oxidation of DMPO (Scheme 4.1 and Equation 4.3)? Can HO\(^{-}\) concentration ever truly quantify via the DMPO-OH\(^{-}\) signal under conditions where the spin trap has been electrochemically oxidised? It has been discussed in the literature, that the presence of an organic radical scavenger, such as ethanol, aids the differentiation of the spin adducts generated from inverted spin trapping (Equation 4.3) to those generated from radical trapping (Equation 4.2). This provides a possible route to differentiate between spin adducts generated from EC oxidation of DMPO from those produced via the spin trapping of HO\(^{-}\), in potential regions where both radical generation processes are thought to occur.

In theory, for the specific case of DMPO (spin trap) and ethanol (radical scavenger), once DMPO has been electrochemically oxidised ethanol can act as a nucleophile and react through the more nucleophilic oxygen to form the DMPO-OCH\(_2\)CH\(_3\)\(^{-}\) spin adduct. In contrast, when HO\(^{-}\) are electrochemically generated (via Equation 4.1), they will react with ethanol by scavenging an \(\alpha\)-hydrogen (i.e. with the single electron) to generate a carbon-centred radical.\(^{33}\) This will subsequently react with DMPO to form a different DMPO-CH(OH)CH\(_3\)\(^{-}\) spin adduct. Each ethanol-based spin adduct has distinctive splitting patterns in EPR spectroscopy enabling the two different reaction pathways to be distinguished shown in Figure 4.13a.

Figure 4.13a presents the simulated spectra for (i) DMPO-CH(OH)CH\(_3\)\(^{-}\) (HO\(^{-}\) route) and (ii) DMPO-OCH\(_2\)CH\(_3\)\(^{-}\) (DMPO oxidation route). Figure 4.13b shows EPR spectra recorded after 5 min electrolysis of 10 mM DMPO and 5 M ethanol (pH 6.15, 0.083
mole fraction) in 0.10 M HClO$_4$ aqueous solutions at potentials between +1.66 to +2.86 V vs SCE in 0.20 V increment steps. This covers a region where only oxidation of DMPO occurs to potentials where HO` will be electrochemically produced from water oxidation at the same time as DMPO is also electrochemically oxidised. For a pH of 6.15, E= +2.09 V vs SCE for HO` generation. A sufficiently high concentration of ethanol is required for this experiment so that ethanol can act as a competing nucleophile with water for the DMPO`. To overcome fouling issues previously discussed, a pre-treatment of -1.96 V vs SCE for 60 sec in 0.10 M TBAB in 5 M ethanol was employed to clean the electrode prior to each measurement.
Figure 4.13: Simulated spectra of: (a)(i) DMPO-CH(OH)CH$_3^\cdot$ hyperfine coupling: $a_N = 1.58$ mT G and $a_H = 2.29$ mT (a)(ii) DMPO-OCH$_2$CH$_3^\cdot$ hyperfine coupling: $a_N = 1.32$ mT, $a_H = 0.70$ mT and $a_H = 0.19$ mT. (b) EPR spectra for 5 min electrolysis of 10 mM DMPO and 5 M ethanol in 0.10 M HClO$_4$ at a constant potential of +1.66 V, +1.86 V, +2.06 V, +2.26 V, +2.46 V, +2.66 V and +2.86 V vs SCE respectively using a 7 by 1 cm rectangle BDD electrode. (c) Plot of double integrated intensity (black) and concentrations of DMPO-OH$^\cdot$ (red) and DMPO-CH(OH)CH$_3^\cdot$ (blue) extracted from EPR spectra vs the applied potential.

The two simulated spectra are presented in Figure 4.13a. The spectrum of DMPO-OH$^\cdot$ which has four peaks in a 1:2:2:1 ratio with hyperfine coupling of $a_N = a_H = 1.5$ mT has previously been presented in Figures 4.9 and 4.11. The spectrum for DMPO-CH(OH)CH$_3^\cdot$ has six peaks in equal intensities with a hyperfine coupling of $a_N = 1.58$ mT.
and $a_H = 2.29$ mT. The spectrum of DMPO-OCH$_2$CH$_3$˙ has twelve peaks in equal intensity with a hyperfine coupling of $a_N = 1.32$ mT, $a_H = 0.70$ mT and $a_H = 0.19$ mT. In Figure 4.13b, a ten peak signature can be observed at +1.66 V and +1.86 V vs SCE. Fitting of these spectra indicates that the ten peak signal is due to the combined presence of DMPO-CH(OH)CH$_3$˙ and DMPO-OH˙. The presence of DMPO-OH˙ is expected, as at this potential the EC oxidation of DMPO is occurring in this water-ethanol mix. However, it is surprising to see DMPO-CH(OH)CH$_3$˙, as at these potentials no electrochemically generated HO˙ radicals should be present to oxidise the ethanol. However, up to now, EC oxidation of ethanol has not been considered. As shown in Figure 4.14, for the solvent ethanol with 0.10 M TBAB added to increase solution conductivity, ethanol is oxidised from potentials of +1.56 V vs SCE upwards at 0.1 V s$^{-1}$, on a BDD electrode.

![Figure 4.14: CV of 0.10 M TBAB in ethanol on 1 mm disk BDD macroelectrode at 0.1 V s$^{-1}$ vs Ag/AgCl.](image)

This data indicates ethanol oxidation is electrochemically more facile than water oxidation. Electro-oxidation of ethanol can result in the extraction of $\alpha$-hydrogen producing the 'CH(OH)CH$_3$ carbon-centred radical (shown in Figure 4.15) which is then subsequently able to react with the DMPO spin trap, resulting in the observed DMPO-CH(OH)CH$_3$˙ signal.
At first glance, the EC oxidation of ethanol would hinder the differentiation of DMPO-OH˙ from inverted spin trapping vs direct EC production of HO˙. However, interestingly Figure 4.13b shows that as the potential increases the product distribution between DMPO-OH˙ and DMPO-CH(OH)CH₃˙ (ten peak signal) moves in favour of DMPO-OH˙ (four peak signal) resulting in DMPO-OH˙ becoming the only species observable in the EPR spectrum at potentials ≥ +2.46 V vs SCE. This is even clearer in Figure 4.13c which shows the concentration of DMPO-OH˙ and DMPO-CH(OH)CH₃˙ respectively. A small amount of DMPO-CH(OH)CH₃˙ is still present at the higher potentials but is overwhelmed by the DMPO-OH˙ signal. Due to the difficulties in fitting such a small signal, an assumption that DMPO-CH(OH)CH₃˙ remains roughly constant has been made from the values extracted at +1.66 and +1.86 V vs SCE. This notable change in product distribution indicates a second mechanism has been initiated to promote the production of DMPO-OH˙. We hypothesise this to be EC generation of HO˙ radicals from water oxidation on BDD, where the water is in excess compared to the ethanol. Comparison of the product distribution between DMPO-OH˙ and DMPO-CH(OH)CH₃˙ has allowed the inference of the production of HO˙ from despite, the convolution of EC oxidation of DMPO.

