Electrochemical Reduction of Bromate by a Pd Modified Carbon Fiber Electrode: Kinetics and Mechanism

Ran Mao^{a,b}, Xu Zhao^{a,*}, Jiuhui Qu^a

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, P.R. China

^b University of Chinese Academy of Sciences, Beijing, 100049, P.R. China

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ABSTRACT

The electroreduction of bromate (BrO_3^-) was investigated at a Pd modified carbon fiber (Pd/C) electrode prepared from PdCl_2 via electrodeposition method. Pd particles distributed on the carbon fiber substrate uniformly. Under various cathode potentials, electroreduction removal of BrO_3^- at pure carbon fiber electrode and the Pd/C electrode were firstly compared. It was observed that nearly no BrO_3^- removal was observed within the bias potential of -2.0 V at the carbon fiber electrode. At the Pd/C electrode, the removal efficiency of BrO_3^- was sharply increased from 24.0% to 58.4% at the cathode potential of -1.0 to -1.5 V , which was further increased to be 87.2% at -2.0 V . The electrochemical reduction of BrO_3^- was strongly pH-dependent at -0.5 V and the reduction rate could be enhanced at low pH. While at the potential of -2.0 V , a slight pH effect was observed. BrO_3^- electroreduction follows pseudo first-order kinetics; the rate constant k was firstly increased from 0.016 to 0.031 min^{-1} with the increase of the Pd loading amount from 0.31 to 0.73 mg/cm^2 , and then was decreased to 0.018 min^{-1} at a higher Pd loading amount of 1.05 mg/cm^2 . The Pd(0) nanoparticles played a significant role in forming atomic H^* to realize indirect BrO_3^- reduction. The electrochemical reduction of BrO_3^- produces accumulated intermediates of HOBr and OBr^- , which were subsequently reduced to Br^- with the time evolution.

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1. Introduction

Bromate (BrO_3^-) is an oxyhalide disinfection byproduct frequently detected in drinking water from ozonation or chlorination of bromide (Br^-)-containing source waters [1,2]. BrO_3^- has been recognized as a potential carcinogen to humans, thereby the World Health Organization (WHO) has strictly regulated BrO_3^- level in drinking water [3]. Thus, it is highly desirable to develop effective treatment methods to remove BrO_3^- pollutants.

Conventionally, BrO_3^- can be removed by various technologies including filtration, photocatalysis, arc discharge, chemical reduction, activated carbon techniques, and biological remediation [4–7]. Among these technologies, the iron-based chemical reduction and biological activated carbon (BAC) treatment has been well discussed in the research papers [8–11]. Although these two approaches can efficiently reduce BrO_3^- to Br^- , their feasibility in water treatment was limited because of the extended reaction time for BAC treatment and requirement for post-treatment to remove

Fe^{2+} or residual biomass [12,13]. In recent years, there has been an increased interest in environmental applications of electrochemical processes, which are chemical-free, electricity driven, highly efficient and selective, and easy to realize automatic operation [14–18]. The compact reactor size, minimal formation of byproducts and low maintenance requirements of the electrochemical process make it highly attractive as point of use drinking water treatment [19]. Electrochemical technologies have been proven effective for eliminating BrO_3^- from water. For example, Kishimoto and Matsuda reported a novel electrochemical method to reduce BrO_3^- to Br^- using an activated carbon felt electrode [20]. BrO_3^- contamination can be removed within a few minutes. But, this process required acidic conditions. Zhao et al. studied the effectiveness of BrO_3^- removal by electrochemical reduction at a boron-doped diamond electrode, which can remove nearly 90% of BrO_3^- with the applied bias potential of -1.0 V within 2 h [21]. The electrochemical process can reduce BrO_3^- to Br^- with enhanced reaction rates, and no additional treatment processes are required.

