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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)):

$$H_2O + BDD \rightarrow BDD(OH^\bullet) + H^+ + e^- \quad (1)$$

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.

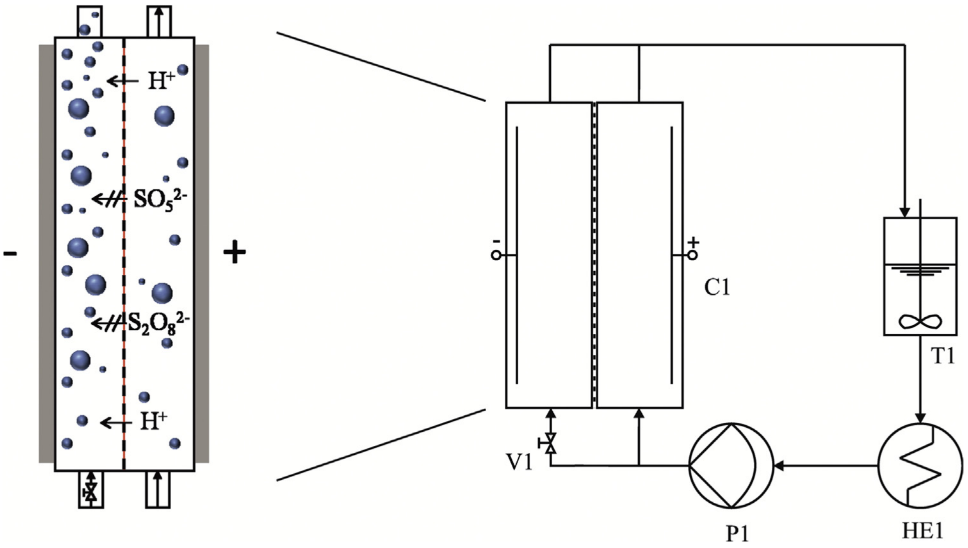

Fig. 1. Schematic description of the modified electrolyte cell with two half cells separated by a manufactured Nafion membrane (left) and technical drawing of the setup used for electrolysis of H_2SO_4 on BDD (right); C1 electrolytic flow cell, P1 PTFE membrane pump, HE1 PFA heat exchanger, V1 valve,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

Small-angle X-ray scattering data were collected using a NANOSTAR instrument from Bruker with Cu-$K_{\alpha1}$ radiation. The scattering was detected from 0 to 3 °2θ. Samples were activated and located within a copper sample holder for measurement. Atomic force microscopy was performed on a *Dimension D3100 from Veeco Digital Instruments* and the surface roughness was determined with a *RS-232* portable surface measurement device from *ATP-Messtechnik*. X-ray photoelectron spectroscopy measurements were carried out using a *SPECS Phoibos 100* with Mg-$K_{\alpha1}$ radiation and an acceleration voltage of 12.5 kV.

4. RESULTS AND DISCUSSION

The BDD electrode is characterized regarding to its morphology, chemical composition and electrochemistry in order to get a better understanding of the peroxodisulfuric acid formation and consumption at boron-doped diamond electrodes. Moreover, the formation of $H_2S_2O_8$ in an electrochemical flow cell under galvanostatic conditions is studied under real working conditions. These experiments influenced directly the specific tailoring of the experimental flow cell equipment.

4.1. Electrode characterization

The morphology of the boron-doped diamond electrodes was investigated by atomic force microscopy. The sample exhibits randomly ordered diamond crystallites with an average size of 3 µm and round aggregates indicating amorphous regions (Fig. 2) being revealed by Raman spectroscopy (see supporting information). The electrode surface shows a R_a and R_z roughness of 4 and 23.5 µm, respectively, measured by a portable surface measurement device (see supporting information). X-ray photoelectron spectroscopy of the electrode determined a boron concentration of 8700 ppm.

