Electrochimica Acta 150 (2014) 68–74

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Understanding Persulfate Production at Boron Doped Diamond Film Anodes

Jake Davis, James C. Baygents, James Farrell *

Department of Chemical & Environmental Engineering, University of Arizona, Tucson, AZ 85721-0011, USA

ARTICLE INFO

Article history:
Received 13 August 2014
Received in revised form 30 September 2014
Accepted 21 October 2014
Available online 25 October 2014

Keywords:
Boron Doped Diamond
BDD
Anode
Persulfate
Electrosynthesis

ABSTRACT

This research used molecular modeling and rotating disk electrode experiments (RDE) to investigate possible reaction pathways for persulfate production via electrolysis of sulfuric acid solutions using boron doped diamond (BDD) film anodes. Density functional theory (DFT) modeling indicated that uncatalyzed oxidation of SO_4^{2-} and HSO_4^- occurs at lower potentials than water oxidation, and that sulfate radical species ($SO_4^{-\bullet}$ and $HSO_4^{\bullet}$) may be produced via direct electron transfer, or via reaction with hydroxyl radicals. The RDE experiments indicated that rates of persulfate generation were strongly dependent of the condition of the electrode surface, and that aged electrode surfaces favored water oxidation over direct SO_4^{2-} and HSO_4^- oxidation. Combination of sulfate radical species in solution is the lowest energy pathway for persulfate production. Sulfate radical species may also react with radical sites on the electrode surface and produce chemisorbed intermediates that can stabilize sulfate radical species. Reaction of the chemisorbed intermediates with a bisulfate radical can produce persulfate via a surface catalyzed pathway. However, the activation barriers for this pathway are much higher than those for persulfate production via solution phase species.

1. Introduction

Peroxodisulfuric acid ($H_2S_2O_8$) is a strong oxidizing agent that is used in a wide variety of commercial applications, such as food additives, as a free radical generator in organic chemistry, as a bleaching agent, and as an etchant in printed circuit board manufacturing [1]. The peroxodisulfate anion, also known as persulfate, contains sulfur in the +6 oxidation state, similar to sulfate, but also contains a peroxide bond that makes it a strong oxidant. The standard reduction potential (E°) for the persulfate anion ($S_2O_8^{2-}$) is 2.1 V, which is greater than the value for H_2O_2 ($E^\circ = 1.8$ V) and permanganate (MnO_4^-) ($E^\circ = 1.7$ V) [2,3].

At the commercial scale, persulfate is most commonly produced via oxidation of ammonium sulfate solutions using platinum (Pt) or platinized titanium electrodes at high current densities [4]. Smit and Hoogland extensively investigated the mechanisms associated with persulfate production on platinum electrodes [5–8]. These studies concluded that persulfate formation occurs via discharge of sulfate ions (SO_4^{2-}) on sulfate covered portions of the Pt electrode. Discharge of bisulfate (HSO_4^-) ions followed by reaction with hydroxyl radicals ($HO^\bullet$) was reported to produce peroxomonosulfuric acid (H_2SO_5), also known as Caro's acid. A mechanism involving oxidation of sulfate with hydroxyl radicals ($OH^\bullet$) produced from water oxidation has been proposed by other investigators [9,10].

Recently, several studies have investigated the production of persulfate via oxidation of sulfuric acid using boron doped diamond film (BDD) electrodes [11,12]. These studies have reported that persulfate can be produced at Faradaic current efficiencies greater than 95% using low current densities in sulfuric acid solutions with concentrations greater than 2 M. A previous study in our laboratory found that Faradaic efficiencies for persulfate generation were only 59 to 66% in 2.5 M sulfuric acid at current densities ranging from 80 to 280 mA cm^{-2} [13]. This difference in Faradaic efficiencies suggests that there may be different mechanisms contributing to persulfate production at low and high current densities. Seranno *et al.* studied persulfate production at a current density of 23 mA cm^{-2} using H_2SO_4 concentrations ranging from 0.25 to 5.0 M [12]. The proposed persulfate production

---

* Corresponding author at. 1133 E James E. Rogers Way, Room 108, Tucson, AZ 85721, USA. Tel.: +1 520 621-2465.

E-mail address: farrellj@email.arizona.edu (J. Farrell).

http://dx.doi.org/10.1016/j.electacta.2014.10.104
0013-4686/

mechanism involved the three reactions:

$$HSO_4^- + HO^\bullet \rightarrow SO_4^{-\bullet} + H_2O \tag{1}$$

$$H_2SO_4 + HO^\bullet \rightarrow SO_4^{-\bullet} + H_3O^+ \tag{2}$$

$$SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow S_2O_8^{2-} \tag{3}$$

Note that no sulfate species are oxidized via direct electron transfer in the proposed mechanism. The only competing reaction was the recombination, and subsequent oxidation, of hydroxyl radicals to form oxygen (O_2) and two protons (H^+).

The mechanism of persulfate generation may not only be affected by the current density, but also by the condition of the BDD electrode. Prior to being anodically polarized, the surface of virgin BDD electrodes is hydrogen terminated, and this results in a hydrophobic electrode surface that has little catalytic activity [14–17]. With increasing time and potential of anodic polarization, oxygenated functional groups are incorporated into the electrode surface. These oxygenated functional groups make the surface hydrophilic and change the catalytic activity of the electrode [15–17]. These groups include carboxyl (-COH), carbonyl (C=O) and carboxylate (-COOH). Carbon atoms bound to oxygen on the surface of aged electrodes may be as high as 50% [16], and only a small fraction of this oxygen incorporation is reversible with cathodic polarization [14].