It is recognized that the reduction of contaminants at cathode surfaces may occur through both direct and indirect mechanisms [22]. Direct reduction occurs by electron tunneling, and indirect reduction of contaminants occurs via reaction with atomic

* Corresponding author. Tel.: +86 10 62849160; fax: +86 10 62849160.
E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

hydrogen adsorbed on the cathode [23]. Nevertheless, the direct reduction of contaminants at the cathode required suitable electrocatalytic electrode materials, which usually worked at high overpotentials to obtain vigorous reduction conditions [24]. Apart from this, H_2 generated at the cathode by water electrolysis during the electrochemical process was considered to reduce the efficiency and consumed the energy [25]. Recent studies have shown that H_2 produced at the cathode can be delivered for palladium (Pd)-catalytic hydrodechlorination of contaminants, thus providing an alternative to reduce the dependence on costly electrode materials [26,27]. For example, Bonin et al. exhibited that Pd-modified cathodes had high dechlorination efficiencies for chlorinated organics, as Pd can activate H_2 as well as catalyze the electrochemical reduction of H^+ or H_2O to produce continuously adsorbed nascent H^* [28,29]. This indirect electroreduction process known as electrocatalytic hydrogenolysis, in which reductive atomic hydrogen is generated at the electrode surface, is indeed a very useful tool for the reductive transformation of contaminants. Therefore, the Pd-modified cathodes are expected to be effective in BrO_3^- reduction. However, for BrO_3^- reduction, the electrochemical activity and the electrocatalytic reduction process with a Pd-modified cathode have not been investigated.

The objective of this study was to explore the reaction mechanism of the electrocatalytic reduction of BrO_3^- on the Pd/C electrode. BrO_3^- reduction at different cathode potentials, pH values, supporting electrolyte concentrations and Pd loadings was investigated. The direct and indirect reduction processes were specifically elucidated.

2. Experimental

2.1. Chemicals

The carbon fiber was purchased from Beijing LN Power Source Company (Toray 120). Proton exchange membrane used in the experiments was Nafion-117 (Du Pont). Other chemicals including sodium bromate, sodium bromide, palladium chloride and ammonium chloride were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals used in this study were analytical grade. High-purity water (specific conductivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$) obtained from a Millipore Milli-Q system was used in all the experiments.

2.2. Electrode preparation

The Pd/C electrode was prepared via our previously reported electrodeposition method [30]. Briefly, the carbon fiber was first immersed in a 0.1% (w/w) Triton X-100 solution for 24 h and then in de-ionized water for 2 h for the purpose of lowering the hydrophobicity and the extent of metal agglomeration [31,32]. The electrodeposition of Pd(0) was carried out by dipping the cleaned carbon fiber in dichlorodiammine palladium $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ complex (plating solution, $\text{pH} = 1$), composed of 1 mM palladium chloride (PdCl_2) and 10 mM ammonium chloride solution [33]. The desired amount of Pd particles were electrodeposited onto the carbon fiber with a current density of 2 mA/cm^2 for 30 min. The as prepared Pd/C electrode was subsequently reduced at 200°C for 2 h with rates of 100 mL/min H_2 to immobilize the catalysts.

2.3. Apparatus

The electrocatalytic reduction of BrO_3^- in aqueous solution was conducted in an electrochemical reactor separated into two cells by the proton exchange membrane (Figure S1). The cathode and the anode compartments were filled with 50 mL aqueous solution of BrO_3^- with Na_2SO_4 (supporting electrolyte) and Na_2SO_4 , respectively. The reactor was connected with an EG&G model 263A

workstation (Princeton Applied Research, USA). The prepared Pd/C electrode was used as the cathode with a geometric surface area of 7.5 cm^2 ($2.5 \text{ cm} \times 3 \text{ cm}$), and the anode was a platinum wire with 72 mm in length and 1.5 mm in diameter. A saturated calomel electrode (SCE) was positioned near the cathode as the reference electrode. To ensure the homogeneity of the catholyte, the system was magnetically stirred at a rate of 700 rpm. The potentiostatic electrolysis was applied in the experiments and Na_2SO_4 was employed as the background electrolyte. All electrolysis experiments were completed at 5 mM Na_2SO_4 unless otherwise noted. During the electrolysis, samples were periodically withdrawn from the cathode cell for analysis. The solution pH was adjusted with diluted H_2SO_4 and NaOH solution (guaranteed grade).

2.4. Analysis

The concentrations of BrO_3^- and Br^- were measured with an ion chromatograph (IC) (Dionex 2000) using an IonPac AS-19 anion-exchange analytical column and an IonPac AG19 guard column. Mobile phase eluent for the IC was KOH solution, and the flow rate was 1.0 mL/min. The chromatogram of BrO_3^- and Br^- was obtained under gradient elution conditions (0.0–18.0 min: 10.0 mM KOH; 18.1–26.0 min: 35.0 mM KOH; 26.1–31.0 min: 10.0 mM KOH).