4.2. Electrochemical measurements

Due to their high overpotential for oxygen- and hydrogen generation, as well as their weak interactions with redox couples, the electrochemical properties of BDD electrodes are unique and favorable. The cyclic voltammogram of a BDD electrode shows a wide potential range between -1.0 V and 2.0 V vs. SCE in which aqueous electrolytes remain stable (Fig. 3). Moreover, the BDD electrode indicates a low background current in the double layer domain. To investigate the electrochemical behavior in terms of the generation of peroxodisulfuric acid, cyclic voltammograms with different amounts of sulfuric acid and peroxodisulfuric acid were measured. In pure 1 M H_2SO_4, the measured reversible redox couple at 1.5 V vs. SCE is attributed to semi-hydroquinone/semi-benzoquinone functional groups, which were proposed to be present on the surface of the BDD electrode by Kapałka et al. (Fig. 3) [14]. This observation is consistent with graphitic and amorphous carbon regions at the electrode's surface (Fig. S1). Comninellis and co-workers assigned the cathodic peak at -1.0 V (inset) vs. SCE to the reduction of $H_2S_2O_8$ (Eq. (4))[20], however, the reduction peak at 0.1 V vs. SCE remains still unclear.

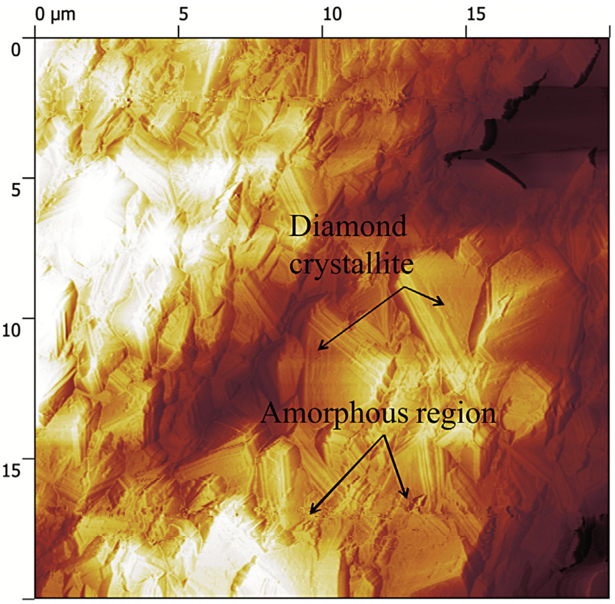

Fig. 2. Atomic force microscopy of the BDD electrode surface scanned in tapping mode with a resonance frequency of 150 kHz.

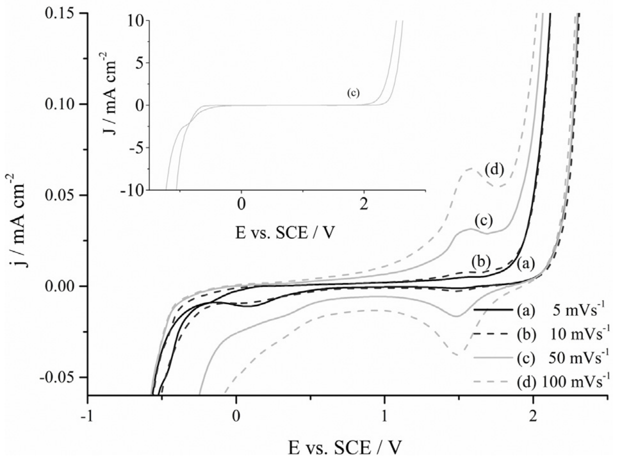

Fig. 3. Cyclic voltammogram of boron-doped diamond electrodes in 1 M H_2SO_4 at different scan rates, T = 21 °C, reference electrode SCE, counter electrode platinum, lower magnification in the inset.

$$H_2S_2O_8 + 2H^+ + 2e^- \rightarrow 2H_2SO_4 \qquad (4)$$

Since it is known that BDD electrodes show no significant adsorption peaks for hydrogen [28], the reduction peak at 0.1 V vs. SCE may originate from another redox couple on the surface of the diamond, as its intensity increases with higher scan rates and is suppressed in highly concentrated H_2SO_4.

