**Boron-doped Diamond Electrocatalyst for Enhanced Anodic H2O2 Production**

Sotirios Mavrikis†‡, Maximilian Göltz§, Stefan Rosiwal§, Ling Wang‡, Carlos Ponce de León†‡\*

†Electrochemical Engineering Laboratory, Faculty of Engineering and Physical Sciences, University of Southampton SO17 1BJ, United Kingdom

‡National Centre for Advanced Tribology at Southampton (nCATS), Faculty of Engineering and Physical Sciences, University of Southampton SO17 1BJ, United Kingdom

§Materials Science and Engineering for Metals, Faculty of Engineering, Friedrich-Alexander University of Erlangen-Nürnberg, D-91058, Germany

AUTHOR INFORMATION

Corresponding Author

\*Email: [capla@soton.ac.uk](mailto:capla@soton.ac.uk) (Carlos Ponce de León)

ABSTRACT

Electrochemical production of hydrogen peroxide (H2O2) constitutes a cost-effective and alternative method to the complex and energy-intensive anthraquinone oxidation process. The two-electron water oxidation reaction (WOR) pathway, whilst unconventional, is an attractive option for H2O2 generation as it can be combined with suitable reduction reactions to effectuate simultaneous electrosynthesis of valuable chemicals at a large scale. In this work we demonstrate that a carbon-based catalyst, boron-doped diamond (BDD), achieves an H2O2 concentration and production rate of 29.0 mmol dm-3 and 19.7 µmol min-1 cm-2, respectively, illustrating the capability of BDD as a suitable electrocatalyst for H2O2 formation from water.

**Keywords**: boron-doped diamond; electrocatalyst; electrosynthesis; hydrogen peroxide; water oxidation

**TOC GRAPHIC**

A close up of a logo

Description automatically generated

Hydrogen peroxide, a powerful oxidising and bleaching agent, is amongst the world’s most produced chemicals, with a wide range of industrial applications, including paper and textile bleaching, chemical synthesis and wastewater treatment. The current standard for manufacturing H2O2 is the anthraquinone autoxidation process, which is characterised by its energy intensity due to low conversion efficiencies, and its rife waste stream generation owing to the formation of non-reactive by-products.1 A more sustainable method for on-site production of H2O2 locally is therefore highly desirable, and electrochemistry may offer one such alternative route. Cathodic electro-generation of H2O2 via the oxygen reduction reaction (ORR) is a well-established process2, with researchers attaining impressive current efficiencies and H2O2 production rates utilising carbonaceous materials like activated carbon3, hierarchically porous carbon4, carbon nanotubes5, N-doped carbon6,7 and cobalt-porphyrin carbon electrodes.8 Far fewer studies have been carried out on the unorthodox two-electron water oxidation reaction (WOR), where H2O2 is electrocatalytically synthesized from H2O directly at the anode.9 This approach remains a relatively unexplored field of electrochemistry, primarily due to reservations concerning the thermodynamic feasibility of the reaction, yet is highly desirable for the efficient and integrated electro-production of valuable chemicals via redox reactions, at an industrial scale.

The anodic, WOR toward H2O2 can be described by **Equation 1**:

|  |  |  |
| --- | --- | --- |
| **2H2O (l) ⇌ H2O2 (aq) + 2H+(aq) + 2*e-*** | ***E***° **= 1.760 V *vs.* SHE** | **(1)** |

The three primary reactions that compete with the WOR are the relatively effortless hydrogen peroxide oxidation reaction (**Equation 2**), the thermodynamically favourable four-electron water oxidation reaction that results in oxygen evolution (**Equation 3**) and the spontaneous decomposition of H2O2 due to its chemical instability (**Equation 4**).10,11

|  |  |  |
| --- | --- | --- |
| **H2O2 (aq) ⇌ O2 (g) + 2H+(aq) + 2*e-*** | ***E***° **= 0.670 V *vs.* SHE** | **(2)** |
| **2H2O (l) ⇌ O2 (g) + 4H+(aq) + 4*e-*** | ***E***° **= 1.23 V *vs.* SHE** | **(3)** |
| **2H2O2 (aq) ⇌ O2 (g) + 2H2O (l)** |  | **(4)** |

Several recent studies have demonstrated the capability of various metal oxidesto catalyse the two-electron WOR. These materials, while demonstrating impressive Faradaic efficiencies (70 %, 76 % and 81 % for BiVO4, CaSnO3 and ZnO, respectively)11–13suffer from low current densities (0.2 - 1.0 mA cm-2 for MnOx)14,15 and H2O2 production rates (1.0 µmol min-1 cm-2 and 1.5 µmol min-1 cm-2 for TiO2 and SnO2, respectively),11 deeming their large-scale implementation questionable.

