



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



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## ABSTRACT

The electroreduction of bromate ( $\text{BrO}_3^-$ ) was investigated at a Pd modified carbon fiber (Pd/C) electrode prepared from  $\text{PdCl}_2$  via electrodeposition method. Pd particles distributed on the carbon fiber substrate uniformly. Under various cathode potentials, electroreduction removal of  $\text{BrO}_3^-$  at pure carbon fiber electrode and the Pd/C electrode were firstly compared. It was observed that nearly no  $\text{BrO}_3^-$  removal was observed within the bias potential of  $-2.0\text{ V}$  at the carbon fiber electrode. At the Pd/C electrode, the removal efficiency of  $\text{BrO}_3^-$  was sharply increased from 24.0% to 58.4% at the cathode potential of  $-1.0$  to  $-1.5\text{ V}$ , which was further increased to be 87.2% at  $-2.0\text{ V}$ . The electrochemical reduction of  $\text{BrO}_3^-$  was strongly pH-dependent at  $-0.5\text{ V}$  and the reduction rate could be enhanced at low pH. While at the potential of  $-2.0\text{ V}$ , a slight pH effect was observed.  $\text{BrO}_3^-$  electroreduction follows pseudo first-order kinetics; the rate constant  $k$  was firstly increased from  $0.016$  to  $0.031\text{ min}^{-1}$  with the increase of the Pd loading amount from  $0.31$  to  $0.73\text{ mg/cm}^2$ , and then was decreased to  $0.018\text{ min}^{-1}$  at a higher Pd loading amount of  $1.05\text{ mg/cm}^2$ . The Pd(0) nanoparticles played a significant role in forming atomic  $\text{H}^*$  to realize indirect  $\text{BrO}_3^-$  reduction. The electrochemical reduction of  $\text{BrO}_3^-$  produces accumulated intermediates of HOBr and OBr<sup>-</sup>, which were subsequently reduced to  $\text{Br}^-$  with the time evolution.

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## 1. Introduction

Bromate ( $\text{BrO}_3^-$ ) is an oxyhalide disinfection byproduct frequently detected in drinking water from ozonation or chlorination of bromide ( $\text{Br}^-$ )-containing source waters [1,2].  $\text{BrO}_3^-$  has been recognized as a potential carcinogen to humans, thereby the World Health Organization (WHO) has strictly regulated  $\text{BrO}_3^-$  level in drinking water [3]. Thus, it is highly desirable to develop effective treatment methods to remove  $\text{BrO}_3^-$  pollutants.

Conventionally,  $\text{BrO}_3^-$  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  $\text{BrO}_3^-$  to  $\text{Br}^-$ , their feasibility in water treatment was limited because of the extended reaction time for BAC treatment and requirement for post-treatment to remove

$\text{Fe}^{2+}$  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  $\text{BrO}_3^-$  from water. For example, Kishimoto and Matsuda reported a novel electrochemical method to reduce  $\text{BrO}_3^-$  to  $\text{Br}^-$  using an activated carbon felt electrode [20].  $\text{BrO}_3^-$  contamination can be removed within a few minutes. But, this process required acidic conditions. Zhao et al. studied the effectiveness of  $\text{BrO}_3^-$  removal by electrochemical reduction at a boron-doped diamond electrode, which can remove nearly 90% of  $\text{BrO}_3^-$  with the applied bias potential of  $-1.0\text{ V}$  within 2 h [21]. The electrochemical process can reduce  $\text{BrO}_3^-$  to  $\text{Br}^-$  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

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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  $18.2 M\Omega cm^{-1}$ ) 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 [ $Pd(NH_3)_2Cl_2$ ] complex (plating solution, 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  $200^\circ C$  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  $7.5 cm^2$  ( $2.5 cm \times 3 cm$ ), 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  $Cu K\alpha$  irradiation from  $5^\circ$  to  $90^\circ$  (in  $2\theta$ ).

## 3. Results and Discussion

### 3.1. Characterization of the Pd/C electrode

The Pd/C electrodes with various Pd loading amounts were first 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<sup>2</sup> Pd/C electrode is approximately 3.4-fold and 1.4-fold higher than that of 0.31 mg/cm<sup>2</sup> and 0.73 mg/cm<sup>2</sup> 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  $26.5^\circ$  is attributed to the highly structured (graphitic) carbon, and the diffraction peaks occurring at  $40.2^\circ$  and  $46.8^\circ$  are assigned to typical Pd metal with face centered cubic crystallographic structure [34,35]. The peaks at  $68.3^\circ$  and  $82.3^\circ$  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

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