For the application as a resist removal bath in the semiconductor

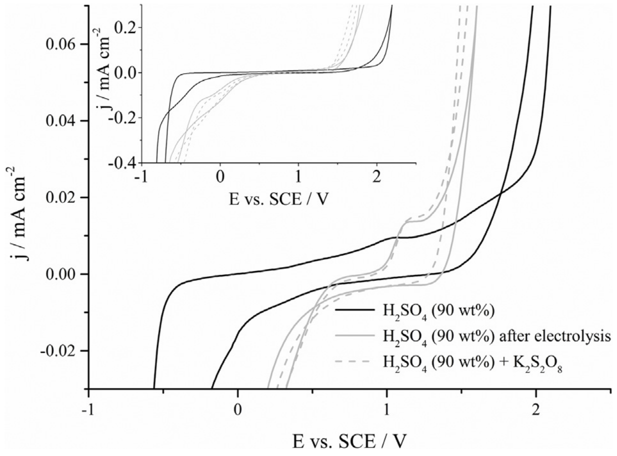

Fig. 4. Cyclic voltammogram of boron-doped diamond electrodes in H_2SO_4 (90 wt %), before and after electrolysis, and after addition of $K_2S_2O_8$, scan rate = 50 mV s^{-1}, T = 21 °C, reference electrode SCE, counter electrode platinum, lower magnification in the inset.

industry or for the production of peroxodisulfates, the electrolyte concentration of 1 M H_2SO_4 is too low. Thus, we investigated the electrochemical behavior of BDD in 90 wt% H_2SO_4 before and after electrolysis. Under these conditions the semi-hydroquinone/semi-benzoquinone redox couple is fully suppressed (Fig. 4). After 400 min of electrolysis, a peroxodisulfuric acid concentration of 0.16 mol l^{-1} was determined by titration. In addition to the cathodic reduction peak at 0 V vs. SCE, the cyclic voltamogramm shows another peak of an anodic, irreversible reaction at 1.1 V vs. SCE. To elucidate the origin of the latter peak, an equal amount of $K_2S_2O_8$ was added to 90 wt% H_2SO_4. The resulting cyclic voltammogram shows the same cathodic reduction peak at 1.1 V vs. SCE and is therefore attributed to an oxidation reaction of either peroxomonosulfuric acid or peroxodisulfuric acid. It is known that peroxodisulfate undergoes an acid catalyzed hydrolysis forming sulfuric acid and peroxomonosulfuric acid (Eq. (5))[6]:

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \quad (5)$$

To gain further information, we performed an Iodometric titration, which confirms the hydrolysis of peroxodisulfate to peroxomonosulfate in 90 wt% H_2SO_4 during the electrolysis, even at ambient temperature (Table 1). Additionally, peroxodisulfate remains stable in 1 M H_2SO_4, due to the absence of this peak at 1.1 V vs. SCE in diluted H_2SO_4 (Fig. 3). Therefore, we conclude that this behavior can be attributed to the oxidation of peroxomonosulfate (Eq. (6)):

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + O_2 + 2H^+ + 2e^- \quad (6)$$

This oxidative consumption was only described for platinum electrodes [28] and implies a distinctive interaction between the electrolyte and the electrode [29]. The observed oxidation potential of 1.1 V vs. SCE is by 0.711 V higher than the standard potential J. Balej gave (0.389 V vs. SCE). This over voltage is attributed to a high electrolyte concentration (90 wt%) and weak interactions between boron doped diamond and the electrolyte [30]. The anodic and cathodic consumption reactions of peroxodisulfuric acid, as well as the side reactions of the hydroxyl radicals affect the process described below and considerably reduce the current efficiency.