We address these challenges by demonstrating the electrocatalytic capability of a synthetic BDD film, coated on a titanium substrate, to promote H2O2 generation via water oxidation. Electrolysis was performed at constant potentials to quantify the concentration, production rate and efficiency of the BDD electrocatalyst. The applied potential range for these electrochemical experiments is selected following analysis of the cyclic voltammogram depicted in **Figure S1**, in the Supporting Information.

The capability of the BDD electrode to electrochemically catalyse the WOR toward H2O2 is evaluated by measuring the concentration of H2O2 yielded as a function of the electrode potential applied (**Figure 1a**). At the lowest potential applied (2.67 V *vs.* RHE), 0.54 mmol dm-3 of H2O2 is detected. The applied electrode potential is increased at increments of 0.1 V, and it was observed that the concentration of H2O2 rises correspondingly. At 3.47 V *vs.* RHE, a value of 29.0 mmol dm-3 of H2O2 is attained, the highest recorded concentration of H2O2 to date produced via water oxidation, approximately four times larger than the reported concentration of 7.5 mmol dm-3 of H2O2 accumulated using Al2O3/BiVO4.16



**Figure 1**.Results from electrochemical experiments at a constant potential range of 2.67 – 3.47 V *vs.* RHE for 300 s, in 25 cm3 of 2.0 mol dm-3 KHCO3 using a 7.4 cm2 BDD-Ti working electrode. **(a)** H2O2 concentration expressed in mmol dm-3 *vs.* the applied electrode potential. **(b)** *FE* for H2O2 production *vs.* the applied electrode potential. **(c)** Kinetic curve of H2O2 concentration over time at a constant potential of 3.17 V *vs.* RHE for 7200 s in 1.0 mol dm-3 KHCO3 (red line) and 2.0 mol dm-3 KHCO3 (blue line).

The selectivity of BDD towards H2O2 synthesis was examined by measuring the Faradaic efficiency (*FE*) (**Figure 1b**) of the oxidation process, using **Equation 5** and **Equation 6**:

|  |  |
| --- | --- |
| ***FE*** **(%): [*n*H2O2 experimental (mol) / *n*H2O2 theoretical (mol)] × 100** | **(5)** |

*n*H2O2 theoretical (mol) is quantified by Faraday’s Law:

|  |  |
| --- | --- |
| ***Q* (C) *= n* (mol) *× z*e *× F* (C mol-1)** | **(6)** |

Where *Q, n, z*e and *F* are the charge passed, the number of moles, the interchanged electrons and the Faraday constant, respectively.

At 2.67 V *vs.* RHE the *FE* is approximately 10.5 % and a gradual increase is observed at a more positive electrode potential, with the *FE* reaching a peak value of 28 % at 3.17 V *vs.* RHE, after which a gradual decrease is noted. The observed trend of the *FE* reaching an optimum value at a specific electrode potential and current, before steadily decreasing suggests that there is a particular potential range where the surface of the BDD catalyst favours H2O2 production slightly more compared to the evolution of oxygen **(Equation 3)**.

The BDD electrode is subsequently subjected to electrolysis at a constant potential of 3.17 V *vs.* RHE (the applied electrode potential where the maximum *FE* of 28% was recorded) for a period of 7200 s to examine the concentration of H2O2 over time. The concentration of H2O2 was initially measured every 180 s until the 900 second mark after which the concentration was then measured every 900 s (**Figure 1c**). It is observed that the concentration of H2O2 rapidly rises to 23.6 mmol dm-3 within the first 1000 s of the experiment (blue line), before stabilising and reaching a plateau until around 4000 s. During that time the concentration of H2O2 reaches a peak value of 24.7 mmol dm-3. Subsequently, a gradual decrease is observed and, at the end of the experiment, the concentration of H2O2 is 17.5 mmol dm-3. The undesirable decline of the H2O2 concentration can be attributed to: i) a decrease in the electrolyte’s conductivity due to the depletion of available K+ ions in the solution, ii) a water shift toward the catholyte via cation diffusion through the Nafion membrane, iii) further oxidation of accumulated H2O2 near the surface of the BDD electrode and in the bulk solution, and iv) spontaneous decomposition of H2O2 (**Equation 4**).

