



The competition between cathodic oxygen and ozone reduction and its role in dictating the reaction mechanisms of an electro-peroxone process



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ABSTRACT

Previous studies indicate that effective generation of hydrogen peroxide (H₂O₂) from cathodic oxygen (O₂) reduction is critical for the improved water treatment performance (e.g., enhanced pollutant degradation and reduced bromate formation) during the electro-peroxone (E-peroxone) process (a combined process of electrolysis and ozonation). However, undesired reactions (e.g., O₃, H₂O₂, and H₂O reductions) may occur in competition with O₂ reduction at the cathode. To get a better understanding of how these side reactions would affect the process, this study investigated the cathodic reaction mechanisms during electrolysis with O₂/O₃ gas mixture sparging using various electrochemical techniques (e.g., linear sweep voltammetry and stepped-current chronopotentiometry). Results show that when a carbon brush cathode was used during electrolysis with O₂/O₃ sparging, H₂O and H₂O₂ reductions were usually negligible cathodic reactions. However, O₃ can be preferentially reduced at much more positive potentials (ca. 0.9 V vs. SCE) than O₂ (ca. -0.1 V vs. SCE) at the carbon cathode. Therefore, cathodic O₂ reduction was inhibited when the process was operated under current limited conditions for cathodic O₃ reduction. The inhibition of O₂ reduction prevented the desired E-peroxone process (cathodic O₂ reduction to H₂O₂ and ensuing reaction of H₂O₂ with O₃ to •OH) from occurring. In contrast, when cathodic O₃ reduction was limited by O₃ mass transfer to the cathode, cathodic O₂ reduction to H₂O₂ could occur, thus enabling the E-peroxone process to enhance pollutant degradation and mineralization. Many process and water parameters (applied current, ozone dose, and reactivity of water constituents with O₃) can cause fundamental changes in the cathodic reaction mechanisms, thus profoundly influencing water treatment performance during the E-peroxone process. To exploit the benefits of H₂O₂ in water treatment, reaction conditions should be carefully controlled to promote cathodic O₂ reduction during the E-peroxone process.

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1. Introduction

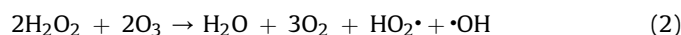
The electro-peroxone (E-peroxone) process is an emerging electrochemically driven advanced oxidation process (AOP) that combines conventional ozonation with *in situ* H₂O₂ production from cathodic oxygen reduction to improve the performance of

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water treatment (Li et al., 2013, 2015; Yao et al., 2017; Yuan et al., 2013). During the E-peroxone process, ozone (O₃) is produced from an oxygen (O₂) feed gas using an ozone generator, then sparged (with unconverted O₂) into an ozone contactor, which is the same as in conventional ozonation. However, the ozone contactor is retrofitted with a carbon-based cathode that can effectively convert the sparged O₂ to hydrogen peroxide (H₂O₂, Eq. (1)) (Yuan et al., 2013). The *in situ* generated H₂O₂ can then in turn enhance O₃ transformation to •OH via the so-called “peroxone reaction” (Eq. (2), simplified according to Fischbacher et al. (2013); (von Sonntag and von Gunten, 2012), and thus significantly

enhance organic pollutant degradation, especially ozone-refractory pollutants (e.g., 1,4-dioxane and oxalic acid) compared to conventional ozonation (Wang et al., 2015a, 2015b). In addition, the electro-generated H_2O_2 can effectively reduce the formation of bromate (BrO_3^-) (Li et al., 2015; Yao et al., 2017), which is a potentially carcinogenic by-product that may form during ozonation of bromide-containing water (Hubner et al., 2015; Pisarenko et al., 2012; von Gunten, 2003). Thus, by utilizing O_2 that would otherwise be wasted in conventional ozonation to electrochemically produce H_2O_2 , the E-peroxone process can considerably improve water treatment performance in many aspects.



Effective generation of H_2O_2 from cathodic O_2 reduction is crucial to the success of the E-peroxone process (Li et al., 2015; Yuan et al., 2013). However, side reactions may occur in competition with O_2 reduction to H_2O_2 at the cathode during the E-peroxone process (see Table 1), thus affecting the process performance. For example, depending on reaction conditions (e.g., electrode materials and cathodic potentials), cathodic O_2 reduction can proceed via a direct four-electron pathway to form OH^- (Eq. (3)) or the two-electron pathway to HO_2^- (conjugate base of H_2O_2 , Eq. (4)) (Šljukić et al., 2005; Yeager, 1984). Moreover, the electro-generated H_2O_2 can also undergo further cathodic reduction to OH^- (Eq. (5)) (Paliteiro et al., 1987). In addition, hydrogen evolution from H_2O reduction (Eq. (6)) is often an important cathodic reaction during electrolytic water treatment. More importantly, for the E-peroxone process, O_3 that is sparged with O_2 can also be electrochemically reduced at the cathode (Eqs. (7) and (8)) (Johnson et al., 1968; Kishimoto et al., 2005; Ochiai et al., 2006). These side reactions are undesired for the E-peroxone process because they impair H_2O_2 electro-generation and thus its beneficial effects on water treatment. It is therefore desirable if these side reactions can be minimized during the E-peroxone process.

