Peroxodisulfate Measurement Using Boron-Doped Diamond Electrodes

Ch. Provent, Ph. Rychen

Diamond electrodes were used for the amperometric measurement of peroxodisulfate concentrations in various media. A linear relationship of the current density as a function of the concentration was observed for both highly concentrated solutions and more diluted ones. Such results consider the monitoring of peroxodisulfate during production and disinfection processes.

Peroxodisulfates are strong oxidizing species with various applications. Among others two particularly interesting applications of these compounds are, on one hand, their use as the efficient oxidizing reagent for chemical synthesis, and on the other hand their capacity to act as a non-halogenated agent for water disinfection, e.g. in swimming pools [1]. For these applications, as well as for the control of the peroxodisulfate production processes, it would be of interest to monitor the peroxodisulfate concentration with a maintenance-free and cost-effective electrochemical sensor.

Thanks to their wide potential window and high stability in the presence of strong oxidizing species, boron-doped diamond (BDD) electrodes are particularly suited to perform electrochemical reactions with the peroxodisulfate/sulfate redox couple. Boron-doped diamond electrodes are known to be particularly efficient to oxidize sulfate into peroxodisulfate for production [2] and analytical purposes. Some results show how the possibility to reduce peroxodisulfate with BDD-electrode can be used for the on-line measurement of its concentration.

Electrochemical measurements were performed with a conventional three-electrode system using a classical Ag/AgCl/KCl 3 M reference electrode. Diamond rotating disk electrodes (RDE) and microdisc-array electrodes were both used as working electrodes, with platinum and an integrated doped-diamond counter-electrode, respectively. Measurements were performed in mineral acid (H_2SO_4) and sodium sulfate solutions (Na_2SO_4).

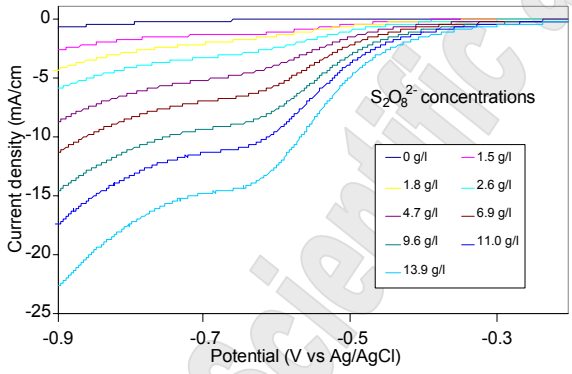

Figure 1: Voltametric curves of solutions of sodium peroxodisulfate in 1 M sulfuric acid (RDE 2000 rpm)

Figure 1 represents the voltametric curves obtained by measuring solutions with concentrations between 0 and 14 g/l of peroxodisulfate in sulfuric acid. In this medium, the limiting current for the reduction of peroxodisulfate into sulfate is observed between –0.6 and –0.8 V vs. Ag/AgCl/KCl 3M. Figure 2 shows the linearity of the current density for a potential of -0.7 V as a function of the peroxodisulfate concentration.

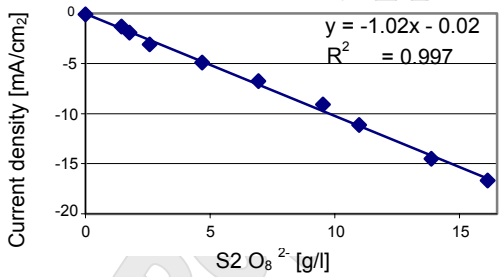

Figure 2: Evolution of the current measured at -0.7 V vs Ag/AgCl/KCl 3 M as vs. the peroxodisulfate concentration in sulfuric acid

With the aim of monitoring the disinfectant concentration, measurements were performed in typical pool water. In this media, the peroxodisulfate reduction takes place at –0.8 V vs. Ag/AgCl/KCl 3M and the limit of the reliable detection with RDE is approximately 1 g/l. With microdisk arrays, minimum detectable concentrations in the range of 50 ppm is expected.

The monitoring of industrial processes, such as peroxodisulfate production in acidic solutions or recycling of peroxodisulfate micro-etchant baths, is an interesting issue for a robust electrochemical sensor based on boron doped diamond technology. Typical process data for sodium peroxodisulfate production are: sulfuric acid concentration from 140 to 280 g/l, sodium sulfate concentration from 250 to 420 g/l and sodium peroxodisulfate from 50 to 280 g/l. Even in those highly concentrated solutions, amperometric measurements with diamond electrodes show a good linearity under higher cathodic potential (–1.3 V vs Ag/AgCl/KCl 3M) (Fig. 3).

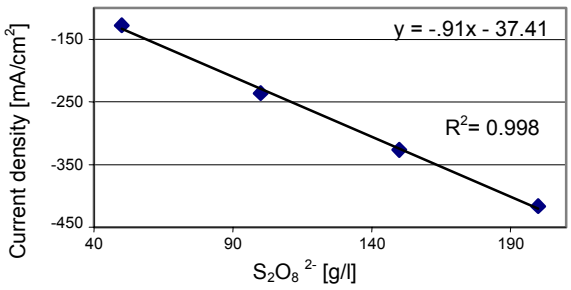

Figure 3: I(at -1.3V) = f ($C_{peroxodisulfate}$) in a H_2SO_4 (160 g/l) / Na_2SO_4 (240 g/l) solution (RDE 2000 rpm)

These results represent the basis for future development projects.

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[1] See www.hygieneinspektoren-nrw.de/bvh-info-schwimmbadwasser.pdf

[2] P.A. Michaud, E. Mahé, W. Haenni, A. Perret, Ch. Comninellis, "Preparation of Peroxodisulfuric Acid Using Boron-Doped Diamond Thin Film Electrodes", Electrochemical and Solid-State Letters, 3(2) (2000) Letters online