Elucidating the reactions occurring on an electrode surface using only experimental evidence is difficult due to the complex chemistry of the electrode surface and the myriad reactions that may occur to both solution phase and adsorbed species. In recent years, there has been increasing use of density functional theory (DFT) and molecular dynamics (MD) modeling for understanding the reactions occurring at electrode surfaces [18–21]. DFT modeling can be used to calculate the energy barriers for both direct electron transfer reactions and for chemical reactions occurring in the vicinity of the electrode surface. Molecular dynamics simulations are useful for understanding the physical properties of the electrode surface and how these properties affect adsorption of reactant and product species.

Previous studies investigating the reactions leading to persulfate production at BDD electrodes have proposed that H_2O is the only species that undergoes a direct electron transfer reaction at the electrode surface [12]. In contrast, there is strong evidence that persulfate production at Pt electrodes involves discharge of both SO_4^{2-} and HSO_4^- ions [5–8]. Thus, it may be possible that sulfate species are also directly oxidized by BDD anodes. One goal of this research was to investigate whether H_2SO_4, HSO_4^- and SO_4^{2-} can be oxidized via direct electron transfer during persulfate production using BDD anodes. Another goal of this research was to determine the most likely reaction pathways for producing persulfate via electrolysis of sulfuric acid solutions using BDD electrodes. Towards that end, DFT simulations were performed to determine the potential dependence of H_2O, SO_4^{2-}, HSO_4^-, and H_2SO_4 oxidation. DFT simulations were also used to determine the activation barriers and reaction energies for the elementary reactions leading to persulfate production. Rotating disk electrode experiments (RDE) were performed to determine the effect of the electrode surface condition on catalyzing reactions. Lastly, MD modeling was used to investigate the effects of oxygen incorporation into the electrode surface on adsorption of H_2O and sulfate species.

2. Experimental

2.1. Reagents and Analysis

All experiments employed reagent grade sulfuric acid, sodium persulfate and potassium peroxomonsulfate obtained from Fisher Scientific, and 18.2 MΩ cm ultrapure water (UPW). Concentrations of persulfate, peroxomonosulfate, and sulfate were determined using a Dionex ICS-5000 ion chromatograph equipped with a Dionex AS-16-2 column. Solutions were sampled using a 5 mL pipette and 5 mL Dionex auto-sampler vials and were analyzed in triplicate. Samples were immediately analyzed to minimize the effect of persulfate decomposition.

2.2. Rotating Disk Electrode Experiments

A BDD film on a p-silicon substrate with a surface area of 1 cm^2 (Advanced Diamond Technologies (ADT), Romeoville, IL) was used as the working electrode. The ADT electrodes were housed in a Princeton Applied Research (PAR) model 616 RDE asembly and rotated at 1500 rpm. Currents or potentials were controlled using a Gamry Series G model 750 potentiostat/galvanostat Fig 1. A 5 cm long by 0.3 mm diameter platinum wire served as the counter electrode. The counter electrode was housed in Nafion tubing (Permapure, Toms River, NJ) to prevent persulfate reduction. A PAR mercury/mercury sulfate electrode (MSE) saturated with potassium sulfate (E^0 = 0.654 V) served as the reference. The RDE experiments were performed in a jacketed Pyrex® reactor containing 50 mL of sulfuric acid maintained at 20 °C using a recirculating water bath. The electrolysis time was 5 minutes and current densities ranged from 10 mA cm^{-2} to 280 mA cm^{-2}. All electrode potentials are reported with respect to the standard hydrogen electrode (SHE). The effects of electrode aging were investigated by comparing persulfate generation rates on a new electrode with those from an electrode that had been used for more than 10 hours in electrolyzing 1 M sulfuric acid solutions at current densities ranging from 100 mA cm^{-2} to 300 mA cm^{-2}.

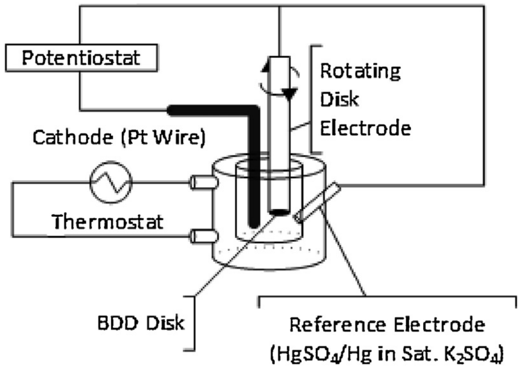

Fig. 1. Schematic diagram of the RDE apparatus.

2.3. DFT Modeling

DFT calculations were performed using the $DMol^3$ [22,23] package in the Accelrys Materials Studio [24] modeling suite using a personal computer. Double-numeric with polarization (DNP) basis sets [25] and the gradient corrected VWN-BP functional for exchange and correlation were used in unrestricted spin calculations. Implicit solvation was incorporated using the COSMO-ibs polarizable continuum solvation model [26]. Simulations with solvated protons also included two explicit water molecules in order to allow for hydrogen bonding and better outlying charge correction for negatively charged species [27]. The BDD surface was modeled using a 10-carbon atom cluster that has been used in previous investigations [16,28].

Apparent activation barriers (E_a) for chemical reactions were calculated by varying the reaction coordinate, defined as the bond length of the bond that was formed or broken during the reaction,