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were carried out in a JSM 6301 instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos AXIS Ultra X-ray photoelectron spectrometer. X-ray powder diffraction (XRD) patterns of samples were obtained with an X'Pert PRO Powder diffractometer machine (PANalytical Co.), by using Ni-filtered $\text{Cu K}\alpha$ irradiation from 5° to 90° (in 2θ).

3. Results and Discussion

3.1. Characterization of the Pd/C electrode

The Pd/C electrodes with various Pd loading amounts were firstly characterized by SEM and EDX analysis. As presented in Fig. 1 (a), the bare carbon fiber is comprised of hundreds of carbon fiber. The ample inner space of carbon fiber can provide optimal channels for targeted BrO_3^- anions to transfer to the catalytic active sites. Abundant sphere-like electrodeposited Pd particles disperse evenly on the carbon fiber as can be seen from images with higher magnification (Fig. 1 (b), (c), (d)). The size of the Pd particles is around 40 nm in diameter. The effect of Pd loading amount on the catalytic behavior of the Pd/C electrode will be addressed subsequently. In fact, the Pd loading amount of 1.05 mg/cm^2 Pd/C electrode is approximately 3.4-fold and 1.4-fold higher than that of 0.31 mg/cm^2 and 0.73 mg/cm^2 Pd/C electrode, respectively. Data in Figure S2 also indicates the same feature, namely 0.72% Pd atoms percent is also nearly 3.4-fold and 1.6-fold as large as 0.21% and 0.44% Pd atoms percent, respectively. Therefore, the EDX results confirm the existence of increased Pd loading amounts on the Pd/C electrodes.

XRD spectra of the carbon fiber electrode and the prepared Pd/C electrode were given in Figure S3. The peak at 26.5° is attributed to the highly structured (graphitic) carbon, and the diffraction peaks occurring at 40.2° and 46.8° are assigned to typical Pd metal with face centered cubic crystallographic structure [34,35]. The peaks at 68.3° and 82.3° are respectively for (220) and (311) planes, indicating the polycrystalline state of Pd particles electrodeposited onto the carbon fiber.

3.2. Effect of cathode potential

Electroreduction of BrO_3^- on the Pd/C electrode at different cathode potentials is investigated and the results are presented in

Fig. 1. SEM images of the Pd/C electrodes with various Pd loading amounts. (a) 0 mg/cm²; (b) 0.31 mg/cm²; (c) 0.73 mg/cm²; and (d) 1.05 mg/cm².

Fig. 2 (a). Nearly no loss of BrO₃[−] is observed at the applied potential of −0.3 V (vs. SCE) and −0.5 V within 60 min. 24.0% of the BrO₃[−] is removed at −1.0 V. BrO₃[−] removal is largely increased to be 87.2% at −2.0 V under the same otherwise conditions. Further decrease of the applied bias potential to −2.5 V does not increase the removal efficiency.

The pseudo first-order reaction kinetics is used to fit the BrO₃[−] removal with the reaction time. The model is given by the equation of (1)

$$C_t = C_0 \exp(-kt) \quad (1)$$

where t is the reaction time (min), k is the rate constant (min^{−1}), and C_0 and C_t are the BrO₃[−] concentrations (μM) at times of $t=0$ and $t=t$, respectively. The kinetic analysis of the data in Fig. 2 (a) gives an average correlation coefficient for the $\ln[\text{BrO}_3^-]$ versus t plot in the linear region of 0.993, suggesting the suitability of the pseudo first-order reaction kinetics used to fit BrO₃[−] removal. As shown in Fig. 2 (b), the value of k remains low until the applied bias potential is −1.0 V, where it begins to rise sharply with the potential decreasing to −2.0 V, and then reaches a plateau of 0.031 min^{−1} when the cathode is operated at more reducing values. A similar trend was reported by Li et al. in the reduction dehalogenation of chloroacetic acids [36]. It was exhibited that the electrocatalytic dehalogenation happened at potentials lower than −1.0 V where molecular hydrogen would evolve. Pd(0) played important roles in the chemisorption and decomposition of hydrogen into atomic H*, a highly activated intermediate hydrogen radical [37]. Atomic H* adsorbed on the surface of the electrode at low cathode potentials is beneficial for the electroreduction of BrO₃[−]. Moreover, it is reasonable to hypothesize that the relatively low removal efficiency at potentials higher than −1.0 V is due to absence of atomic H* so that BrO₃[−] can only be removed by the direct reduction at the Pd/C electrode.