4.4. Electrochemical generation of Caro's acid by oxidation of sulphuric acid

Due to the reduced current efficiency the described consumption reactions (4), (5), and (6) will limit the yield of the product. Sulfuric acid was oxidized in an electrochemical flow cell and different parameters were adjusted to elucidate the influence of the side reactions on the current efficiency under real working conditions. For this purpose, the temperature of the electrolyte, the current density, and the electrolyte concentration have been systematically altered and the results were investigated by titration of the reaction products. The electrolyte circuit and the flow cell were used as described in chapter 2, except that Valve V1 was opened during the electrolysis and the membrane was removed. Hence, anodic and cathodic reactions can take place.

Table 1
H_2SO_5 and $H_2S_2O_8$ sum and H_2SO_5 single concentration in 90 wt% H_2SO_4 at different working temperatures and different time determined by iodometric titration and back titration with $FeSO_4$ and $KMnO_4$ respectively.

T/°C	$c_{H2SO5+H2S2O8}$/mol l^{-1}	c_{H2SO5}/mol l^{-1}
10	0.055	0.056
21	0.135	0.144
55	0.064	0.064

During the electrolysis the concentration of H_2O_2 and $H_2S_2O_8$ (representative for the sum of H_2SO_5 and $H_2S_2O_8$, determined by titration against Fe^{2+}, even though the predominant peroxosulfate species in solution is H_2SO_5) was constantly monitored to verify how ongoing reactions interact. In the early stage of the electrolysis, the concentration of the peroxodisulfuric acid increases rapidly and the current efficiency reaches 40% (see supporting information). A steady state is achieved at 21 °C after 1000 min and the current efficiency decreases to 0% until the peroxodisulfuric acid reaches a plateau of 0.13 mol l^{-1} (Fig. 5). The current is completely extinguished by side reactions, due to complex anodic and cathodic consumption reactions (*vide supra*) (Fig. 6). One byproduct of the electrolysis is hydrogen peroxide, which was detected by titration. A plateau concentration of 0.01 M was observed after 600 min at 21 °C and was formed either by the recombination of two hydroxyl radicals (Eq. (7)) or by the hydrolysis of Caro's acid (Eq. (8)):

$$2OH^{\bullet} \rightarrow H_2O_2 \quad (7)$$

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2 \quad (8)$$

Hydrogen peroxide decomposes thermally and electrochemically [31]. Another side-reaction is the generation of oxygen, which was detected by hydrogen-oxygen reaction, and the formation of ozone [29]. These competitive reactions of the hydroxyl radical limit the current efficiency in the early stage of the electrolysis, even when the product concentration is still low. Iodometric titration revealed that the major peroxosulfuric species is Caro's acid even at 10 °C (Table 1). This shows that $H_2S_2O_8$, being the primary reaction product, forms immediately H_2SO_5 and is consumed at both cathode and anode, following reactions (4) and (6). The consumption rate increases with the concentration of H_2SO_5 and limits the current efficiency in the later stage of the electrolysis when the plateau concentration is reached. In previous works, the side reactions have not been taken into account, because the electrolyte concentrations have been much lower and the final product concentration only reached levels that do not cause significant electrochemical decomposition [17,20,32]. Recently, Davis et al. reported the formation of a plateau concentration in a circulated electrolyte bath at even lower sulfuric acid concentrations, which stands in good agreement with our results [33].