The observed decrease in this study contrasts with the trend reported by Michaud et al., who attained a constant H2O2 concentration for over 18,000 s, using BDD films coated on silicon wafers in a solution of 1.0 mol dm-3 perchloric acid.17 It should be noted however that the H2O2 concentration achieved in this work (24.7 mmol dm-3 at a total current density of 88.2 mA cm-2, **Figure S2**) is approximately 30 times larger than that accumulated by Michaud et al. (0.8 mmol dm-3 at a total current density of 160 mA cm-2), which can account for the noted decomposition trend.

An identical set of experiments was also carried out, at the same potential, using a lower concentration of the supporting electrolyte, 1.0 mol dm-3 of KHCO3 (**Figure 1c**, red line). The trend observed using the lower concentration of KHCO3 is similar to that of the higher concentration of supporting electrolyte, with H2O2 rapidly being produced within the first 1000 s of the experiment, reaching a peak concentration of 10.8 mmol dm-3 before gradually declining to 7.6 mmol dm-3 at the end of the experiment.

The amount of H2O2 accumulated using 2.0 mol dm-3 of KHCO3 is, on average, 2.4 times larger than the concentration of H2O2 measured when 1.0 mol dm-3 of electrolyte is used. This highlights the role of the hydrogen-carbonate ion in promoting continuous H2O2 synthesis while also curtailing H2O2 decomposition during electrolysis, as initially reported by Fuku and Sayama.18

An important parameter for scaling up the two-electron WOR process is the production rate of H2O2 (*ν*H2O2), defined as the number of moles of H2O2 (µmol) generated, per the duration of electrolysis (min), per geometric surface area of the working electrode (cm2). The production rate of H2O2 on BDD is compared with other studies reported in literature11,12 on WOR towards H2O2 (**Figure 2a**). BDD’s rate of H2O2 production (black line) rises exponentially as the electrode potential is increased, and at 3.07 V *vs.* RHE, the *ν*H2O2 is measured at 7.5 µmol min-1 cm-2, higher than the respective H2O2 production rate of the metal oxide catalystsreported. Whereas the production rate for metal oxides reaches a peak at a certain potential and gradually decreases, BDD’s H2O2 production rate continues to grow at more positive electrode potentials. At 3.5 V *vs.* RHE, a value of 19.7 µmol min-1 cm-2 is reached, approximately four times higher than the production rate of BiVO4 (red line), as a result of BDD’s exceptional stability and the high current density attained (**Figure S3**). This trend demonstrates BDD’s noteworthy capability to produce H2O2 via the two-electron WOR pathway and establishes BDD as a competent carbon-based alternative to metal oxide catalysts.

A close up of a map

Description automatically generated

**Figure 2**.Comparison of the results achieved in this work to metal oxide catalysts. **(a)** production rate (µmol min-1 cm-2) of BDD and reported metal oxides *vs.* the applied electrode potential converted to RHE. **(b)** Peak *FE* for H2O2 synthesis using BDD achieved in this work compared to maximum reported *FE*s for metal oxides. Metal oxide data used for Fig. 3a kindly provided by the authors of (11,12).

The efficiency of BDD to catalyse the water oxidation reaction toward H2O2 is evaluated by comparing the peak *FE* achieved in this work to the maximum efficiencies of thereported metal oxide catalysts (**Figure 2b**). Boron-doped diamond’s peak *FE* of 28 % is well below that of calcium tin oxide (CaSnO3) or BiVO4 at 76 % and 70 %, respectively, however it is worth noting that the current densities attained in this study (up to 295 mA cm-2 at 3.47 V *vs.* RHE) are at least an order of magnitude larger than the reported current densities reached using the metal oxide catalysts. A more positive electrode potential will result in rapid oxygen evolution, competing with H2O2 production and can also gradually increase the electrolyte’s temperature, leading to thermal decomposition of accumulated H2O2, which could account for the diminished *FE* measured using the BDD catalyst. Improvements to the electrochemical cell used and modification of BDD’s selectivity toward H2O2, by tuning the degree of boron doping are possible options for enhancing the overall efficiency of the reaction.

