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Continuous electrooxdiation of sulfuric acid on boron-doped diamond electrodes

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ABSTRACT

This study reports on the electrochemical oxidation of highly concentrated sulfuric acid by Diachem® boron-doped diamond electrodes. The scope of this work was to evaluate a proposed continuous electrooxidation process in order to prepare a resist removal bath that contains equivalent amounts of peroxosulfuric compounds as a common SPM (sulfuric acid and hydrogen peroxide mixture) bath. The electrochemical processes at the electrode surface were investigated by cyclic voltammetry and by titration of the reaction products under real working conditions (> 80 wt% H_2SO_4). Furthermore, an alternative electrolysis test cell setup, exhibiting a thin and mechanically stable ion exchange membrane will be used. For this process only one electrolyte circuit is performed. The initial electrolysis product $H_2S_2O_8$ immediately undergoes hydrolysis and forms H_2SO_5. The obtained concentration of H_2SO_5 was similar to a reference SPM bath (> 0.14 mol l^{-1} H_2SO_5 in 90 wt% H_2SO_4), even though the current efficiency was lower than for more diluted solutions. This can be attributed to a complex interplay of side and consumption reactions of peroxosulfuric compounds. This electrolysis bath has the potential to be a very promising alternative to standard SPM baths, as it operates as a continuous and sustainable process.

1. INTRODUCTION

Peroxosulfuric compounds are widely used as bleaching and cleaning agents due to their strong oxidizing properties. The SPM (sulfuric acid and hydrogen peroxide mixture) process is used in the semiconductor industry to remove patterned photoresist after lithography. The mixing of hydrogen peroxide and sulfuric acid forms Caro's acid (H_2SO_5, peroxomonosulfuric acid), which oxidizes the resist [1]. However, a SPM bath becomes diluted by adding more hydrogen peroxide leading to lesser oxidizing ability. Thus, the SPM bath has to be removed, which causes problems in sustainability and long down times. Therefore, it is highly desirable to replace the SPM bath by a continuously working process and in situ regeneration of the oxidant. The electrolysis of sulfuric acid on platinum was often used to produce peroxodisulfuric acid ($H_2S_2O_8$), which was an important intermediate in the production of hydrogen peroxide [2,3]. Peroxodisulfuric acid is known to form peroxomonosulfuric acid at low pH-values. Sulfuric acid is recovered after Caro's acid is consumed, hence the process can in principle be run continuously [4–6]. The efficiency of the peroxodisulfuric production depends strongly on the nature of the anode material. As the discharge of water is a possible side reaction, anodes with a high overpotential for oxygen evolution are required. Usually, carbon electrodes show high overpotentials, but they lack the necessary electrochemical stability towards sulfuric acid. In recent years, synthetic boron-doped diamond (BDD) electrodes have been intensively investigated as a promising electrode material due to their high electrochemical stability [7] and high overpotential for both oxygen and hydrogen evolution [8,9]. Outer sphere reactions proceed completely reversible [10], whereas inner sphere reactions are strongly inhibited at diamond surfaces and only take place in the potential region of water discharge [11]. This is part of the special electrochemistry of BDD in aqueous media, which can basically be attributed to the in-situ formation of loosely adsorbed hydroxyl radicals at the electrode surface [12,13]. The initial step is the decomposition of water to adsorbed hydroxyl radicals (Eq. (1)):

$$H_2O + BDD \rightarrow BDD(OH^{\bullet}) + H^{+} + e^{-} \qquad (1)$$

These radicals desorb and exist in a thin diffusion layer at the electrode due to weak adsorption properties of diamond. They can recombine to hydrogen peroxide or react with a suitable reduction agent in a following reaction step [14]. This can lead to the formation of e. g. exotic and strong oxidation agents such as

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Ag(II) (AgO) [15], Fe(VI) (FeO_4^{2-}) [16], or peroxodisulfate [17]. The assumed electrochemical mechanism on BDD surfaces is different compared to the mechanism of commonly used platinum electrodes. The sulfate anions SO_4^{2-} and HSO_4^- are oxidized directly on the platinum surface to sulfate radicals SO_4^-, which recombine to $H_2S_2O_8$ [18,19]. At the BDD electrode, however, the hydroxyl radical reacts with H_2SO_4 (Eq. (2)) or HSO_4^- (Eq. (3)) to sulfate radicals:

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

$$HSO_4^- + OH^\bullet \rightarrow SO_4^{-\bullet} + H_2O \tag{3}$$

Serrano et al. proposed the above mentioned mechanism and reported on the electrochemical preparation of peroxodisulfuric acid using boron-doped diamond thin film electrodes and sulfuric acid with concentrations below 5 mol l^{-1}, by observing current efficiencies of nearly 95% [17,20]. Recently, Kurita Water Industries published a study about the resist removal properties of electrolyzed sulfuric acid [21]. Both, Zwicker et al. [22] and Hayamizu et al. [23] patented a process using boron-doped diamond electrodes and sulfuric acid as a cleaning system, while Comninellis et al. patented the electrochemical production of peroxodisulfates itself using BDD electrodes [24]. However, up to now, the electrolysis in especially highly concentrated sulfuric acid (≥85 wt%) per se is not further described in the literature.