4.4.1. Influence of the working temperature on the process

No significant differences between 10 °C, 21 °C, and 55 °C working temperature are observed at the early stage of the

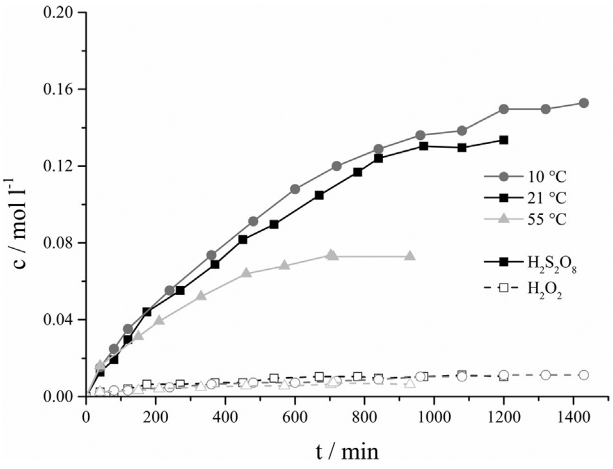

Fig. 5. Concentrations of $H_2S_2O_8$ and H_2O_2 vs. time in sulfuric acid (90 wt%) using three different working temperatures, current density = 0.15 A cm^{-2}.

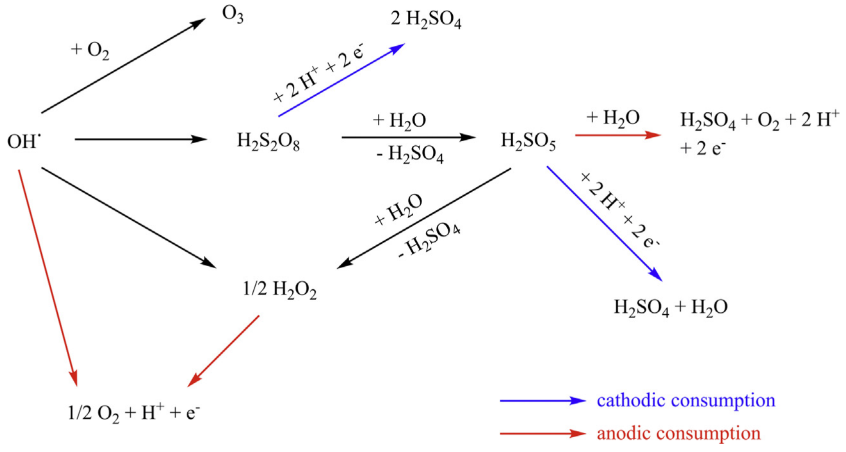

Fig. 6. Possible reaction paths of hydroxyl radicals after desorption, including anodic and cathodic consumption reactions.

electrolysis (<150 min), whereas the plateau concentration reaches only 0.07 mol l^{-1} for 55 °C instead of 0.14 mol l^{-1} for 10 °C (Fig. 5). Thus, the anodic and cathodic consumption reactions are influenced much more by increased temperatures than the competitive side reactions. The thermal decay of H_2SO_5 can be neglected at this temperature values, because the product concentrations remained stable for 2 h at 55 °C. The setup had to be cooled down to 21 °C for further experiments, as the process generates heat and the electrolyte's temperature rises without a heat exchanger cooling down the electrolyte.

4.4.2. Influence of current density on the process

The current density was examined in the range from 0.05 to 0.5 A cm^{-2} (Fig. 7). An increasing current density leads to a higher concentration of hydroxyl radicals causing a faster increase of the peroxodisulfuric acid concentration. The formation rate of peroxodisulfuric acid increases linearly with the current density and the plateau concentration is already reached at 600 min for 0.5 A cm^{-2}, (note that other settings still generate peroxosulfate after 600 min). Hence, the formation and the consumption reactions of peroxodisulfuric acid are accelerated to the same degree by increasing current densities and no diffusion processes or slow reaction steps seem to limit the process in the observed current density range. The influence of the current density is less pronounced (Fig. S4). Davis et al. reported a similar behavior for current densities from 0.1 to 0.3 A cm^{-2} and more diluted electrolyte concentrations showing that this process runs current limited over a wide range of parameters [33]. As a result of higher peroxodisulfuric acid concentrations, the hydrogen peroxide concentration increases as well. This supports the formation of H_2O_2 via Reaction (5) and (8) rather than via reaction (7).