3.3. Effect of solution pH

A comparison of BrO₃[−] reduction at −0.5 and −2.0 V with various pH values was performed in order to explore the role of H⁺ in the electroreduction of BrO₃[−]. As shown in Fig. 3 (a), the relative moles vs time plot at −0.5 V shows that the BrO₃[−] removal rate strongly depends on the solution pH. The electroreduction rate of BrO₃[−] is decreased from 0.0203 to 0.0014 min^{−1} upon increasing pH from 2.73 to 9.39. By contrast, in the electrochemical reduction of BrO₃[−] at −2.0 V, a negligible influence of solution pH is observed (Fig. 3 (b)). The electroreduction rate of BrO₃[−] remains around 0.031 min^{−1} when pH is increased from 2.09 to 9.88, reflecting a stable electrocatalytic activity of the Pd/C electrode with a wide pH range. The different electroreduction behavior with various pH ranges indicated that the electroreduction of BrO₃[−] proceed with a different reduction process at −2.0 V.

The similar strong dependence of BrO₃[−] reduction on pH value was observed by Kishimoto et al. and Chen et al. [20,38]. They pointed out that low solution pH can accelerate the BrO₃[−] removal. Reactions occurring at the electrode are heterogeneous and aqueous electrons coupled with H⁺ are considered to take part in the direct reduction of BrO₃[−] on the cathode surface. Therefore, H⁺ concentration is important to the chemical equilibrium of the overall reaction. Nevertheless, when the applied bias potential is decreased to −2.0 V, the notably increased atomic H* gathered on the Pd particles may efficiently reduce BrO₃[−] to Br[−] [29]. On the basis of the above analysis, the electrochemical reduction of BrO₃[−] proceeds with indirect mechanism at low cathode potentials, and H⁺ concentration seems insignificant due to the high catalytic ability of the Pd particles for the indirect BrO₃[−] reduction. This electrochemical reduction behavior of BrO₃[−] is in agreement with reports in the literature in which slight pH effects were observed for TCE reduction in the Pd modified electrode reactor [22]. They reported that although the higher pH values contributed to decreased cathodic production of hydrogen in both the untreated and Pd modified

Fig. 2. (a) Electrocatalytic reduction of BrO_3^- and Br^- generation at different applied potentials (filled symbols denote normalized BrO_3^- concentration and open symbols denote normalized Br^- concentration), (b) effect of applied bias potential on the BrO_3^- reduction kinetics at the Pd/C electrode (5 mM Na_2SO_4 ; 0.66 μM initial BrO_3^- concentration; Pd loading amount: 0.73 mg/cm^2). The inset in (b) illustrates the effect of applied bias potential on the BrO_3^- removal efficiency.

iron reactors, the palladium could concentrate the available hydrogen, leading to smaller pH effects than that in the iron reactor. Their observation also supported the conclusion that atomic H^* was involved in the BrO_3^- reduction by the Pd modified electrode.

3.4. Effect of Na_2SO_4 concentration

As shown in Fig. 4, within 120 min, the BrO_3^- concentration decreases by 25.5% and 57.1% with Na_2SO_4 concentration of 0.1 mM and 1.0 mM at the constant potential of -2.0 V, respectively. When the Na_2SO_4 concentration is increased to 10 mM, a sharp decline in BrO_3^- concentration within 30 min is observed and the residual concentration is below detection limits of the analytic method used in this study (0.5 $\mu\text{g}/\text{L}$). Actually, there is a rise in electrolytic current upon increasing Na_2SO_4 concentration, and thus more atomic H^* cover the surface of the cathode, thereby the adsorbed BrO_3^- are more likely to acquire atomic H^* . The results are consistent with the hypothesis that indirect reduction was predominant under the tested conditions.

3.5. Effect of Pd loading amount

The effect of Pd loading amount on BrO_3^- reduction and corresponding pseudo first-order rate constant (k , min^{-1}) are

Fig. 3. Effect of solution pH on BrO_3^- reduction at the Pd/C electrode at applied potential of (a) -0.5 V and (b) -2.0 V (5 mM Na_2SO_4 ; 0.66 μM initial BrO_3^- concentration; Pd loading amount: 0.73 mg/cm^2). Inset is the effect of solution pH on the BrO_3^- reduction kinetics.