The aim of this work is to prepare a solution of peroxodisulfuric acid in sulfuric acid equivalent to a common SPM resist removal bath by electrolysis on boron-doped diamond electrodes. Therefore, cyclic voltammetry was performed in highly concentrated H_2SO_4 of more than 85 wt%, which should help to understand the formation and consumption reactions of peroxodisulfuric acid at boron-doped diamond electrodes. Moreover, the formation of $H_2S_2O_8$ in an electrochemical flow cell under galvanostatic conditions is studied in order to investigate the influence of consumption reactions on the formation rate of peroxodisulfuric acid under real working conditions. These experiments play an important role for the design of a test setup to fulfill the special requirements of this process.

3. EXPERIMENTAL

Sulfuric acid was electrolyzed in a symmetric electrolytic flow cell. Both, cathode and anode were boron-doped diamond electrodes (Diachem®) supplied by *Condias*. The boron-doped diamond was coated on p-silicon substrates using hot-filament chemical vapor deposition. The electrodes were inserted in PVDF blocks and pressed against a PVDF frame. The resulting electrolysis chamber had a geometric electrode surface of 20 cm^2 and an inter-electrode gap of 6 mm. The BDD electrodes were contacted on their whole area of the electrode from the back side of the cell in order to avoid inhomogeneous current distributions. A thin cation exchange membrane was placed between cathode and anode to exclude the reaction products from the cathode chamber. Therefore, a very thin membrane was manufactured by infiltrating an ethanolic Nafion solution (*DuPont*) into a hydrophilic Gore PTFE separator as a kind of framework with an average pore size of about 5 μm. This procedure is reported elsewhere [25] and resulted in a very thin, but mechanically stable cation exchange membrane, which was used to separate the cathode chamber from the anode chamber. The separated electrolyte cell was placed in an unconventional setup as it will be described in the following (Fig. 1). Instead of using two half circuits for the anolyte and catholyte, only the anode chamber is flushed with fresh electrolyte. The total electrolyte volume measured 1 liter for all experiments with the flow cell. Electrolysis products are removed from the cell with the electrolyte flow and stored in PP-bottles, in which they were mixed with the residual electrolyte, thermally equilibrated by a temperature control device, and pumped into the electrolyte cell back again by PTFE membrane pumps as fast as possible assuming homogeneous mixing of the electrolyte and equilibrium between the electrolysis cell and electrolyte reservoir. The only convection at the cathode surface is caused by gaseous electrolysis products (Fig. 1).

The concentration of electrolysis products were determined offline by titration. H_2O_2 was titrated using $KMnO_4$. The sum of peroxosulfuric species was back titrated with $FeSO_4$ and $KMnO_4$. The electrolyte was titrated iodometrically with KI and NaS_2O_3 to determine the peroxomonosulfuric acid concentration [26,27].

Cyclic voltammetry measurements were carried out using a double walled three electrode glass cell (*Radiometer Analytical*). A saturated calomel electrode was used as a reference electrode, boron-doped diamond as the working electrode and a platinum plate (*Alfa Aesar*, 99.9%) as the counter electrode. The data was collected using a potentiostat from *Iviumstat*. The electrolyte was degassed under argon flow for 30 min before the measurement was started.

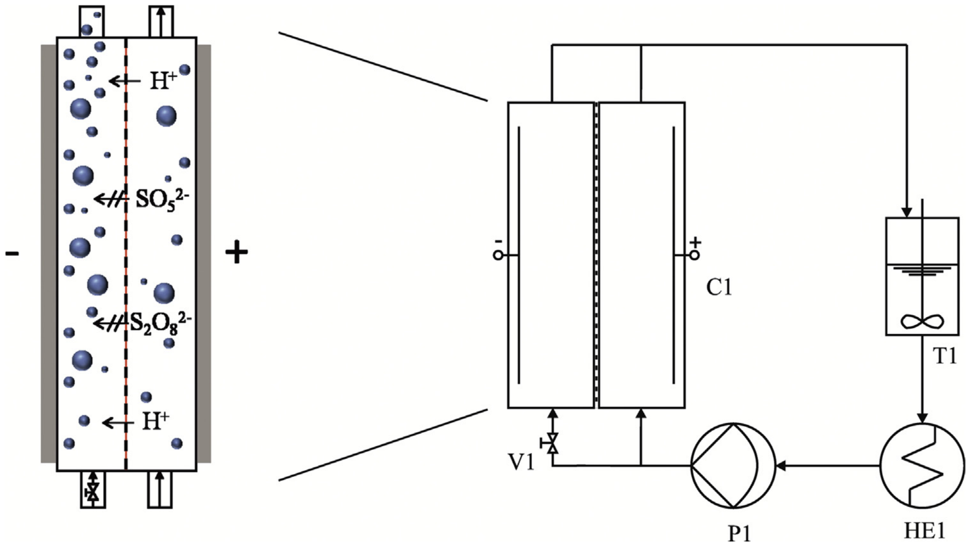

Fig. 1. Schematic description of the modified electrolyte cell with two half cells separated by a manufactured Nafion membrane (left) and technical drawing of the setup used for electrolysis of H_2SO_4 on BDD (right); C1 electrolytic flow cell, P1 PTFE membrane pump, HE1 PFA heat exchanger, V1 valve, T1 electrolyte reservoir.