In this work, we studied the catalytic ability of synthetic boron-doped diamond films to promote H2O2 formation via the two-electron WOR pathway. Conducted in a two-compartment, three-electrode batch cell, we have demonstrated that BDD is a promising catalyst for anodic H2O2 electrosynthesis, presenting reasonable selectivity alongside excellent stability and rate of reaction.

* Applying a constant electrode potential within the range of 2.67 – 3.47 V *vs.* RHE for 300 s, we found that BDD generated 29.0 mmol dm-3 of H2O2 at 3.47 V, the highest reported value to date for the WOR, exclusively, in neutral media.
* Electrolysis conducted at 3.17 V *vs.* RHE, for 7,200 s, using different concentrations of KHCO3, showed that the amount of H2O2 synthesized in 2.0 mol dm-3 of KHCO3, was on average 2.4 times larger than the amount produced in 1.0 mol dm-3 of KHCO3. This accentuates the importance of hydrogen-carbonate in stimulating H2O2 synthesis and minimising H2O2 decomposition.
* When comparing BDD’s catalytic performance to state-of-the-art materials, we acquire an H2O2 production rate of 19.7 µmol min-1 cm-2, amongst the highest recorded values for the two-electron WOR, almost four times larger than the rate achieved using BiVO4. The *FE* of the reaction using a BDD working electrode reaches a peak value of 28 % at 3.17 V *vs.* RHE, yet this is accomplished at total current densities of at least 120 mA cm-2.

These results indicate that diamond-carbon structures like BDD are stellar catalyst options for the two-electron WOR toward H2O2. Further optimisation of the electrochemical cell used and tailoring of the boron content of BDD have been identified as future steps to improve the selectivity of the catalyst and boost the progression of large-scale electrosynthesis of H2O2 using just water.

**Experimental Methods**

Electrochemical experiments were carried out in a two-compartment, three-electrode and low-volume electrochemical cell, where a Nafion 115 proton-exchange membrane (Fuel Cell Store) separated the anodic and cathodic compartments (**Figure 3**) to prevent H2O2 degradation by exposure to the hydrogen evolution reaction (HER) occurring in the CE compartment (**Equation 7**).



**Figure 3**. Low-volume, two-compartment and three-electrode electrochemical cell. **(1)** BDD/Ti working electrode (WE), surface area, A = 7.4 cm2; **(2)** Pt-mesh counter electrode (CE), surface area, A = 25 cm2; **(3)** silver/silver chloride reference electrode (saturated KCl); **(4)** Nafion115 cation exchange membrane, pre-treated in 1 mol dm-3 H2SO4; **(5)** 2.0 mol dm-3 aqueous KHCO3 electrolyte, pH 8; **(6)** borosilicate-coated magnetic stirring bar; **(7)** WE compartment, and **(8)** CE compartment.

|  |  |  |  |
| --- | --- | --- | --- |
| |  | | --- | | **2H+ (aq) + 2*e-* → H2 (g)** | | ***E***° **= 0.0 V *vs.* SHE** | **(7)** |

The anodic compartment contained a BDD working electrode (A = 7.4 cm2) and a silver/silver chloride (≥ 99.0 %, saturated KCl) reference electrode (Bio-Logic Science Instruments Ltd), while a Pt mesh (A = 25 cm2) was used as a counter electrode in the cathodic compartment. An aqueous solution of 2.0 mol dm-3 KHCO3 (>99.5 %, pH 8, V = 25 cm3 per compartment), was used as an electrolyte, and the anolyte was stirred at 500 rpm using a borosilicate-coated magnetic stirring bar. The working electrode was subjected to a range of different potentials (Metrohm Autolab PGSTAT302N, Booster20A), to investigate the catalyst’s performance while the current was measured as a function of time. The concentration of H2O2 produced was quantified using Quantofix Peroxide test strips and a Quantofix Relax reflection photometer. Samples containing H2O2 were titrated with potassium permanganate (>99.9 %, Fischer Scientific) and sulfuric acid (99.999% H2SO4) to further corroborate the accuracy of the results attained, based on the following reaction (**Equation 8**):

|  |  |
| --- | --- |
| **2MnO4- (aq) + 6H+(aq) + 5H2O2 (aq) → 2Mn2+(aq) + 8H2O (l) + 5O2 (g)** | **(8)** |

