Diamond Electrode Facilitated Electrosynthesis of Water and Wastewater Treatment Oxidants

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ABSTRACT

While diamond electrodes have been commonly used to generate ˙OH to treat a variety of persistent water and wastewater micropollutants, mass transfer limitations and the non-selective, short-lived nature of the ˙OH restrict the degradation to the solution at, or near, the electrode surface. However, diamond electrodes can generate oxidizing species that facilitate micropollutant degradation in the bulk water solution. These include persulfate, sulfate radicals, peroxodiphosphate, ferrate, permanganate, reactive chlorine species, hydrogen peroxide, and ozone, which have been reported during electrochemical treatment of water with diamond electrodes. Although still restricted to specialized applications, recent studies, summarized in this review, have proven the electrogeneration of these additional oxidant species to be effective. They have shown the adaptability and potential of diamond electrode-based water treatment to mitigate the presence of micropollutants in water.

Keywords: boron-doped diamond; water; wastewater; electrosynthesis; oxidant; oxidation

Introduction

Electrochemical technologies present a promising alternative to conventional water and wastewater treatment processes for niche applications, such as small, remote, and decentralised systems. Their attractiveness towards these applications is partly due to their ability to eliminate the chemical supply chain associated with conventional treatment processes, whereby treatment chemicals are electrochemically generated on-site and on-demand. Two electrochemical processes have received much research attention: electro-oxidation (EO) and electro-reduction (ER). One of the most promising and widely investigated electrode materials for EO applications is boron-doped diamond (BDD), which has been shown to effectively treat several common and recalcitrant raw water and wastewater pollutants [1–3]. Direct ER at the cathode, including with the use of BDD, is also a promising water treatment process for the abatement of various common pollutants, such as halogenated compounds like per- and polyfluoroalkyl substances [4].

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BDD EO can occur by various mechanisms, including direct oxidation at the electrode surface and through the generation of reactive oxygen species (ROS), most notably hydroxyl radicals ($^\bullet$OH) [5,6]. $^\bullet$OH oxidation has been observed to be the primary mechanism for pollutant degradation during BDD EO, particularly for the most common water and wastewater organic micropollutants [1–3]. Although $^\bullet$OH is highly effective at pollutant degradation, it is a high reduction potential oxidant but non-selective in terms of reactivity. Thus, electrochemically generated hydroxyl radicals are often limited to reactions occurring on the electrode surface or within the electrical double layer. Furthermore, EO and ER are often mass transport limited, which limits electrochemical treatment exclusively to the electrode surface. However, BDD electrodes can be used either for EO or ER for generation of secondary chemical oxidants for downstream oxidation or disinfection during transport in water distribution systems [7,8]. Given these prospects, many research groups are exploring a wide variety of applications employing diamond electrodes for anodic and cathodic electrochemical water or wastewater treatment, for the efficient generation of alternative high reduction potential oxidants that include persulfate, sulfate radical, peroxodiphosphate, ferrate, permanganate, reactive chlorine species, hydrogen peroxide, and ozone.

Anodic Electrosynthesis Processes

Synthetic diamond electrodes have been used for the generation of alternative oxidants from bromide [9], nitrate, carbonate [10–17], phosphate [9,18,19], sulphate [20–22] and chloride [9,14,23–34]. In most instances, the generation of these oxidants is a by-product due to the parasitic side reactions involving electrolyte species during a water/wastewater EO process. However, the targeted electrosynthesis of oxidant species during EO is being explored to increase pollutant transformation at the electrode surface via direct- and $^\bullet$OH-mediated oxidation and in the bulk-phase water. In particular, oxidants such as persulfate ($S_2O_8^{2-}$, E^0=+1.96 V_{SHE}) [35], sulfate radical anion ($SO_4^{\bullet-}$, E^0=+2.44 V_{SHE}) [36], peroxodiphosphate ($P_2O_8^{4-}$, E^0=+2.07 V_{SHE}) [37], ferrate (FeO_4^{2-}, E^0=+2.2 V_{SHE}) [38], permanganate (MnO_4^-, E^0=+1.51 V_{SHE}) [39], and reactive chlorine species (RCS) [40,41] during EO on BDD have been reported to increase micropollutant degradation rates [42].