Fig. 4. Effect of supporting Na_2SO_4 electrolyte concentration on BrO_3^- reduction at the Pd/C electrode during the potentiostatic electrolysis. Filled symbols denote BrO_3^- concentration and open symbols denote Br^- concentration (0.66 μM initial BrO_3^- concentration; applied potential: -2.0 V; pH 7.25; Pd loading amount: 0.73 mg/cm^2).

Fig. 5. Effect of Pd loading amount on BrO_3^- reduction and kinetics (inset) during potentiostatic electrolysis. Filled symbols denote normalized BrO_3^- concentration, open symbols denote normalized Br^- concentration, and the lines denote the non-linear curve fit of the data points in the same color (5 mM Na_2SO_4 ; pH 7.25; 0.66 μM initial BrO_3^- concentration; applied potential: -2.5 V).

investigated at the constant potential of -2.5 V. As shown in Fig. 5, the rate constants k of BrO_3^- removal at the 0.73 mg/cm^2 Pd/C electrode is nearly doubled in comparison to that at the 0.31 and 1.05 mg/cm^2 Pd/C electrode, suggesting that the electrochemical activity of the Pd/C electrode is not proportional to the Pd loading amount. It is obvious that the electroreduction removal of BrO_3^- is promoted at the Pd/C electrode in comparison with that at the pure carbon fiber electrode, however, increase of the Pd loading amount does not continually improve the removal efficiency. As demonstrated by SEM images, the aggregation of large metallic Pd(0) particles becomes clear when the Pd loading amount is increased to be 1.05 mg/cm^2 , leading to the locally excessive H_2 evolution, which may be responsible for the electrocatalytic performance of BrO_3^- reduction at the 1.05 mg/cm^2 Pd/C electrode.

It is also worth mentioning that for unmodified carbon fiber electrode (Pd loading of 0 mg/cm^2), the BrO_3^- content is found to remain nearly constant throughout the experiment at cathode potentials from -0.15 V to -2.0 V (Figure S4). And, a vigorous evolution of H_2 has been observed at the carbon fiber electrode at -2.0 V. If the BrO_3^- removal mechanism involves indirect reduction, BrO_3^- should be reduced by atomic H^* which can be generated in the step before H_2 evolution [39]. This result indicates that the unmodified carbon fiber is not an efficient substrate for the reduction of BrO_3^- . It can also be deduced that the electrochemical reduction of BrO_3^- at -2.5 V occurs through direct reduction mechanism. Cheng et al. found that the direct electroreduction at the carbon electrode surface could not promote reductive dechlorination of 4-chlorophenol within -1.1 V vs SCE because hydrogen gas escapes relatively easily from the surface [40]. By contrast, the Pd modified carbon cloth electrode exhibited the unique property to promote dechlorination of organic compounds due to the ability of Pd to absorb hydrogen into its lattice and to maintain a high surface concentration of hydrogen. In our case, the electroreduction of BrO_3^- at -2.5 V on the carbon fiber electrode may be attributed to the more reducing cathode potentials employed in this study which can significantly enhance the direct electron transfer on its surface.

3.6. Proposed mechanisms for electrocatalytic reduction of BrO_3^-

In order to investigate the electrochemical reduction of BrO_3^- at the Pd/C electrodes, linear sweep voltammograms (LSVs) with various BrO_3^- concentrations are recorded in the presence of 1.0 mM

Fig. 6. Linear sweep voltammograms at 10 mV/s of (a) 0.73 mg/cm^2 Pd/C electrode with gradient concentration of BrO_3^- in 1.0 mM Na_2SO_4 and (b) Pd/C electrodes with different Pd loading amounts in 1.0 mM Na_2SO_4 and 0.5 mM BrO_3^- , pH 7.25.