4.4.3. Influence of electrolyte concentration on the process

This parameter is limited to concentration restrictions of a resist removal bath and was varied from 95 wt% to 90 wt% and 85 wt%, respectively (Fig. 8). Serrano et al. reported an increasing formation rate of peroxodisulfuric acid with rising electrolyte concentration up to 40 wt% H_2SO_4 since hydroxyl radicals only react with molecular sulfuric acid or hydrogen sulfate and their amount rises constantly with higher mass fractions of H_2SO_4 [20,34]. In contrast, the formation rate of $H_2S_2O_8$ and the plateau concentration decrease with increasing concentrations from 85 wt % to 90 wt%. An explanation for this observation might be that in a solution of more than 76 wt% of pure H_2SO_4 in H_2O practically contains no free water, which is not solvated to a proton and the equilibrium (Eq. (9)) is strongly shifted to the right side.

$$5H_2SO_4 + H_2O \leftrightarrow HSO_4^- + H_3O^+ \qquad (9)$$

Water is essential for the first step of the peroxodisulfate formation comprising the water discharge and the hydroxyl radical formation. Consequently, the hydrogen peroxide and peroxodisulfate concentration decreases and electrochemical consumption reactions must increase to consume the electrical charge at the electrodes under galvanostatic conditions. Lower overvoltages and

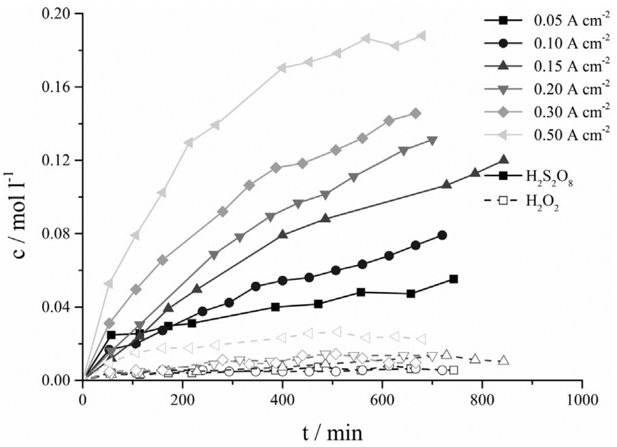

Fig. 7. Concentrations of $H_2S_2O_8$ species and H_2O_2 vs. time in sulfuric acid (90 wt%), constant temperature (21 °C) using six different current densities.

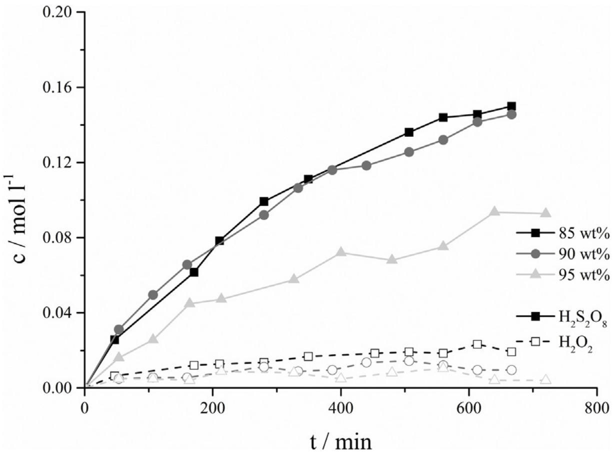

Fig. 8. Concentrations of $H_2S_2O_8$ and H_2O_2 vs. time at constant temperature (21 °C), constant current (0.15 A cm^{-2}) using three different H_2SO_4 concentrations.

current densities minimize this effect. It is not clear which consumption reaction is more crucial regarding to the current efficiency. At these concentrations, no free water is present in solution and H_2SO_4 molecules are not fully hydrated and may even form polysulfuric acids. Hence, there are many details involved in this electrolysis, which are not fully understood at this point.