It is also noted, in Figure 4.13 no evidence of the oxygen-centred ethoxy radical has been observed at potentials where it is believed the HO˙ can oxidised ethanol to produce ethoxy radicals. This could be due to the low mole fraction (0.083) of ethanol in the mixture or DMPO-OCH₂CH₃˙ undergoing a further 1 electron oxidation to form acetaldehyde an EPR-silent nitrone.²⁶ Note, in this study, no evidence of the two stage EC oxidation process (i.e. 2 sequential oxidation steps) for the spin trap radical DMPO-OH˙ to DMPO-X˙ and/or HDMPO-OH˙ (Figure 4.7) even up to +5.00 V vs SCE (Figure
4.12) was observed. This contrasts with Pei and co-workers who observed a triplet signal in addition to DMPO-OH\(^\cdot\) at +5.62 V vs SHE.\(^{39}\)

Although, DMPO is the most ubiquitously used spin traps for EC-EPR, it is expected other commonly used spin traps to be prone to the same pitfalls experienced by DMPO, when the potential required to electrochemically generate the radical is greater than the oxidation potential of the spin trap. Whilst EC measurements have been made on PBN (POBN and MNP have not previously been looked at) using a Pt WE,\(^{36}\) which is electrocatalytically much more active to water oxidation. In this case the water oxidation signal obscured any EC signal due to oxidation of the spin trap and oxidation potentials were inferred from non-aqueous conditions. By using a BDD electrode, as water is electrocatalytically retarded, it should be possible to observe the oxidation signals of the spin trap molecules. This is illustrated by the data shown in Figure 4.16 which presents the EC oxidative window for MNP, PBN and POBN all at 10 mM in 0.10 M HClO\(_4\) recorded at 0.1 V s\(^{-1}\) on a 1 mm diameter BDD electrode. MNP contains a nitroso functional group to stabilise the radical whilst PBN and POBN contain nitrone functional groups.

![Figure 4.16](image.png)

**Figure 4.16**: Oxidative windows for 10 mM (a) MNP, (b) PBN and (c) POBN in 0.10 M HClO\(_4\) at a scan rate of 0.1 V s\(^{-1}\) on a 1 mm BDD electrode.

Similar to DMPO, a clear peak in the anodic region is observed at +1.91 V and +1.88 V vs SCE for MNP and POBN respectively in Figure 4.16. In the case of PBN, two oxidation peaks can be observed at +1.97 and +2.19 V vs SCE. It’s not surprising the spin traps tested are oxidised at similar potentials within a small window as they are structurally similar. In addition the nitrone or nitroso functional groups required to stabilise free
radicals in the spin traps are electrochemically active. The observation of EC oxidation peaks for these three spin traps demonstrates that the EC oxidation of spin traps in EC-EPR experiments is likely to occur for all spin trap and thus obscure the results obtained.

4.4. Conclusions

This study has demonstrated the onset of EC DMPO oxidation in acidic aqueous media (i.e. 0.10 M HClO₄) occurs from +1.40 V vs SCE onwards reaching a peak maximum at +1.90 V vs SCE on BDD. The EC oxidation of DMPO was also shown to trigger fouling effects at the electrode surface and that cleaning steps were required for repeat EC measurements in a DMPO containing solution. Furthermore, EC-EPR work at low potentials in a DMPO containing solution, prior to the onset of HO’ formation, revealed that DMPO-OH’ is formed. This is as a result of EC oxidation of DMPO as soon as current passes for DMPO oxidation. Even with cleaning steps in place, the signal for DMPO-OH’ was seen to gradually drop off with small fluctuations when the potential was increased. This raises some serious concerns over the use of DMPO in EC-EPR experiments to detect HO’. This study has also demonstrated that adding a radical scavenger in order to confirm the presence of free radicals, in this case ethanol, is also fraught with issues. This is because ethanol can also get electrochemically oxidised. However, by carefully monitoring how the product distribution changes over a potential range from oxidation only to radical production regime, with ethanol present in solution in the minority can indicate as to where EC generation of free radicals happens. The mixture of DMPO-OH’ and DMPO-CH(OH)CH₃’ present due to DMPO oxidation and ethanol oxidation became predominantly DMPO-OH’ from +2.26 V vs SCE due to electrochemically generation of HO’.

When carrying out EC-EPR experiments, consideration of the magnitude of the applied potential is a critical factor. Below +1.40 V vs SCE, DMPO can be used without needing to consider inverted spin trapping effects as DMPO is not electrochemically oxidised at this potential. However, the data presented in this chapter shows that if the experiment is producing HO’ (from water oxidation) at a potential close to the onset
of DMPO oxidation, then it is highly likely that the DMPO-OH\(^{-}\) signal will contain mixed contributions from DMPO oxidation and trapped HO\(^{-}\). This would lead to an overestimation of the real HO\(^{-}\) concentration. For many EAOPs, a constant current is used thus having knowledge of the applied potential is useful. As the potential moves further away from the DMPO oxidation potential it is likely to play less of a role. However, as shown in this chapter, as the potential is increased the DMPO-OH\(^{-}\) signal actually drops which we attribute to competing EC processes i.e. formation of a fouling layer and/or further oxidation of DMPO-OH\(^{-}\) to an EPR silent species. The fouling effects/consumption of DMPO-OH\(^{-}\) seen in this work puts doubt over whether DMPO can be used as an effective spin trap at the higher potentials used in EAOPs. Although, the development of different cell geometries such as a flow cell could be beneficial to minimise fouling events and prevent further oxidation of DMPO-OH\(^{-}\).

### 4.5. References


13343.


Chapter 5: Production of Diamond Membranes - The Critical Role of Radicals in the Non-Contact Electrochemical Etching of $sp^2$ Carbon

5.1. Overview

Diamond is an exceptional material well known for its extreme properties of hardness, thermal conductivity, and wide optical transmission making it a material of significant interest in emerging technologies.\(^1\) To develop the next generation of optical, quantum, and electronic devices,\(^2\)\(^-\)\(^4\) nano-structuring of the diamond is often required. In particular for quantum technology applications, high-quality single crystal diamond membranes of sub-micron thickness, containing negatively charged nitrogen vacancy defects are essential.\(^2\),\(^3\),\(^5\) While diamond membranes can be prepared using mechanical polishing, this is possible down to only ca. 10 µm thickness.\(^4\) Such membranes are typically wedge-shaped due to the complexities of achieving co-planarity at this thickness over a large area (mm\(^2\)). Moreover, mechanical polishing can result in sub-surface damage, penetrating microns deep, which requires further processing steps to achieve the surface quality required for quantum applications.\(^6\)\(^-\)\(^8\)

Ion implantation is used to amorphise a well-defined sub-surface region of the diamond, followed by high temperature annealing to convert this amorphised diamond to $sp^2$ carbon. After the sub-surface $sp^2$ carbon layer has been prepared the membrane can be removed via etching of this layer, also known as “lift-off”. This method has been proposed as an alternative to mechanical polishing for producing thin, uniform diamond membranes.\(^4\),\(^9\)\(^-\)\(^12\) Diamond membrane thickness is determined by the implantation energy and as the amorphise layer implants parallel to the top surface, the resulting membrane has a consistent thickness at all points. Oxygen dry etching\(^12\) has been used, but was found to be slow (5 hrs for separation of a 2 by 2
mm membrane) with some damage to the membrane also observed due to etching of the diamond as well as the sp$^2$ carbon layer.\(^{12}\)

Electrochemical (EC) etching has also been proposed as an etch method, due to the advantages electrochemistry brings in terms of reduced cost of the set-up and negligible damage to the diamond.\(^9\) However, unlike traditional EC etching/electropolishing where direct contact is made to the conductive material and a potential applied to promote oxidative dissolution of the material itself,\(^{13,14}\) a non-contact EC set-up is required due to the nano-sized features of the embedded sp$^2$ carbon. In order for the implanted sp$^2$ carbon to experience a potential difference across the sp$^2$ carbon, the use of low conductivity solutions was advocated;\(^9\) to drop a meaningful potential across the sp$^2$ carbon/electrolyte interface, the resistance of the solution must be higher than that of the sp$^2$ carbon layer. This concept is often referred to as bipolar electrochemistry.\(^{15,16}\) Unfortunately, using this approach, etch rates were found to be slower than reported for dry etching,\(^{12}\) taking 10 hrs to separate a 3 by 3 mm membrane in a dilute chromic acid solution, even with an applied voltage of 100 V.\(^9\) Thus, despite the importance of this process to the quantum optical communities, the EC etch process is still far from optimised for efficient sp$^2$ carbon removal rates.\(^4,12,17–20\)