Research has been focused on the generation of phosphate and sulphate radical anions since the parent ions are common constituents in water and wastewater. The BDD electrosynthesis of peroxodiphosphate, $P_2O_8^{4-}$, has been studied as functions of applied potential, current density, pH, and temperature [18,43]. Sánchez *et al.* electrochemically synthesized peroxodiphosphate under optimized conditions using a thin diamond layer (1.05 μm), high boron content (8000 ppm), with a high sp^3/sp^2 (diamond/graphite) carbon ratio of 80:1exhibited both direct electron transfer and $^\bullet$OH-mediated oxidation at the BDD surface [37]. Similar factors have been explored during the electrosynthesis of persulfate ($S_2O_8^{2-}$) and sulfate radicals ($SO_4^{\bullet-}$) [36]. For example, Martínez-Huitle *et al.* observed that lower sp^3/sp^2 ratios favored the synthesis of

$S_2O_8^{2-}$ due to the increased adsorption sites on graphite for sulfate, whereby $SO_4^{•-}$ is formed and reacts (with other adsorbed $SO_4^{•-}$) to form $S_2O_8^{2-}$ [44]. The role of $^•OH$ on sp^3 sites in the oxidation of $SO_4^{•-}$ to $S_2O_8^{2-}$ has also been noted [35].

The electrochemical generation of RCS has been widely investigated using mixed metal oxide electrodes [45], as well as with BDD for the synthesis of chloramines [41], and the volatile chlorine species Cl_2, ClO_2, and Cl_2O [40]. Chloramines were observed to be efficiently synthesized via electro-oxidation of chloride anions to chlorine radicals and the subsequent chlorination of ammonia. The electrochemical production of ClO_2 and Cl_2O during BDD electro-oxidation may explain observed increases in performances during electrochemical production of RCS to conventional chlorination systems [40]. The role of sp^3/sp^2 on RCS generation has also been investigated. Electrodes containing a greater diamond content yielded greater generation of desirable active chlorine species, like Cl_2 and ClO_2, while higher graphite content lead to active chlorine conversion to undesirable specie, such as perchlorate (ClO_4^-) [46].

The electrochemical synthesis of high valence state iron and manganese oxidants such as ferrate (VI) (FeO_4^{2-}) and permanganate (MnO_4^-) is currently of interest [47]. Ferrate has been observed to be generated from several different iron precursor species including Fe_2O_3, FeO, and $FeCl_3$ [47,48] during oxidation of BDD electrodes even at very low initial iron concentrations (9 μM $FeCl_2$) [38], The production mechanism involves both direct electron transfer to BDD and a $^•OH$-mediated oxidation at the anode surface [49]. The electrochemical synthesis of permanganate from low initial $[Mn^{2+}]$ = 39 μM has recently been reported [39]. Permanganate synthesis was observed to progress less readily than ferrate under similar conditions, as the electro-oxidation of Mn^{2+} proceeded principally to intermediate oxidation state species of insoluble manganese in the +3, +4, and +5 valence states. However, even low levels of ferrate and permanganate generation were observed to increase the degradation of water pollutants such as atrazine [50,51] and perfluorooctane sulfonate [52] during electro-oxidation processes. However, the roles of the boron content, sp^3/sp^2 carbon ratio and other BDD modifiers or co-dopants are still largely unknown.