Na_2SO_4 at a scan rate of 10 mV/s . A shoulder like reduction current maximum is observed at about -2.0 V, which is consistent with the results reported before as the maximum reduction rate is obtained at the same cathode potential (Fig. 6 (a)). It is clear that peak current increases with the increment of BrO_3^- concentration, indicating that more electrons take part in the reduction process. In comparison with the unmodified carbon fiber electrode, the current intensities of the Pd/C electrodes with three Pd loadings are significantly increased (Fig. 6 (b)). Combined with the kinetics analysis in Fig. 5, it is concluded that Pd particles on the carbon fiber facilitate the electron transfer reaction and improve the cathode performance in BrO_3^- reduction. Among the three Pd/C electrodes with different Pd loadings, the current densities are first increased and then decreased with the Pd loading amount. It is possible that the negative effect on BrO_3^- removal at high Pd loading amount is due to the presence of aggregation of large metallic Pd(0) particles. This unexpected appearance can result in locally excessive H_2 evolution and thus hamper BrO_3^- migration and its reaction with atomic H^* on the catalytic active sites. By contrast, Chen et al. reported that increase of the Pd loading amount led to the increase in the initial BrO_3^- reduction rate without the negative influence [38]. It is important to note the difference in terms of catalytic system between the two studies. Chen et al. carried out the reduction experiments in a heterogeneous catalytic system using Pd/ Al_2O_3 and exogenous H_2 as catalysts. However, the Pd/C electrode used in this study serves two purposes: it is the conducting matrix on which protons are reduced electrochemically to atomic or molecular hydrogen as well as available hydrogen is converted to atomic H^* , and it also furnishes catalytic sites for the chemical reaction of atomic H^* with BrO_3^- . At lower catalyst loadings, the

Fig. 7. XPS spectra of Pd on the Pd/C electrode before and after the electrochemical reduction (5 mM Na₂SO₄; pH 7.25; 0.66 μM initial BrO₃[−] concentration; applied potential: −2.0 V; Pd loading amount: 0.73 mg/cm²).

electrochemical process fails to produce enough atomic H* in the Pd lattice for BrO₃[−] reduction. At high catalyst loadings, the cathode may restrict access of BrO₃[−] to the interior portions where H₂ is excessively electrogenerated, which can be responsible for the decreased catalytic activity of the Pd/C electrode.

In the dechlorination reaction catalyzed by Pd in the electroreduction process, it is recognized that transitional C-Pd-Cl bond were formed, resulting in the presence of Pd(II) species. The chloroacetic acids were then attacked with atomic H*, followed by the C-Cl scission [30]. Herein, XPS is used to investigate the valence state of Pd coated on the Pd/C electrode in the electroreduction of BrO₃[−] ions. A typical XPS survey spectrum is presented in Fig. 7. The Pd 3d spectra before and after the electrochemical reduction exhibit spin-orbit doublet i.e. 3d_{5/2} at 335.7 eV and 3d_{3/2} at 340.9 eV respectively, which are attributed to the presence of metallic palladium Pd(0). According to the hydrodeoxygenation mechanism proposed by Chaplin et al., the reaction pathway of Pd-based catalytic reduction of BrO₃[−] was characterized by the removal of oxygen atoms from oxanions (BrO₃[−]) by hydrogenation to water [29]. In this oxygen atom transfer mechanism, the roles of Pd for monometallic catalysts are to (1) dissociate H₂ (ignoring the electroreduction of H⁺ or H₂O on polarized Pd particles due to that the electrons are provided by cathode) and (2) facilitate H₂O formation from abstracted oxygen atoms. So it is concluded that neither palladium-bonding between the Pd atoms and the targeted oxanions nor any oxidation species that can interact with Pd(0).

It is noteworthy that only 64% of the total Br[−] is detected within 30 min with the 10 mM Na₂SO₄, although BrO₃[−] is almost completely removed in the same time scale. The molar concentration of Br[−] increases successively during the subsequent electrolysis, which is nearly identical to the initial BrO₃[−] concentration within 90 min. This observation indicates that some kinds of intermediates are generated under these conditions; otherwise, the increment of Br[−] should be identical to the decrement of BrO₃[−] during the electrocatalytic reduction process according to the stoichiometric relationship. Data in Fig. 8 shows that nearly 0.15 mg/L HOBr/OBr[−] is generated during the BrO₃[−] reduction at the carbon fiber electrode with initial 400 mg/L BrO₃[−], and around 0.20 mg/L HOBr/OBr[−] is detected at the 0.73 mg/cm² Pd/C electrode under the same conditions. As reported by Qu et al., although the intermediates of BrO₃[−] reduction involved BrO₂, HBrO₂ and HBrO which would undergo electrochemical reduction to produce Br₂ rapidly, Br₂ must then be reduced to Br[−] at the potential of the catalytic reduction, thus the final product of BrO₃[−] reduction was Br[−] [41].