This work demonstrates a new non-contact EC nanofabrication method which can be used to etch conductive nanomaterials, where direct electrical contact to the conductive material is challenging. Rather than relying on a bipolar etch mechanism and low conductivity solutions, this method uses high conductivity, fully dissociated electrolytes in conjunction with EC initiation of radical generating chemical pathways in solution. Etch rates of the sp$^2$ carbon layer are measured using in-situ optical microscopy. How the choice of electrolyte and electrolyte concentration can significantly enhance sp$^2$ carbon etch rates is explored.
Chapter 5: The Critical Role of Radicals in Non-Contact Electrochemical Etching of sp² Carbon

5.2. Experimental

5.2.1. Reagents and solutions

All solutions were prepared from deionised water (>18.2 MΩ cm, Milli-Q, Millipore Corp.). Etch solutions comprised either 400 mM boric acid (H₃BO₃, 99.97%, Sigma Aldrich) or 250 mM electrolyte salts in deionised water. Salts investigated included potassium nitrate (KNO₃, 99.97%, Sigma Aldrich), potassium chloride (KCl, ≥99%, Sigma Aldrich), and potassium sulfate (K₂SO₄, Pure, Acros Organics). Sulfuric acid (H₂SO₄, >96%, Merck) was used at 0.3% v/v (50 mM) in deionised water. Mixed K₂SO₄/H₂SO₄ solutions were made to 250 mM total sulfate concentrations in deionised water. Solutions for electron paramagnetic resonance (EPR) spectroscopy comprised of KNO₃, KCl, and K₂SO₄ (Analysis Grade, Sigma Aldrich) at a concentration of 250 mM or 400 mM boric acid in deionised water.

5.2.2. Diamond sample preparation

Standard grade chemical vapour deposition (CVD) and high pressure high temperature (HPHT, type 1b) single crystal diamond plates (Element Six Ltd.) which are ca. 500 µm thick, and either 3.5 mm (3.5 by 3.5 mm), 4.1 mm (4.1 by 4.1 mm) or 4.2 mm (4.2 by 4.2 mm) in size were used as the substrates for all studies, unless otherwise stated. The front face of each sample was mechanically polished to ca. nm roughness, and the rear face lapped to ca. µm roughness. Before ion implantation, samples were acid cleaned described in Chapter 2 Section 2.2. After acid cleaning the implantation surface was cleaned in an oxygen/argon plasma (Emitech, K1050X Plasma Asher, 80 W, 60 s). The polished face was then implanted (Ion Beam Centre, University of Surrey) with 2 × 10¹⁶ carbon atoms (at 2 MeV) per square centimetre, to produce an amorphised layer ca. 9400 nm below the surface, and ca. 400 nm thick, as estimated from stopping range of ions in matter (SRIM) simulations. The implanted samples were annealed at 1300 °C for 2 hrs, to convert the amorphised region into sp² carbon. After annealing the samples were then acid cleaned using the method described above and then characterised by Raman spectroscopy to verify that a sub-
surface $sp^2$ carbon layer was present. Note, due to the limited availability of the samples used, it was necessary to complete some work without repeats.

5.2.3. Electrochemical etching

Etching of single crystal diamond substrates took place in a custom designed 3D printed (Taz 6, Lulzbot) polyethylene terephthalate cell. The electrodes used were two Pt wire electrodes (0.75 mm in diameter and 2 cm in length) spaced 6 mm apart, as shown in Figure 5.1. A variable DC power supply (EA-PS 9750-04, Elektro-Automatik GmbH) was employed to apply a potential between the two electrodes, operating in a potential limiting mode at 30 V (approximately +15 V and −15 V vs ground), with a current value dependent on the solution composition. The diamond substrate, with embedded $sp^2$ carbon layer was bonded (lapped face on) to a polycarbonate (RS Components) support using a low-bloom cyanoacrylate adhesive (Loktite 460, Henkel), making sure no adhesive was visible to solution. This piece of polycarbonate was then placed into a slot, for centring purposes, with the polycarbonate face on which the diamond is adhered, held against the Pt electrodes (Figure 5.1). This ensures that the diamond plate was orientated such that the square face was perpendicular to the base of the etch cell, aligning the $sp^2$ carbon layer in plane with the Pt wire electrodes. The cell was designed with a light path for transmission imaging of samples undergoing etching (Figure 5.1).
Chapter 5: The Critical Role of Radicals in Non-Contact Electrochemical Etching of \( \text{sp}^2 \) Carbon

Figure 5.1: Schematic of the etch cell showing the arrangement of diamond sample (yellow), electrodes (grey), and polycarbonate support (light blue). Front: a front view as seen by the USB microscope) showing the diamond sample attached to the polycarbonate support and placed between the two Pt electrodes. Top: a top view showing how the diamond sample is aligned in plane with the electrodes. Side: a side view with the electrodes omitted for clarity which shows how the USB microscope images through the solution and polycarbonate support in transmission using a backlight to maximise the contrast between etched and unetched areas of the \( \text{sp}^2 \) carbon.

A digital USB microscope (VMS-001, ×20–90 magnification, Veho, UK) was used to capture time lapse images of etch progress. All etches were performed at 25 °C. Etch solution was circulated from this reservoir into the cell and returned via an outflow at a flow rate of 200 mL min\(^{-1}\). The inlet and outlet were intentionally placed away from the Pt electrodes to minimise solution flow across the diamond sample and electrodes. Although flow will increase mass-transport to and from the electrodes it is likely the production of gas bubbles from water electrolysis at the Pt electrodes will be a much more significant contributor to increased mass-transport.
5.2.4. Image analysis

A MATLAB (Version 2017b, MathWorks) script was used to analyse all time-lapse data of the etch processes. Each frame from the video capture was extracted. The region of interest (i.e. the diamond substrate) is defined on the first image and the script used to calculate what proportion of that area corresponds to the etched region; these match RGB values provided in the script. This proportion is then converted to an area and the area etched is then plotted vs etch time to create an etch profile.

5.2.5. Electron paramagnetic resonance spectroscopy

For EPR measurements, electrolysis of solutions containing either 250 mM K$_2$SO$_4$, 250 mM KCl, 250 mM KNO$_3$ or ca. 400 mM H$_3$BO$_3$ was performed with no recirculating flow, in a single compartment cell. 30 V was applied between the two Pt electrodes of the same geometry as those used in the etch cell in the solution of interest. After an electrolysis time of 15 min the potential was switched off and approximately 10 mM of the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO; > 98%, Enzo Life Sciences) was added to the solution and mixed thoroughly. Note: the time from switching off the potential to adding the spin trap was ca. 30 s. From the resultant solution, an aliquot of the electrolysis mixture was sampled and the EPR spectrum recorded. Based on the findings of Chapter 3, the EPR signals for the DMPO spin adduct were recorded on a continuous wave (CW) X-band spectrometer (EMX, Bruker, Germany) fitted with a cylindrical resonator (4119HS/0207, Bruker, Germany). Measurements were performed in a 1 mm inner diameter (ID) quartz EPR tube (Wilmad® quartz (CFQ) EPR tubes, Sigma-Aldrich). For all measurements the following spectrometer parameters were used: a non-saturating microwave (MW) power of 20 mW; central magnetic field, 352 mT; scan width, 10 mT and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans. Fitting and simulation of the EPR spectra was performed using the MATLAB package EasySpin (Version 5.2.25).
5.2.6. Monitoring of H$_2$O$_2$ in etch solutions