The anodic production of H_2O_2 using BDD electrodes has been demonstrated, with Faradaic efficiencies increasing from 12 to 32% and production rates increasing from 0.27 to 3.9 μmol min^{-1} cm^{-2} between 2.57 and 2.9 V_{RHE} [53]. A similar trend in H_2O_2 anodic electrosynthesis was observed by Mavrikis *et al*. [54]. Their research found higher production rates and current efficiencies at higher anodic potentials. When operating between 2.67-3.47 V_{RHE}, an H_2O_2 concentration and Faradaic efficiency of 29 mmol dm^{-3} and 28% were achieved at 3.47 and 3.17 V_{RHE}, with corresponding production rates of 19.6 and 10.6 μmol min^{-1} cm^{-2}, respectively [54]. In a related study, H_2O_2 concentrations of 0.79, 1.57, 3.5 and 4.34 mg L^{-1} and Coulomb efficiencies of 19, 18, 15 and 6.3% after 30 min of electrolysis were reported for potentials of 2.0, 2.5, 3.0 and 3.5 $V_{Ag/AgCl}$, respectively [55]. In addition, the generation of ozone using BDD electrodes has also been reported. For example, ozone concentrations as high as 5.6 mg L^{-1} were achieved with current

densities of 20 and 40 mA cm^{-2} (pH = 3, [Na$_2$SO$_4$] = 0.05 M, T = 23 °C and Q = 4.7 L min^{-1}) [56]. In contrast, at 60 mA cm^{-2}, the O$_3$ concentration decreased from 5.6 mg L^{-1} at 60 min down to 2.9 mg L^{-1} at 360 min of electrolysis [56].

Cathodic Electrosynthesis Processes

While the generation of H$_2$O$_2$ by a BDD anode was reported in the previous section, it has more commonly been explored during the cathodic reduction of oxygen. Even though simple carbon materials have been extensively used for H$_2$O$_2$ generation via O$_2$ reduction at the cathode, BDD has also been used successfully. Santana-Martínez *et al*. reported H$_2$O$_2$ concentrations of 0.72, 0.52 and 0.33 mg L^{-1} after 360 min of electrolysis at current densities of 20, 40 and 60 mA cm^{-2} (pH = 3, [Na$_2$SO$_4$] = 0.05 M, T = 23 °C and Q = 4.7 L min^{-1}), respectively [56]. Furthermore, the electrogenerated H$_2$O$_2$ can be oxidized to O$_2$ and H$^+$, which can subsequently react with the electrogenerated O$_3$ to produce ROS, such as $^\bullet$OH and $\bullet$O$_2^-$, as well as O$_2$. This can also be facilitated by the recombination of $\bullet$OH generated at the anode. These processes explain why the measured concentration of H$_2$O$_2$ is, roughly, one order of magnitude lower than that of O$_3$. A similar difference in oxidant concentrations was also observed when electrolysis was conducted at pH 7. Similarly, Thostenson *et al.* reported H$_2$O$_2$ concentrations of 0.24, 1.35 and 5.0 mg L^{-1} and Coulombic efficiencies of 47, 53 and 19 % after 30 min of electrolysis at potentials of -1.0, -1.5 and -2.0 V$_{Ag/AgCl}$, respectively [55].

For the electrosynthesis processes herein reviewed, further efforts should consider the improvement of reactor design, aimed to reduce mass transfer limitations in the electrochemical cell, to increase the electrosynthesis efficiency and micropollutant degradation. Moreover, current efficiencies can be further improved with increased oxidation and/or reduction selectivity, through the modifications and addition of co-dopants to diamond electrode materials [57].

Applications

Commercial EO and ER operations using diamond electrodes are still limited to niche applications on a relatively small scale. The versatility and tunability of EO and ER provide tailored solutions to specific wastewater treatment needs, such as the on-site removal of non-biodegradable toxic compounds in industrial wastewaters, or systems with small space requirements [58]. Like other electrochemical devices for water and wastewater treatment [59–61], EO and ER using diamond electrodes can be used as an off-grid solution using renewable energy sources for the generation of oxidants, where grid electricity is scarce or non-existent, such as rural areas of low- and middle-income countries [62]. Electrolysis cells are electrodes directly connected to a power supply operating in DC in a monopolar or bipolar electrochemical (BPE) configuration. In the BPE configuration, an electric field is generated by an extra pair of electrodes,

avoiding an electrical connection to the internal electrode(s). EO and ER can be separated using an ion-specific membrane or can be together in a single chamber configuration in batch or flow-through modes. Different possibilities of electrochemical reactor design specifics for BDD-driven electrosynthesis are presented in **Table 1** with examples of applications from academia and industry. More comprehensive reviews and analysis can be found in the literature [63–66].