5.1. Development of an adjusted flow cell design

The previous experiments revealed that both competitive reactions and consumption reactions limit the current efficiency. The current density does not show any significant influence on these mentioned reactions. A promising approach concerning the efficiency enhancement is to remove the anodic reaction products frequently, thus to prevent cathode contact as well as critical concentrations.

Usually, an electrolyte cell is separated by an ion exchange membrane to isolate the cathode from the anode chamber. Commercially available membranes such as Nafion failed under these conditions. Their ion conductivity is too low to ensure the required current densities. As a result, the electrical current collapsed after a few seconds. Verbrugge et al. showed that the ion conductivity of perfluorosulfonic acid membranes decreases with increasing sulfuric acid concentrations due to the decreasing water content of the membrane [35]. Small angle X-ray scattering showed that the ionomer peak still exists after treatment with 90 wt % H_2SO_4, but it is shifted to higher q-values (Fig. 9). A higher q-value indicates a smaller average distance L between the solvent clusters in the membrane (Eq. (9)), which is attributed to the partial dehydration of the membrane and therefore, decreasing ion conductivity [36–38]:

$$L = 2\pi/q \qquad (10)$$

A thinner membrane gives better ion conductivities, but thinner membranes usually suffer from the mechanical stability being required in a flow cell. Therefore, a commercial, hydrophilic, and porous PTFE separator was impregnated with an ethanolic Nafion solution according to Nouel and Fedkiw [25]. This thin, but mechanically stable cation exchange membrane was implemented in a special setup that was designed to meet the requirements of this process. The membrane divides the electrolyte cell in two compartments. Usually, such a cell requires two different electrolyte loops. Recently, Kobayashi et al. patented a setup in which the electrolyte circulates successively in the cathotic chamber before it enters the anodic chamber. Anodic and cathodic compartments are separated only by a diaphragm [39]. If the electrolyte enters the anodic chamber in a consumed and peroxodisulfate depleted condition (after it was used in a resist removal bath), less peroxodisulfuric acid will face the cathode and the cathodic reduction of $H_2S_2O_8$ (Eq. (4)) will be reduced. If the electrolyte enters the cathode chamber after recirculation containing considerable amounts of $H_2S_2O_8$, reaction (4) will take place.

In our work, the electrolyte is pumped exclusively through the anode chamber. The cathode chamber is filled with electrolyte and closed by a valve prior to the electrolysis start. Only one electrolyte loop is necessary, which is highly desirable in an industrial process. The proton gradient, which is formed during electrolysis, can only be destroyed by convection of the rising hydrogen bubbles and diffusion (Fig. 1). In contrast to the setup of Kobayashi et al. using a diaphragm and a series connection of anode and cathode chamber, peroxodisulfuric acid is excluded from the cathode chamber by the membrane in order to avoid the reductive consumption (Eq. (4)). After the electrolysis was started, no electrolyte leaching was observed from the cathode chamber demonstrating that the membrane works successfully as a pneumatic barrier. A maximum current density of 0.25 A cm^{-2} was reached and no loss of membrane material was detected after an electrolysis period of 3.9 Ah cm^{-2}. No significant benefits were noticed until the peroxodisulfuric acid concentration reaches 0.08 mol l^{-1} (Fig. 10). After this point, the new Nafion/PTFE hybrid membrane setup produces more peroxodisulfuric acid compared to the setup without membrane. The membrane is expected to eliminate only the cathodic consumption reaction. Hence, the competitive reactions, which are dominating the early stage of the electrolysis, are not suppressed and anodic consumption is still present leading into a plateau of 0.16 mol l^{-1} $H_2S_2O_8$. Nevertheless, the plateau concentration could be increased by 0.02 mol l^{-1} due to the implementation of the developed membrane. This is the first time, a mechanically stable Nafion membrane was implemented in electrolysis process for the generation of peroxodisulfuric acid in highly concentrated sulfuric acid. Furthermore, a membrane is essential for industrial use, because gaseous byproducts, namely oxygen and hydrogen, can form explosive mixtures.