For detection of H$_2$O$_2$ by ultra-violet (UV-Vis) spectroscopy, a TiSO$_4$ dye was prepared by refluxing titanium (IV) oxide anatase (99.7 %, Alfa Aesar) in concentrated H$_2$SO$_4$ for 12 hrs at 150 °C.$^{25}$ This reflux solution was left for 16 hrs so the excess titanium (IV) oxide anatase sediments from solution. The supernatant was collected, diluted to make 1 L with deionised water and finally filtered through a 0.2 micron filter before use. A calibration curve was produced for a range of H$_2$O$_2$ concentrations between 0.75 µM and 7.5 mM, by serially diluting a stock H$_2$O$_2$ (30 % w/w uninhibited, Fischer Scientific) solution (9.8 M). UV-Vis spectra were collected between 200 to 600 nm (Lambda 850, PerkinElmer). Electrolysis of three individual solutions containing either 250 mM KNO$_3$, 250 mM KCl, or 250 mM K$_2$SO$_4$ was performed in a one-compartment cell by applying 30 V between two Pt electrodes (electrode area, 0.50 cm$^2$) using a power supply (Elektro-Automatik GmbH, EA 9750-04) under static conditions for 1, 2, 3, 4, 5 and 6 min per electrolyte. The electrolysis solution was then mixed with the prepared TiSO$_4$ solution in a 4:5 ratio and measured for H$_2$O$_2$ quantification using UV-Vis spectroscopy.

5.3. Results and Discussion

5.3.1. Measuring the material etch rate

The etch rate, as a function of solution composition, of the ca. 400 nm thick sp$^2$ carbon layer embedded in the freestanding single crystal diamond substrates, was monitored optically, in transmission mode, using a USB microscope (Figure 5.1). An exemplar optical image of the time-dependent removal of the sp$^2$ carbon layer is shown in Figure 5.2, here recorded over a period of 2 hrs in 250 mM K$_2$SO$_4$. Images were recorded every 10 sec from application of the potential. At time, t= 0 min, the image appears black, due the presence of a complete sp$^2$ carbon layer. EC etching of this layer is monitored via the colour change of the sample from black to colourless, the latter representing the translucent diamond as the sp$^2$ carbon layer is removed. This colour change was used to quantify the area of sp$^2$ carbon removed as a function of etch time. The heterogeneous nature of the etch process, as shown by Figure 5.2, is
typical of all etches in the different solutions observed under these flow conditions, the only difference being the timescale of the removal process.

Figure 5.2: Optical image capture of the etch progress on a 4.2 mm by 4.2 mm HPHT diamond in aerated 250 mM K₂SO₄ solution with 30 V applied between two Pt electrodes, from t= 0 to t= 2 hrs. Each image is separated by approximately 8 min of etching in 250 mM K₂SO₄. Anode and cathode positioned to the left and right of the frame (out of view), respectively.

All etches in all solutions examined (n= 27 in total) had a sigmoidal shape, as shown in the exemplar etch rate data (area etched vs time) in Figure 5.3, for a 250 mM K₂SO₄ solution. All data was fitted with a sigmoid (black line) and this fit used to provide insight into the etch characteristics. The curve could be divided into four distinct sections. First, the induction period (yellow shaded area), second the bulk etch region where the rate of etching is highest and linear and where most of the material removal occurs (pink shaded area). Third, the bulk etching limit, where the limited amount of material remaining leads to a decrease in rate (blue shaded area), before finally reaching the final region, the etching complete region (grey shaded area) and no sp² carbon remains. Most membranes (~ 90 %) recovered after the etch process were completely intact.
Chapter 5: The Critical Role of Radicals in Non-Contact Electrochemical Etching of \( \text{sp}^2 \) Carbon

Figure 5.3: Exemplar etch profile from in-situ transmission microscope imaging. The raw data points (\( n = 6500 \), red) are fitted with a sigmoidal function (black) and three distinct regions are defined. Etching is considered complete at 3 hrs as no visible remnants of the \( \text{sp}^2 \) carbon layer remains. Conditions: 4.1 by 4.1 mm CVD sample in aerated 250 mM solution of \( \text{K}_2\text{SO}_4 \) with 30 V applied between the electrodes at 25 °C.

The induction period, during which very little etching takes place, varied in length for the range of conditions tested, however faster bulk etch rates typically resulted in shorter induction periods. We speculate that the existence of an induction period is a result of either the \( \text{sp}^2 \) carbon region not extending completely to the edge of the diamond, or a structurally different form of \( \text{sp}^2 \) carbon at the edge vs the interior. In the majority of etches, etching began from two to three randomly distributed individual sites around the plate then continued inwards.

To assess the impact of solution conditions and composition on the etch rate, we focused on the bulk etch region (pink), which is where the majority of material is removed. In the bulk etching limit (blue area), as with the induction period (yellow area), we believe the material properties of the \( \text{sp}^2 \) carbon implanted diamond play a more significant role in controlling the etch characteristics. This will form the subject of further work. Bulk etch rates were thus used as the quantitative metric for comparing the efficacy of different electrolyte solutions. Area etch rates (in \( \text{mm}^2 \text{ hr}^{-1} \)) were determined by analysing the gradient over the region where 20% to 70% of the total area of \( \text{sp}^2 \) carbon had been removed (i.e. 3.5 mm\(^2 \) to 12.25 mm\(^2 \)) in Figure 5.3).
This threshold was chosen as in all etches conducted it was within the pseudo-linear region of the sigmodal fit. Area, rather than volume, was also employed as a metric to acknowledge the uncertainty in the SRIM estimate if the sp\textsuperscript{2} carbon layer width.

5.3.2. Electrochemical etching in low conductivity solutions and chemical etching

For these EC etch studies, half-saturated aerated H\textsubscript{3}BO\textsubscript{3} (~ 400 mM) was employed as the etch electrolyte, following literature precedent\textsuperscript{4} in order to define a baseline etch rate under “bipolar” etch conditions. It is important to appreciate that whilst the concentration of H\textsubscript{3}BO\textsubscript{3} is high, solution conductivity is very low (only \(40 \mu S \text{ cm}^{-1}\) which equates to a conductance of \(3 \mu S\) based on cell geometry) due to H\textsubscript{3}BO\textsubscript{3} being a weak acid (pK\textsubscript{a} = 9.2) and only partially deprotonated (dissociated).\textsuperscript{26} The conductivity of bulk amorphous sp\textsuperscript{2} carbon is ca. 12.5 S cm\textsuperscript{-1}, which based on layer dimensions represents a conductance of ca. 0.6 mS.\textsuperscript{27} As such, the sp\textsuperscript{2} carbon layer is over two orders of magnitude more conductive than the solution, and the majority of the potential between the two Pt wire electrodes will be dropped across the solution. Consequently, a large potential will be present at the sp\textsuperscript{2} carbon-electrolyte interface, which is capable of driving electron transfer reactions directly at this electrode surface. EC etching in this media gave an etch rate of 0.7 mm\textsuperscript{2} hr\textsuperscript{-1} (for a 4.2 by 4.2 mm substrate), taking 20 hrs for complete separation once the induction period had passed.