Fig. 8. HOBr/OBr[−] generation at the carbon fiber electrode and the 0.73 mg/cm² Pd/C electrode during the potentiostatic electrolysis (10 mM Na₂SO₄; 400 mg/L initial BrO₃[−] concentration; applied potential: −2.5 V; pH 7.25).

Therefore, the electrochemical reduction of BrO₃[−] produces intermediates (BrO₂, HBrO₂, HBrO, Br₂), and these intermediates may have accumulated in the solution because of the fast reduction of BrO₃[−] at high Na₂SO₄ concentrations, which are subsequently reduced to Br[−] with the time evolution.

In our case, in the bias potential range from −0.3 to −1 V, the generation of atomic H* is so weak that the direct reduction of BrO₃[−] by electrons provided at the cathode becomes the main process which was responsible for the BrO₃[−] removal, i.e. the direct electron transfer on the cathode surface might be predominant, which is consistent with our observation that evolution of H₂ (the electrogenerated H₂ may be the main source for atomic H*) can only be found at potentials more negative than −1.0 V. The direct pathway can be expressed by Eq. (2):

Therefore, the electrochemical reduction of BrO₃[−] can be enhanced at low pH through the transition of the chemical equilibrium of the reduction reaction.

While in the range from −1.0 to −2.0 V, the sharp increase of the BrO₃[−] removal efficiency from 24.0% to 87.2% is likely due to the fact that BrO₃[−] electroreduction mainly proceeded via the indirect reduction process, as in this process, the notably enlarged atomic H* generated at the potential more negative than −1.0 V on the Pd/C surface can efficiently reduce BrO₃[−] to Br[−]. When atomic H* can be effectively generated on the cathode surface, corresponding Eq. (2) turns to be as follows:

Then the reduction of BrO₃[−] on the Pd/C electrode proceeds with the indirect mechanism, as Pd serves to concentrate the available hydrogen which can be converted to atomic H*, thereby reducing the influence of pH on the BrO₃[−] reduction. When the potential is set more negative than −2.0 V, the Pd/C electrode achieves a stable electrocatalytic activity, indicating that the exterior of Pd lattice had been saturated with atomic H*. Accordingly, the electrochemical reduction of BrO₃[−] proceeds with divergent mechanisms at different cathode potentials, thereby resulting in the different dependence of BrO₃[−] removal on the pH.

4. Conclusions

The electrochemical reduction of BrO₃[−] at the Pd/C electrode has been exhibited with the generation of Br[−]. The polycrystalline

Pd particles dispersed evenly on the carbon fiber with ca. 40 nm in diameter. The removal of BrO_3^- followed the pseudo-first order kinetics. The rate constant k remained low when the applied potential was higher than -1.0 V and was largely increased at low pH value. In the range from -1.0 to -2.0 V , the electroreduction rate was greatly increased and was hardly affected by solution pH at a relatively low potential. Accordingly, the electrochemical reduction of BrO_3^- was supposed to proceed with direct mechanism at potentials more positive than -1.0 V , and with indirect mechanism via reaction with atomic H^* at potentials more negative than -1.0 V . The strong pH dependence at -0.5 V can be attributed to the transition of chemical equilibrium of the BrO_3^- direct reduction reaction involving H^+ , while the slight pH dependence at -2.0 V was due to that the atomic H^* concentrated on Pd lattice can efficiently reduce BrO_3^- by indirect mechanism. Although Pd catalyst can actively produce adsorbed nascent H^* , the locally excessive H_2 evolution at high Pd loadings would inhibit the BrO_3^- reduction. HOBr and OBr^- were observed both at the unmodified carbon fiber electrode and at the Pd/C electrode during the electroreduction process, which would finally be reduced to Br^- .

Supporting Information Available

Additional figures (schematic of the electrocatalytic reactor employed in this work, EDX patterns of the Pd/C electrodes with various Pd loading amounts, XRD patterns of the carbon fiber electrode and the 0.73 mg/cm^2 Pd/C electrode, and BrO_3^- removal and Br^- formation at the unmodified carbon fiber electrode at different applied potentials) are included in the Supporting Information.

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