By using carbon-based materials as the cathode, some of the side reactions can be largely suppressed during the E-peroxone process. Many previous studies have indicated that O_2 reduction on carbon electrodes follows predominantly the two-electron pathway to yield H_2O_2 , whereas the four-electron pathway is negligible (Brillas et al., 2009; Paliteiro et al., 1987; Šljukić et al., 2005; Yeager, 1984). For example, Paliteiro et al. (1987) reported that O_2 reduction takes place only as far as H_2O_2 on freshly polished pyrolytic graphite. In addition, carbon materials are known to have low catalytic activity for H_2O_2 decomposition, and therefore may not cause substantial further reduction of the electro-generated

H_2O_2 (Brillas et al., 2009; Paliteiro et al., 1987). Furthermore, carbon electrodes generally have much higher overpotentials for H_2O_2 reduction than for O_2 reduction, and can therefore produce H_2O_2 in the potential region of water stability (Panizza and Cerisola, 2001). Due to these favorable characteristics, carbon-based cathodes (e.g., carbon-polytetrafluoroethylene (carbon-PTFE), reticulated vitreous carbon, and carbon felt) have been widely used to produce H_2O_2 from cathodic O_2 reduction for water and wastewater treatment, typically in the electro-Fenton (E-Fenton) process (Brillas and Martínez-Huitle, 2015; Brillas et al., 2009; Oturan et al., 2000, 2008), and more recently in the E-peroxone process (Hou et al., 2016; Yuan et al., 2013).

However, it is still unclear how the presence of O_3 would affect cathodic O_2 reduction to H_2O_2 during the E-peroxone process. As shown in Table 1, O_3 has a much more positive standard reduction potential than O_2 (Haynes, 2014). In addition, Johnson et al. (1968) reported that the onset potentials of O_3 reduction and O_2 reduction at a platinum (Pt) cathode are ~ 1.3 V vs. SCE and ~ 0.6 V vs. SCE, respectively. Ochiai et al. (2006) also found that O_3 can be reduced at approximately 0 V vs. Ag/AgCl at boron-doped diamond (BDD) electrode, whereas O_2 reduction is inhibited in the potential region more positive than -0.4 V vs. Ag/AgCl. These previous results suggest that O_3 may also be preferentially reduced over O_2 at carbon cathodes, thus affecting H_2O_2 production from cathodic O_2 reduction during the E-peroxone process. Nevertheless, because virtually no studies have investigated the cathodic O_3 reductions at carbon electrodes, the effects of cathodic O_3 reduction on O_2 reduction to H_2O_2 have mostly been overlooked in the previous studies on the E-peroxone process (Wang et al., 2015b; Yuan et al., 2013), as well as studies on a similar cathodic oxidation process, whereby an O_2/O_3 mixture is electrochemically produced from water oxidation at a lead dioxide (PbO_2) anode in the anodic compartment of a divided electrochemical cell and then purged with an O_2 gas stream to a graphite cathode in the cathodic compartment (Amadelli et al., 2000, 2011). For example, it has often been assumed that H_2O_2 can be electrochemically generated at the same rate during the E-peroxone process as during electrolysis with only pure O_2 sparging (Li et al., 2013; Wang et al., 2015b). However, considering that O_3 can be reduced more easily at much higher standard electrode potential than O_2 (Table 1), the validity of this assumption requires further investigation. Due to the critical role of H_2O_2 in the E-peroxone process, it is imperative to get a better understanding of the cathodic reaction mechanisms during the E-peroxone process, especially, how the presence of O_3 would affect cathodic O_2 reduction to H_2O_2 .

To this end, this study investigated the main cathodic reactions (O_2 , O_3 , H_2O , and H_2O_2 reductions) that may occur at the carbon cathode during the E-peroxone process using various electrochemical techniques (e.g., linear sweep voltammetry and stepped-current chronopotentiometry). The effects of applied current and ozone dose on the cathodic reaction mechanisms were evaluated systematically. In addition, to investigate the kinetics and mechanisms of pollutant degradation by the E-peroxone process, the degradation of oxalate and phenol during ozonation, electrolysis, and the E-peroxone process were compared. Phenol is a common pollutant detected in various water sources, and reacts actively with O_3 (Mvula and von Sonntag, 2003). In contrast, oxalate reacts poorly with O_3 and is often a major by-product formed during ozonation of many organic pollutants such as aromatics and natural organic matter (von Sonntag and von Gunten, 2012). They were therefore selected as an ozone-resistant and ozone-reactive model compound, respectively. The evolutions of cathodic potentials, dissolved O_2 , O_3 and H_2O_2 were followed during these processes to analyze the cathodic reactions that occurred during electrolysis with O_2/O_3 sparging.

Table 1
Possible cathodic reactions that may occur during the E-peroxone process and their standard electrode potentials (E^0).

Reaction ^a	E^0 (vs. SHE) ^b	Reference
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (3)	0.401	(Haynes, 2014)
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ (4)	-0.076	(Haynes, 2014)
$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ (5)	0.878	(Haynes, 2014)
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (6)	-0.828	(Haynes, 2014)
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$ (7)	1.24	(Haynes, 2014)
$O_3 + e^- \rightarrow O_3\cdot^-$ (8)	1.23	(Kishimoto et al., 2005)

^a The table lists the cathodic reactions and standard reduction potentials under alkaline conditions, which simulate the high local pH in the cathode diffuse layers.

^b E^0 values are presented against standard hydrogen electrode (SHE) at 298.15 K (25 °C), and at pressure of 101.325 kPa. The activity of all the soluble species (e.g. OH^-) is assumed to be 1.000 mol/L.

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