Under bipolar conditions, etching most likely occurs via direct EC oxidative (Equations 5.1 and 5.2) and/or reductive (Equation 5.3) dissolution of the sp\textsuperscript{2} carbon. Note that the potentials given are thermodynamic potentials, with the experimentally observed potentials often being higher due to kinetic limitations.\textsuperscript{28,29}

\[
\text{C(s)} + \text{H}_2\text{O}_{(aq)} \rightarrow \text{CO}_{(g)} + 2\text{H}^+_{(aq)} + 2\text{e}^- \quad E^0 = 0.52 \text{ V vs SHE} \textsuperscript{30} (5.1)
\]

\[
\text{C(s)} + 2\text{H}_2\text{O}_{(aq)} \rightarrow \text{CO}_2(g) + 4\text{H}^+_{(aq)} + 4\text{e}^- \quad E^0 = 0.21 \text{ V vs SHE} \textsuperscript{30} (5.2)
\]

\[
\text{C(s)} + 4\text{H}^+_{(aq)} + 4\text{e}^- \rightarrow \text{CH}_4(g) \quad E^0 = -0.13 \text{ V vs SHE} \textsuperscript{30} (5.3)
\]
It is also possible electrochemically generated species which are highly oxidising in nature, e.g. radicals, can cause etching of the sp² carbon. For example, at high enough potentials, water can be oxidised to form hydroxyl radicals (HO⁻), in solution (Equation 5.4).\(^{31}\)

\[
\text{H}_2\text{O}(l) \rightarrow \text{HO}^-_{(aq)} + \text{H}^+_{(aq)} + \text{e}^- \quad E^{0\text{e}} = +2.73 \text{ V vs SHE}^{31} (5.4)
\]

However, other pathways for water oxidation are more energetically favourable meaning it is only on surfaces where traditional water oxidation routes are strongly retarded, such as boron doped diamond (BDD) that direct HO⁻_{(aq)} production is significant.\(^{32}\) EC radical generation via oxidation of the electrolyte is also unlikely as oxidation of borate anions / boric acid is not thought to result in radicals. This is also confirmed by the data in Figure 5.4, which shows no EPR evidence of radical formation in the half-saturated aerated H_3BO_3 solution after 30 V electrolysis for 15 min.

![Figure 5.4](image)

**Figure 5.4**: EPR spectra after 15 min of applied 30 V in 400 mM of aerated H_3BO_3. Experimental Conditions: A non-saturating MW power of 20 mW; central magnetic field, 352 mT; scan width, 10 mT and a modulation amplitude, 0.05 mT. Spectrum reported is an average of 9 scans.

Cathodically, on sp² carbon, the oxygen reduction reaction (ORR) favours a 2 electron pathway which results in production of the oxidising agent H_2O_2 (Equation 5.5).\(^{33}\) Dissolved oxygen will always be present due to the use of aerated solutions and the
high potential difference applied across the two Pt electrodes; at the Pt anode, oxygen will be evolved from water oxidation.

\[ \text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2\text{O}_2(aq) \quad \text{E}^0 = 1.76 \text{ V vs SHE}^{34} \quad (5.5) \]

Note, that immersing a sp\(^2\) carbon implanted diamond sample into very high concentrations of H\(_2\)O\(_2\) (30 % w/w), much higher than those generated during ORR, at 25 °C for 24 hrs, with no applied potential, results in no visible etching of the sp\(^2\) carbon layer. This result suggested etching is either extremely slow or not possible using H\(_2\)O\(_2\) alone.

### 5.3.3. Electrochemical etching in high conductivity solutions

For the strong electrolyte (high solution conductivity) experiments three different electrolytes were employed (KNO\(_3\), KCl, and K\(_2\)SO\(_4\)). The anion concentration was fixed at 250 mM, with solution conductivities almost three orders of magnitude higher than that for H\(_3\)BO\(_3\); at 24 mS cm\(^{-1}\) (conductance of 1.8 mS), 28 mS cm\(^{-1}\) (conductance of 2.1 mS) and 42 mS cm\(^{-1}\) (conductance of 3.2 mS) respectively. Note, with this increase in solution conductivity, bipolar contributions towards etching are expected to be significantly reduced due to considerably decreasing the potential drop between the sp\(^2\) carbon layer and electrolyte. Figure 5.5 shows the (a) etch profiles and (b) etch rates for the sp\(^2\) carbon implanted diamond substrate, in the bulk etch regions in the three different electrolytes. H\(_3\)BO\(_3\) is included for comparison in the data in (b).
Figure 5.5: a) Etch profiles for etching of 4.2 mm by 4.2 mm HPHT single crystal diamonds in aerated 250 mM solutions of KNO$_3$ (blue), KCl (black) and K$_2$SO$_4$ (pink). Inset, etch profile for KCl and K$_2$SO$_4$ from 0–2 hrs, the inset has the same units as the larger plot. 30 V was applied between the two Pt electrodes until etching was complete. Data was collected as n= 1. b) Comparison of the bulk etch rates for each different electrolyte, plus aerated 400 mM H$_3$BO$_3$.

Whilst the etch rate in KNO$_3$ was slower (0.3 mm$^2$ hr$^{-1}$) than that obtained using the H$_3$BO$_3$ both KCl (8.0 mm$^2$ hr$^{-1}$) and K$_2$SO$_4$ (13.0 mm$^2$ hr$^{-1}$) resulted in dramatic improvements in etch rate. Sulfate increased the bulk etch rate compared to both nitrate and boric acid by over an order of magnitude.

5.3.4. Electron paramagnetic resonance spectroscopy studies

To explore the origin of these observations in detail, EPR spectroscopy was employed to identify radicals produced during electrolysis. The EPR spectrometer was set up with the optimised conditions from Chapter 3. A cell with Pt electrodes identical to those used for etching, but with no diamond substrate present, was employed for the EPR measurements with 250 mM KNO$_3$, KCl and K$_2$SO$_4$, undergoing electrolysis at 30 V for 15 min. In our non contact high conductivity experiments, the etchant is expected to be generated primarily at the non contact electrodes, via EC means, and must move through solution to the sp$^2$ carbon. Hence, to be effective any radicals produced must either have a sufficiently long lifetime or, as most radicals in aqueous solution are notoriously short-lived e.g. $\leq \mu$s timescale, are continually generated or regenerated through chemical reactions in solution. To show whether radicals were
present at timescales significantly longer than their characteristic lifetimes, the DMPO spin trap was added after electrolysis had completed and the potential had been switched off; a process taking typically 30 sec. This contrasts with the vast majority of EC-EPR experiments where the spin trap is added before starting electrolysis; this circumvents any spin trap oxidation issues discussed in Chapter 4. DMPO was mixed into the solution and an aliquot taken for analysis in the EPR spectrometer, data shown in Figure 5.6. Note, the experiment was performed under stationary conditions which resulted in notable solution heating (~ 90 °C) compared to the flow experiments.

**Figure 5.6:** EPR spectra after 15 min of applied 30 V in 250 mM solutions of aerated KNO₃, KCl and K₂SO₄ (blue), as well as simulated spectra for the DMPO-OH⁺ spin adduct and D’ quartz signal (black). Experimental Conditions: A non-saturating MW power of 20 mW; central magnetic field, 352 mT; scan width, 10 mT and a modulation amplitude, 0.05 mT. All spectra reported are an average of 9 scans.

In all solutions, a clear signature for the DMPO-OH⁺ spin adduct is seen in the EPR spectrum, as well as a D’ signature at 352 mT from the quartz tube (included in the fit). The hyperfine coupling ($a$) extracted from the fitted data gave values of $a_N = 1.50$ mT and $a_H = 1.50$ mT which is in agreement with those expected for DMPO-OH⁺. The
DMPO-OH˙ signature, which is indicative of radical concentration, varies in intensity in the order NO₃⁻ (low) < Cl⁻ < SO₄²⁻ (high). Formation of HO´(aq) via the water oxidation route (Equation 5.4) is unlikely to be significant on Pt, as discussed in Section 5.3.2, this is due to the strong adsorption of HO´ on Pt electrodes leading to the formation of Pt oxide.\textsuperscript{37} Given the extremely high reactivity of HO´, its short lifetime (≤ μs)\textsuperscript{38} and the fact that the spin trap is added after the potential has been switched off, observation of a DMPO-OH˙ signal means that chemical routes in solution (initiated electrochemically) must be acting to generate or regenerate the HO´ radical (discussed below).