This modified setup was used to prepare 0.1 mol peroxodisulfuric acid in 90 wt% sulfuric acid (5.9 V, 3 A), which is equivalent to a reference SPM-bath (50:1H_2SO_4:H_2O_2, 100 °C), with an average current efficiency of 18.8% and a specific energy consumption of 8.66 kWh per kg $H_2S_2O_8$. This concentration stays constant by further electrolysis without changing or diluting the bath.

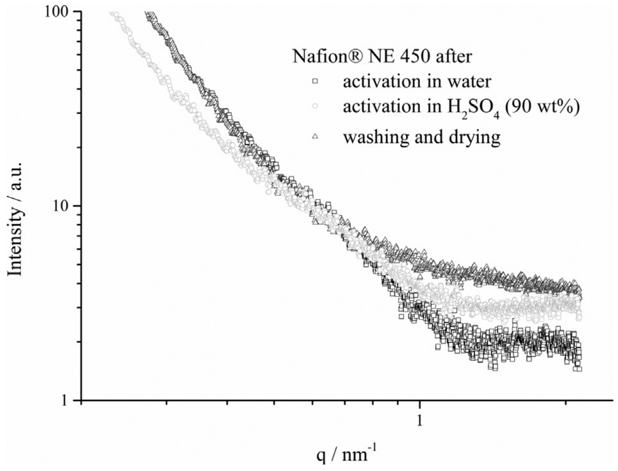

Fig. 9. Small angle X-ray scattering curves of Nafion NE 450 membranes after different activation procedures at room temperature.

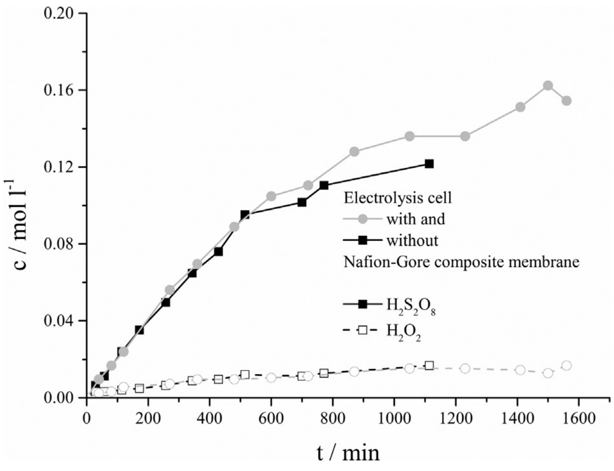

Fig. 10. Concentrations of $H_2S_2O_8$ and H_2O_2 vs. time in sulfuric acid (90 wt%), current density = 0.15 A cm^{-2} for electrolysis cell with and without Nafion membrane.

6. CONCLUSIONS

In this work, the electrolysis of highly concentrated sulfuric acid to peroxodisulfuric acid by BDD electrodes was investigated. The morphology of the BDD electrode was characterized and the electrochemical behavior of BDD in 90 wt% was analyzed by cyclic voltammetry revealing that both anode and cathode consume the electrolysis product. Electric current density only has a marginal influence on the current efficiency in the electrolytic flow cell, whereas the high electrolyte concentration initiates hydrolysis and consumption reactions that are responsible for the lower current efficiency [20]. SAXS measurements confirmed that conventional membranes exhibit too low ion conductivities and are thus not suitable for our requirements. Therefore, a porous PTFE-separator was impregnated with a Nafion solution resulting in a thinner but mechanically stable ion exchange membrane that was implemented in a specifically designed setup for the electrooxidation of sulfuric acid. This approach successfully hindered the peroxosulfuric acid reduction at the cathode and improved the performance of the process. Finally, a peroxodisulfate concentration was achieved as a steady state that is equivalent to a common SPM resist removal bath with a current efficiency of 18.8% without dilution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2014.09.133.

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