The boron-doped diamond electrode used in this study was synthesised by deposition of BDD films on a titanium substrate via hot-filament chemical-vapour-deposition (HF-CVD). The coating process and characterisation of the BDD coating are depicted in **Figure S4** in the Supporting Information.

ASSOCIATED CONTENT

**Supporting Information**

Supporting Information is available free of charge on the ACS Publications website. Contents include additional details on the boron-doped diamond electrode used and data from cyclic voltammograms, and total and partial current densities for the WOR toward H2O2.

AUTHOR INFORMATION

\*Email: [capla@soton.ac.uk](mailto:capla@soton.ac.uk) (Carlos Ponce de León)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The University of Southampton is part of the CO2-based electrosynthesis of ethylene oxide (CO2EXIDE) project consortium, which receives funding from the European Union’s Horizon 2020 research and innovation programme in co-operation with the sustainable process industry through resource and energy efficiency (SPIRE) initiative under grant agreement no. 768789.

The development of the boron-doped diamond electrodes was carried out at the Friedrich-Alexander University of Erlangen-Nürnberg with the aid of the Bayerische Forschungsstiftung.

The authors would like to acknowledge Samuel C. Perry, from the University of Southampton, and Luciana Vieira and Dhananjai Pangotra, from Fraunhofer IGB, for their advice and comments on the manuscript and Moritz Wegener from Schaeffler Technologies AG for the financial support.

REFERENCES

(1) Campos-Martin, J. M.; Blanco-Brieva, G.; Fierro, J. L. G. Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process. *Angew. Chemie - Int. Ed.* **2006**, *45* (42), 6962–6984. https://doi.org/10.1002/anie.200503779.

(2) Otsuka, K.; Yamanaka, I. One Step Synthesis of Hydrogen Peroxide through Fuel Cell Reaction. *Electrochim. Acta* **1990**, *35* (2), 319–322. https://doi.org/10.1016/0013-4686(90)87004-L.

(3) Yamanaka, I.; Hashimoto, T.; Ichihashi, R.; Otsuka, K. Direct Synthesis of H2O2 Acid Solutions on Carbon Cathode Prepared from Activated Carbon and Vapor-Growing-Carbon-Fiber by a H2/O2 Fuel Cell. *Electrochim. Acta* **2008**, *53* (14), 4824–4832. https://doi.org/10.1016/J.ELECTACTA.2008.02.009.

(4) Liu, Y.; Quan, X.; Fan, X.; Wang, H.; Chen, S. High-Yield Electrosynthesis of Hydrogen Peroxide from Oxygen Reduction by Hierarchically Porous Carbon. *Angew. Chemie - Int. Ed.* **2015**, *54* (23), 6837–6841. https://doi.org/10.1002/anie.201502396.

(5) Lu, Z.; Chen, G.; Siahrostami, S.; Chen, Z.; Liu, K.; Xie, J.; Liao, L.; Wu, T.; Lin, D.; Liu, Y.; Jaramillo, T.F.; Nørskov, J.K.; Cui, Y. High-Efficiency Oxygen Reduction to Hydrogen Peroxide Catalysed by Oxidized Carbon Materials. *Nat. Catal.* **2018**, *1* (2), 156–162. https://doi.org/10.1038/s41929-017-0017-x.

(6) Fellinger, T.-P.; Hasché, F.; Strasser, P.; Antonietti, M. Mesoporous Nitrogen-Doped Carbon for the Electrocatalytic Synthesis of Hydrogen Peroxide. *J. Am. Chem. Soc.* **2012**, *134* (9), 4072–4075. https://doi.org/10.1021/ja300038p.