Metal surfaces, such as Pt, can catalyse the decomposition of any H₂O₂ present to produce HO´ via the Weiss mechanism (Equation 5.6).\textsuperscript{39}

\[
\text{Pt}_x(s) + 2\text{H}_2\text{O}_2(aq) \rightarrow \text{Pt}_{x+1}(s) + \text{OH}^-(aq) + \text{HO}´(aq)
\]  \hspace{1cm} (5.6)

Where Pt\(_x\) and Pt\(_{x+1}\) denotes active sites on the Pt surface. Whilst ORR on Pt is typically thought to predominantly occur via the 4 electron pathway to form H₂O (Equation 5.7),\textsuperscript{40} the amount of H₂O₂ produced on Pt via the 2 electron pathway (Equation 5.5) has been shown to be dependent on solution composition.\textsuperscript{41–43}

\[
\text{O}_2(aq) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(aq)
\]  \hspace{1cm} (5.7)

Once formed, HO´ radicals can recombine to form H₂O₂ (Equation 5.8) or react with H₂O₂ (Equation 5.9) to form the hydroperoxyl radical (HO₂´). Although HO₂´ is lower in oxidising ability than HO´, thermodynamically it is capable of direct oxidation of the sp² carbon layer.\textsuperscript{31}

\[
\text{HO}´(aq) + \text{HO}´(aq) \rightarrow \text{H}_2\text{O}_2(aq)
\]  \hspace{1cm} (5.8)

\[
\text{HO}´(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{HO}_2´(aq) + \text{H}_2\text{O}(aq)
\]  \hspace{1cm} (5.9)

As HO₂´ is a much longer lived radical in solution (10 – 100 sec)\textsuperscript{44} compared to HO´, if there is any HO₂´ present when the electrode potential is switched off and DMPO is added to solution, HO₂´ will react with DMPO to form DMPO-OOH´. However, DMPO-
OOH\textsuperscript{−} is not stable (lifetime ca. 1 min) and will decay to give the much more stable
spin adduct DMPO-OH\textsuperscript{−};
\textsuperscript{45–47} a process which will be even quicker in the elevated
solution temperature of this EPR experiment.\textsuperscript{48} Since it takes a few min to transfer the
sample into the EPR and tune the spectrometer, any DMPO-OOH\textsuperscript{−} present will have
likely decayed to DMPO-OH\textsuperscript{−}.

Considering individual electrolytes, in KNO\textsubscript{3}, very small amounts of DMPO-OH\textsuperscript{−} are
observed in the EPR spectra, suggesting a low concentration of radicals are produced,
via either Equation 5.6 and/or Equation 5.9. In KCl, EPR measurements reveal over
twice the amount of DMPO-OH\textsuperscript{−} compared with KNO\textsubscript{3}. Chloride ions have been shown
to adsorb onto Pt surfaces and promote the generation of H\textsubscript{2}O\textsubscript{2} via the 2 electron ORR
route.\textsuperscript{41–43} Interestingly, whilst the EPR data shows a two times increase in the amount
of DMPO-OH\textsuperscript{−} in KCl than compared to KNO\textsubscript{3}, the sp\textsuperscript{2} carbon bulk etch rate data (Figure
5.5) shows a greater than 1 order of magnitude increase in the etch rate in KCl
compared to KNO\textsubscript{3}. As well as radical species the production of non-radical oxidising
species is also possible. For example, EC oxidation of the chloride ions not only results
in chlorine radical production (Equation 5.10) but also the formation of chlorine gas,
hypochlorous acid or hypochlorite (dependent on solution pH).\textsuperscript{49}

\begin{equation}
\text{Cl}^{-} (\text{aq}) \rightarrow \text{Cl}^{-} (\text{aq}) + e^{-} \quad E^0 = +2.43 \text{ V vs SHE}^{31} \quad (5.10)
\end{equation}

However, their subsequent chemical reactions are also possible chemical routes for
generation of oxidising agents and free radicals. All of these chlorine-based species
can interact with hydroxyl radicals in solution and further oxidise into ClO\textsubscript{2}⋅, ClO\textsubscript{3}− and
ClO\textsubscript{4}− generating a portfolio of species available for etching.\textsuperscript{49} Hypochlorous acid itself
is an oxidising agent (E\textsubscript{0} = +1.63 V vs SHE)\textsuperscript{34} capable of etching sp\textsuperscript{2} bonded carbon,\textsuperscript{50} in
addition to the H\textsubscript{2}O\textsubscript{2}. Based on the H\textsubscript{2}O\textsubscript{2} chemical etch data in Section 5.3.2, and the
fact these species have lower thermodynamic oxidising potentials than H\textsubscript{2}O\textsubscript{2},
production of such species alone is unlikely to be sufficient to explain the observed
etch rates. Due to the methodology selected to look for long-lived radicals, no
evidence of chlorine-based radicals was observed in Figure 5.6. Although, these
radicals, as well as the stable chlorine-based species are still expected to be present during etches.

Hypochlorous acid will react with hydrogen peroxide to produce the singlet oxygen (Equation 5.11).\(^{51}\)

\[
\text{HClO}_{(aq)} + \text{H}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}_{(aq)} + ^1\text{O}_2(g) + \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} \tag{5.11}
\]

Singlet oxygen is extremely reactive thus capable of etching \(\text{sp}^2\) carbon or reacting with water to further produce more \(\text{HO}_2^-\) and \(\text{HO}^-\) radicals (Equation 5.12).

\[
^1\text{O}_2(g) + \text{H}_2\text{O}_{(aq)} \rightarrow \text{HO}_2^-_{(aq)} + \text{HO}^-_{(aq)} \tag{5.12}
\]

The EPR spectra after electrolysis of \(\text{K}_2\text{SO}_4\) has the highest concentration of DMPO-OH\(^-\) for all three electrolytes, with the double integrated intensity being nine times larger than that in the \(\text{KNO}_3\) solution. Sulfate radicals (\(\text{SO}_4^-\)), with a lifetime of \(\mu\text{s}\), are highly oxidising \((E^0= +2.44 \text{ V vs SHE})^31\) and can be generated oxidatively on Pt electrodes in sulfate containing media.\(^{52,53}\) Equation 5.13. In the EPR spectrum, the splitting pattern of DMPO-SO\(_4\)\(^-\) is obscured by that of DMPO-OH\(^-\) when DMPO-OH\(^-\) is present in the majority.\(^{54}\)

\[
\text{SO}_4^{2-}_{(aq)} \rightarrow \text{SO}_4^-_{(aq)} + e^- \quad E^0= +2.44 \text{ V vs SHE}^{53} \tag{5.13}
\]

The highly reactive \(\text{SO}_4^-\) radicals are also able to abstract a hydrogen from water and produce \(\text{HO}^-\) (Equation 5.14).\(^{52}\) Given the high concentrations of sulfate ions and water molecules in the high conductivity solution, Equation 5.10 is thought to be a preferred route for \(\text{HO}^-\) generation, resulting in high concentrations of DMPO-OH\(^-\).

\[
\text{H}_2\text{O}_{(aq)} + \text{SO}_4^-_{(aq)} \rightarrow \text{HO}^-_{(aq)} + \text{SO}_4^{2-}_{(aq)} + \text{H}^+_{(aq)} \tag{5.14}
\]

Once \(\text{SO}_4^-\) and \(\text{HO}^-\) radicals have been produced there are a host of reaction pathways that can occur (Equations 5.15 to 5.18).\(^{38,55}\)

\[
2\text{SO}_4^-_{(aq)} \rightarrow \text{S}_2\text{O}_8^{2-}_{(aq)} \tag{5.15}
\]

\[
\text{HO}^-_{(aq)} + \text{S}_2\text{O}_8^{2-}_{(aq)} \rightarrow \text{HSO}_4^-_{(aq)} + 2\text{SO}_4^-_{(aq)} + \frac{1}{2}\text{O}_2(g) \tag{5.16}
\]
These reaction pathways are referred to as chaining mechanisms and will result in the regeneration of the radicals and generation of more stable oxidising species. This, we believe, is the reason for the appearance of the HO' radicals at timescales much longer than their lifetime and their detection in the system once the electrode potential has been switched off. This behaviour is thought to be the dominant factor behind the significant DMPO-OH' signal in sulfate media. Increased HO' levels should also result in an increased prominence of Equation 5.8 and 5.9, compared to KNO₃ solutions. As with KCl, the generation of non-radical species such as S₂O₈²⁻ (E⁰ = +2.01 V vs SHE), and their subsequent reactions with radicals could also be contributing to etching.