The design of electrochemical reactors is still very system-specific without standardized reactor shape and electrode configuration requirements for similar industrial usage [65], and often require extensive modelling and evaluation work and laboratory studies to identify the optimal configuration and operating conditions [67,68].

Table 1. Examples of design-specific reactor configurations used in the electrochemical synthesis of oxidants in water and wastewater treatment and their specific advantages and challenges.

Sub-system	Configuration	Advantages	Challenges	Recent examples of application
BDD electrode configuration	Monopolar	High current density Low electrical potential requirement Higher surface area Can be run in galvanostatic mode	"Dead zones" can be present in large scale reactors	Most electrode configurations used in laboratory studies are monopolar
	Bipolar	Easy assembly	Low current density High electrical potential requirement	Diamox advanced electrochemical reactor (commercially available) [69]
Electrochemical reactor	Single chamber (e.g., batch or CSTR)	Easy to operate Less susceptible to fast changes in wastewater load	Mass transport can be a challenge	Most electrochemical reactors used in laboratory studies are single chambers.
	Flow-through (e.g., PFR)	Small design footprint	Contact time can be too short Outlet concentrations are highly susceptible to inlet variations	Membrane-based electrochemical flow reactor for the generation of ferrates [70]
Electrochemical cell	Separated (e.g., ion-specific membrane)	High residence time of oxidants or reducers Separated fluxes can have a higher added value	High electrochemical resistance	Electrochemical preparation of persulfate in a split-cell or dual-chamber reactor [71,72]

| Undivided (no barrier between anodes and cathodes) | Low electrochemical resistance, Combine EO and ER processes | Low residence time of oxidants or reducers | Treatment of Thiosalts in Contaminated Mine Water [73] |

At the laboratory or bench scale, the use of diamond electrodes for synthesizing oxidants species and their use in the subsequent degradation of various organic micropollutants has been investigated. The oxidation of several aromatic (phenol and naphthol) and aliphatic (2-propanol and maleic acid) organic species, as well as an inorganic pollutant (cyanide), was tested using electrosynthesized peroxodiphosphate [37]. It was observed that the chemical structure of the organic pollutants did not yield specific selectivity towards peroxodiphosphate oxidation, but rather was a function of oxidant concentration. Several studies have been published which investigated the incidental degradation of pesticides, such as propham, in chloride-containing waters [42]. While propham degradation was observed to increase with increasing chloride concentrations, due to the greater rate of RCS synthesis, the overall extent of complete pollutant mineralization was decreased due the formation of stable chlorinated by-products; a phenomenon that has been reported previously for other organic micropollutants [74,75]. Limited studies have also evaluated the degradation of target pollutants by electrochemically synthesized ferrate (e.g., 2,4-D [70] and microcystin-LR [76]). Similarly, the simultaneous EO and electrochemically synthesized ferrate oxidation of pollutants such as blue BR dye [77], atrazine [50] and PFOS [52] were all found to significantly increase overall compound degradation due to the effects of ferrate. Increased degradation of atrazine was observed during an EO and coupled *in situ* permanganate synthesis [51].

Conclusion

The use of electrochemical systems to treat various water and wastewater matrices has been receiving much attention over the last several decades. While the development of novel and powerful electrode materials, like boron-doped diamond, have widened the possibilities for EO and ER technologies, mass-transport-limited to the electrode surface haves restricted their application as oxidation and disinfection unit operations. However, the co-generation of powerful oxidant species, such as $S_2O_8^{2-}$, $SO_4^{\bullet-}$, $P_2O_8^{4-}$, FeO_4^{2-}, MnO_4^-, RCS and ROS, during EO and ER operations, allows for the simultaneous degradation of target pollutants at the electrode surface and in the bulk-phase water solutions. While research in this area is still in progress, and real-world systems are limited to niche applications, the potential use of simultaneous electro-degradation (EO and ER) and oxidant generation is a promising technology worthy of further exploration.

Acknowledgements

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