(7) Park, J.; Nabae, Y.; Hayakawa, T.; Kakimoto, M. Highly Selective Two-Electron Oxygen Reduction Catalyzed by Mesoporous Nitrogen-Doped Carbon. *ACS Catal.* **2014**, *4* (10), 3749–3754. https://doi.org/10.1021/cs5008206.

(8) Yamanaka, I.; Ichihashi, R.; Iwasaki, T.; Nishimura, N.; Murayama, T.; Ueda, W.; Takenaka, S. Electrocatalysis of Heat-Treated Cobalt-Porphyrin/Carbon for Hydrogen Peroxide Formation. *Electrochim. Acta* **2013**, *108*, 321–329. https://doi.org/10.1016/J.ELECTACTA.2013.06.072.

(9) Ando, Y.; Tanaka, T. Proposal for a New System for Simultaneous Production of Hydrogen and Hydrogen Peroxide by Water Electrolysis. *Int. J. Hydrogen Energy* **2004**, *29* (13), 1349–1354. https://doi.org/10.1016/j.ijhydene.2004.02.001.

(10) Perry, S. C.; Pangotra, D.; Vieira, L.; Csepei, L. I.; Sieber, V.; Wang, L.; Ponce de León, C.; Walsh, F. C. Electrochemical Synthesis of Hydrogen Peroxide from Water and Oxygen. *Nat. Rev. Chem.* **2019**, *3* (7), 442–458. https://doi.org/10.1038/s41570-019-0110-6.

(11) Shi, X.; Siahrostami, S.; Li, G. L.; Zhang, Y.; Chakthranont, P.; Studt, F.; Jaramillo, T. F.; Zheng, X.; Nørskov, J. K. Understanding Activity Trends in Electrochemical Water Oxidation to Form Hydrogen Peroxide. *Nat. Commun.* **2017**, *8* (1). https://doi.org/10.1038/s41467-017-00585-6.

(12) Park, S. Y.; Abroshan, H.; Shi, X.; Jung, H. S.; Siahrostami, S.; Zheng, X. CaSnO3 : An Electrocatalyst for Two-Electron Water Oxidation Reaction to Form H2O2. *ACS Energy Lett.* **2019**, *4* (1), 352–357. https://doi.org/10.1021/acsenergylett.8b02303.

(13) Kelly, S. R.; Shi, X.; Back, S.; Vallez, L.; Park, S. Y.; Siahrostami, S.; Zheng, X.; Nørskov, J. K. ZnO As an Active and Selective Catalyst for Electrochemical Water Oxidation to Hydrogen Peroxide. *ACS Catal.* **2019**, *9* (5), 4593–4599. https://doi.org/10.1021/acscatal.8b04873.

(14) Izgorodin, A.; Izgorodina, E.; MacFarlane, D. R. Low Overpotential Water Oxidation to Hydrogen Peroxide on a MnOx Catalyst. *Energy Environ. Sci.* **2012**, *5* (11), 9496–9501. https://doi.org/10.1039/c2ee21832a.

(15) McDonnell-Worth, C.; MacFarlane, D. R. Ion Effects in Water Oxidation to Hydrogen Peroxide. *RSC Adv.* **2014**, *4* (58), 30551–30557. https://doi.org/10.1039/c4ra05296j.

(16) Miyase, Y.; Iguchi, S.; Miseki, Y.; Gunji, T.; Sayama, K. Electrochemical H2O2 Production and Accumulation from H2O by Composite Effect of Al2O3 and BiVO4 . *J. Electrochem. Soc.* **2019**, *166* (13), H644–H649. https://doi.org/10.1149/2.0561913jes.

(17) Michaud, P.-A.; Panizza, M.; Ouattara, L.; Diaco, T.; Foti, G.; Comninellis, C. Electrochemical Oxidation of Water on Synthetic Boron-Doped Diamond Thin Film Anodes. *J. Appl. Electrochem.* **2003**, *33* (2), 151–154. https://doi.org/10.1023/A:1024084924058.

(18) Fuku, K.; Sayama, K. Efficient Oxidative Hydrogen Peroxide Production and Accumulation in Photoelectrochemical Water Splitting Using a Tungsten Trioxide/Bismuth Vanadate Photoanode. *Chem. Commun.* **2016**, *52* (31), 5406–5409. https://doi.org/10.1039/c6cc01605g.