To verify an increased concentration of H₂O₂ in the chloride and sulfate electrolyte, UV-Vis spectroscopy experiments were recorded on the electrolysis solution every min over a six min period (Figure 5.7). Each time point is a separate experiment with fresh solutions used each time.
Figure 5.7: (a) Exemplar UV-Vis spectrum for TiSO₄ dye with 2.5 mM H₂O₂. (b) Calibration curve for H₂O₂ concentrations of 0.75 μM to 2.5 mM in the presence of TiSO₄. (c) Concentration of H₂O₂ produced for each electrolysis time in 250 mM KNO₃ (grey triangle), KCl (pink circle) and K₂SO₄ (blue square) using two Pt electrodes at 30 V per time point.

In Figure 5.7a, an exemplar UV-Vis spectrum has been provided for the detection of H₂O₂ using TiSO₄ showing the peak maximum at λₘₐₓ = 425 nm. A calibration curve
from serial dilution of stock $H_2O_2$ was produced in **Figure 5.7b** giving the equation of line $y = 755.72x + 0.067$ and $R^2 = 0.995$. In **Figure 5.7c**, concentrations of $H_2O_2$ for electrolysis of KNO$_3$ are undetectable within the limits of detection of the UV-Vis experiment. The limit of detection of this method has been determined as the lowest concentration tested (0.75 µM) due to small amounts of remaining titanium anatase particles in solution absorbing at low levels in the baseline. In contrast, for electrolysis of KCl, $H_2O_2$ is clearly present over the entire time span of the experiment in the highest abundance of the three electrolytes tested. This is attributed to the adsorption of chlorides ions on the Pt electrons promoting $H_2O_2$ generation. Finally, in the electrolysis of $K_2SO_4$ solution, $H_2O_2$ could be detected through the experiment demonstrating the chaining mechanism is helping to produce more $H_2O_2$ than compared to KNO$_3$.

### 5.3.5. The effect of concentration and pH in sulfate media

As sulfate containing electrolytes gave rise to the highest bulk etch rates, this electrolyte was chosen for further study. The chaining reactions which are most critical for etching of the sp$^2$ carbon layer are those which increase the number of radicals at the surface of the sp$^2$ carbon layer. Once a sulfate radical, SO$_4^{2-}$, is generated on the Pt electrodes it can react with any solution component; reaction with water results in the generation of HO$^-$ as per Equation 5.14. However, if this happens too far away from the sp$^2$ carbon edge the radical cannot contribute to etching as it will not react with the sp$^2$ carbon during its very short lifetime. In contrast, if HO$^-$ encounters a SO$_4^{2-}$ within its lifetime regeneration of SO$_4^{2-}$ is possible. This chaining can continue until either the SO$_4^{2-}$ or HO$^-$ radical reaches the edge of the sp$^2$ carbon layer and etching can take place.

To test this theory, the effect of sulfate concentration was investigated for concentrations over the range 30 – 250 mM $K_2SO_4$ (**Figure 5.8**). Data for 250 mM KNO$_3$ was also included for comparison and is the data point at 0 mM sulfate, shown in **Figure 5.8a**.
At sulfate concentrations in the range $0 \sim 60$ mM, the etch rate increases linearly (dashed, pink line) with increasing sulfate concentration. This is likely a result of the increased sulfate ion concentration which increases the chances of a HO\textsuperscript{−} encountering SO\textsubscript{4}\textsuperscript{2−} within the distance it can travel during its lifetime. This results in an increased number of chaining events and ultimately results in a higher number of radicals available at the sp\textsuperscript{2} carbon solution interface to etch the sp\textsuperscript{2} carbon material.

As the concentration of SO\textsubscript{4}\textsuperscript{2−} increases, the SO\textsubscript{4}\textsuperscript{2−} – SO\textsubscript{4}\textsuperscript{2−} inter-ion spacing decreases. While the spacing has not decreased to a point where a HO\textsuperscript{−} is guaranteed to encounter a SO\textsubscript{4}\textsuperscript{2−} in its short lifetime, at 60 mM a plateau is still observed (blue line, Figure 5.8a). A likely explanation for this is that as the radical concentration increases, the chances of radical recombination also increase, as shown in Equation 5.8 and 5.15. Hence further increases in SO\textsubscript{4}\textsuperscript{2−} concentration won’t necessarily increase the number of radicals available at the edge of the sp\textsuperscript{2} carbon layer. Note, as the concentration of K\textsubscript{2}SO\textsubscript{4} increases, the conductivity also increases from $7 \sim 42$ mS cm\textsuperscript{−1} across the range, however the plateau region from 60 mM – 250 mM K\textsubscript{2}SO\textsubscript{4} shows no noticeable change in etch rate. This suggests that conductivity has little effect on bulk etch rate in this region.
As the generation of HO’ via SO$_4$’$^-$ shows a pH dependence (Equation 5.14), the effect of pH on etch rate was investigated. Mixtures of K$_2$SO$_4$ and H$_2$SO$_4$ were used to vary solution pH over the pH range 0.8 to 7.1 whilst maintaining the total sulfate concentration at 250 mM (Figure 5.8b). A decrease in pH has the effect of increasing the bulk etch rate and a maximum bulk etch rate of 21.0 mm$^2$ hr$^{-1}$ is achieved at pH 0.8. As shown Figure 5.8a, increasing conductivity again has little effect on the etch rate. The increase in etch rate can therefore be attributed to the increase in proton concentration.

5.4. Conclusions

The impact of EC generation of chemical radical pathways in solution, on increasing the bulk etch rate of implanted thin sp$^2$ carbon layers in single crystal diamond, has been demonstrated. A novel optical etch tracking method was used to monitor etching, via quantification of the colour change associated with removal of the black sp$^2$ carbon layer in the translucent diamond. Electrolyte chemical identity and concentration was found to play a crucial role, with conductive sulfate and chloride solutions showing significantly increased bulk etch rates (an order of magnitude) compared to conductive nitrate solutions and low conductivity boric acid solutions. The highest rate, 42 mm$^2$ hr$^{-1}$, was achieved using sulfate electrolyte in acidic media at elevated temperature. This represents a 40x increase compared to measurements in the industry standard, boric acid solutions of low conductivity using a bipolar arrangement.

Complementary EPR experiments showed the chloride and sulfate electrolytes also produced differing quantities of DMPO-OH’. Boric acid showed no radicals whilst nitrate showed a minimal amount of DMPO-OH’. As the DMPO spin trap was added ca. 30 s after the potential had been switched off, any HO’ (lifetime ≤ μs) produced via electrochemical means should no longer be present. The detection of HO’ demonstrated the existence of electrochemically initiated, solution chemistry radical generation pathways which enabled HO’ to be observed on timescales much longer (> $10^7$) than their lifetime. The chloride and sulfate anions (and their electrochemically
oxidised forms) also contributed to the production of other species e.g. H$_2$O$_2$, which also aided radical production. The existence of these electrochemically initiated solution chemical pathways was also reinforced by the detection of H$_2$O$_2$ which has been postulated to be the main species and involved in the first step in these routes.

The significant reduction in time during the bulk etch region of the process improves the viability of the implantation and non-contact electrochemical etch as a process to produce thin diamond membranes. However, there is still scope for advancement.

5.5. References


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Chapter 5: The Critical Role of Radicals in Non-Contact Electrochemical Etching of sp² Carbon


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Chapter 6: Conclusions and Future Work

In Chapter 3, the electron paramagnetic resonance (EPR) spectrometer configuration was optimised for working in water (a high dielectric solvent) which is necessary for the electrochemical (EC) generation and subsequent detection of HO\(^{\cdot}\). The optimum resonator and sample holder (based on the criteria of best resolution and ease of use) was determined to be the hs resonator and 1 mm inner diameter quartz tube. The flat cell and star-bore tubing did show they could potentially improve the resolution further however, these sample holders were problematic when being manually filled. Going forward, future work developing a flow system through the EPR resonator could remove complications associated with the ease of using with the flat cell and star-bore tubing. The development of this type of flow cell could enhance the resolution possible for this system.

5,5-dimethyl-1-pyrroline N-oxide (DMPO) is often the spin trap of choice for the spin trapping of HO\(^{\cdot}\) to produce DMPO-OH\(^{\cdot}\). Also in Chapter 3, initial EC generation of DMPO-OH\(^{\cdot}\) experiments demonstrated DMPO-OH\(^{\cdot}\)’s short lifetime and resultantly, the EPR parameters were adapted to make measurements in a quick time frame (whilst remaining quantitative) by reducing the time per scan from 10 min to 30 sec. The presence of H\(_2\)O\(_2\) has previously been reported to drastically decrease the lifetime of DMPO-OH\(^{\cdot}\) therefore, in theory the use of a two-compartment where the counter electrode (CE) is isolated behind a porous frit (pore size ca. 10 μm) should help to improve the lifetime of DMPO-OH\(^{\cdot}\). In theory, this will keep unwanted by-products produced at the CE away from the spin trapping reaction at the working electrode (WE). The results showed a very minimal increase in DMPO-OH\(^{\cdot}\) signal when the two-compartment cell was used thus, no real benefit was seen to the two-compartment cell’s use, so it was not utilised for further work. In the future, the use of a cation exchange Nafion™ membrane could boost the DMPO-OH\(^{\cdot}\) signal by better segregation of the CE products. Additionally, the role of oxygen in the EC generation of DMPO-OH\(^{\cdot}\)
was investigated. The removal of oxygen from solution during the experiment showed an enhancement in signal; this could be due to improved electrode efficiency, improvement in stability of DMPO-OH˙ or due to the removal of paramagnetic oxygen which can cause line broadening. However, total exclusion of oxygen is very difficult as oxygen is produced at the WE from water oxidation. Furthermore, in electrochemical advance oxidative processes (EAOPs), deoxygenated conditions are not commonly employed so for the best comparison oxygenated conditions have still been used. Finally in Chapter 3, to determine whether the formation of DMPO-OH˙ via the Forrester-Hepburn mechanism under the conditions used in this thesis was possible, the hydrolysis of DMPO over time was monitored. In the 40 hrs window, tested no artefactual DMPO-OH˙ was observed consequently, the Forrester-Hepburn mechanism can be eliminated.

In Chapter 4, DMPO was shown to be electrochemically oxidised on boron doped diamond (BDD) in acidic aqueous media (i.e. 0.10 M HClO₄) from +1.40 V vs SCE upwards reaching a peak maximum at +1.90 vs SCE. Furthermore, the EC oxidation of DMPO gave rise to fouling effects and the formation of a film at the electrode surface. Cleaning steps were employed to minimise fouling effects but, these effects could not be fully removed during the 5 min generation times for EC-EPR experiments in a DMPO containing solution. EC-EPR experiments performed at low potentials (before the generation of HO˙) in a DMPO containing solution revealed that DMPO-OH˙ is formed via inverted spin trapping as a direct result of the EC oxidation of DMPO. This provokes serious worries over the validity of using DMPO in aqueous environments in EC-EPR experiments to confirm the presence of HO˙. In some fields the confirmation of free radicals (and that the spin adduct is not formed via inverted spin trapping or the Forrester-Hepburn mechanism) in solution is achieved by the addition of a radical scavenger to the spin trapping experiment. In Chapter 4, it was demonstrated that the addition of ethanol to EC-EPR experiments is also fraught with issues; this is because ethanol is also electrochemically oxidised. Though by careful observation of how the product distribution changes as a function of potential (from a potential of DMPO oxidation only to a potential for free radical production) with ethanol present in
solution can reveal where EC generation of HO’ occurs. The blend of DMPO-OH’ and DMPO-CH(OH)CH₃’ observed due to EC oxidation of DMPO and ethanol became predominantly DMPO-OH’ from +2.26 V vs SCE due to electrochemically generation of HO’.

When performing EC-EPR experiments, determining what applied potential is being used is a critical factor for experimental design. Under potentials of +1.40 V vs SCE, DMPO in acidic aqueous environments can be employed without concern. However, the results reported in Chapter 4 shows that if HO’ is being electrochemically generated at a potential near or exceeding the onset of DMPO oxidation, then it is highly probable that the DMPO-OH’ signal will contain mixed contributions from DMPO oxidation and spin trapped HO’. This would lead to inaccurate reporting of HO’ concentration or could result in false identification of HO’. For many EAOPs and electrosynthesis experiments, a constant current approach is exploited thus being able to relate the constant current to the applied potential is advantageous. As the applied potential increases further away from the onset of DMPO oxidation, DMPO oxidation is likely to play less of a role. Though, this was not verified in this thesis due to the overwhelming DMPO fouling/consumption of DMPO-OH’ issues. Furthermore, as the potential is increased the DMPO-OH’ signal declines beyond +1.90 V vs SCE which is due the formation of a fouling layer blocking the electrode and/or further oxidation of DMPO-OH’ to an EPR silent species. The drop off in DMPO-OH’ seen in this work puts doubt over whether DMPO can be used as an effective spin trap at the higher potentials used in EAOPs. In the future, fouling effects and the consumption of DMPO-OH’ could be minimised by the development of different cell geometries such as a flow cell. This would remove the EC products away from the electrode surface before they can undergo further EC reactions.

In Chapter 5, the knowledge gained from the previous chapters was applied to studying a novel EC etch method to produce diamond membranes. The benefit of initiating chemical pathways in solution from EC generation on increasing the bulk etch rate of thin sp² carbon layer implanted in single crystal diamond was exhibited. The chemical identity as well as the concentration of supporting electrolyte used was
found to play a crucial role in enhancing the etch rate. In particular, sulfate and chloride solutions showed a significant increase in bulk etch rates (by an order of magnitude) compared to nitrate and boric acid solutions. The highest etch rate (42 mm² hr⁻¹) was achieved using sulfate electrolyte under acidic conditions at elevated temperature. This etch rate represents an improvement of 40x compared to measurements in the industry standard conditions which uses low conductivity boric acid solutions in a bipolar arrangement.

Furthermore in Chapter 5, complementary EPR experiments showed that all three electrolytes (nitrate, chloride and sulfate) produced differing quantities of DMPO-OH⁻ at 30 V for 15 min whereas, boric acid showed no evidence of free radicals under the same conditions. As the DMPO spin trap was added after the potential had been turned off, any HO⁻ produced via EC means would no longer be present due to their lifetime of ≤ μs. This spin trapping method also alleviated any EC oxidation of DMPO concerns. The detection of HO⁻ revealed the existence of electrochemically initiated pathways for solution radical regeneration mechanisms which facilitated HO⁻ to be seen on timescales much longer (> 10⁷) than their lifetime. H₂O₂ production was monitored and shown to be produced in chloride and sulfate but not in nitrate media. The detection of H₂O₂ also reinforced the solution radical chemistry reactions as H₂O₂ has been postulated to be the predominant species involved in the first step of these routes.