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Boron-doped diamond electrodes and microelectrode-arrays for the measurement of sulfate and peroxodisulfate

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Abstract

Measurements of sulfate and peroxodisulfate concentrations with boron-doped diamond (BDD) electrodes and microelectrode array electrodes have been performed in various media. Diamond electrodes allow the measurement of sulfate on the anodic side of the electrochemical window through its oxidation into peroxodisulfate, and detection of peroxodisulfate on the cathodic side through the reverse reduction reaction. In all cases, current density was proportional to solution concentrations. The effect of the doping level (boron concentration) of the diamond films on these measurements was evaluated. Some industrial applications of this technology are foreseen.
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1. Introduction

Synthetic diamond films have attracted much attention during the last decades due to their unique properties. Conductive boron-doped diamond (BDD) films have been shown to be particularly interesting materials for electrochemical purposes [1–10]. These films have properties such as high stability in the presence of strong oxidizing species, good chemical and electrochemical stability and low background current. The latter is especially attractive for electroanalytical applications. One interesting property of BDD electrodes is their wide potential window and the high potential at which oxygen evolution occurs by water oxidation [4,5]. These properties make BDD electrodes particularly suited for electrochemical reactions with compounds that have highly positive standard potentials and which cannot be detected or produced using classical electrode materials.

BDD films can be used without further modification as macroelectrodes or can be micro-structured to get microelectrode designs. With disc microelectrodes, a very efficient hemispherical diffusion is achieved. This enhanced diffusion brings: (1) much higher current density, which translates into a higher signal to noise ratio; (2) a low dependence on hydrodynamic conditions, because sensing is done within the diffusion layer; (3) a short equilibration time after applying a potential step; (4) the possibility to work in high resistive media, due to the limited ohmic drop within a small area close to the electrode. The disadvantage is a small total current which can be a problem particularly for trace detection. But this drawback is largely avoided by the use of an array of microelectrodes, instead of a single microelectrode. In a well-designed array the current is greatly increased (100-fold) while retaining the single microelectrode benefits. CSEM has developed various designs of microdisc array electrodes (with microelectrodes of 5–15 μm in diameter, each of them separated by 150 or 300 μm), in materials such as BDD, amorphous carbon or metal (Au, Pt), and used them for analytical method for the analysis and monitoring of aqueous media [5,11,12]. Some of the work presented here has been performed with a chip that contains boron-doped diamond microdisc array electrodes (BDD/Si MDA) such as that represented in Fig. 1. This chip is composed of an array of microelectrodes each of them having a diameter of 5 μm. The distance between two micrelectrodes is 150 μm. This chip also integrates a crook-shaped boron-doped diamond counter electrode, which surround the microdisc array. The three-electrode

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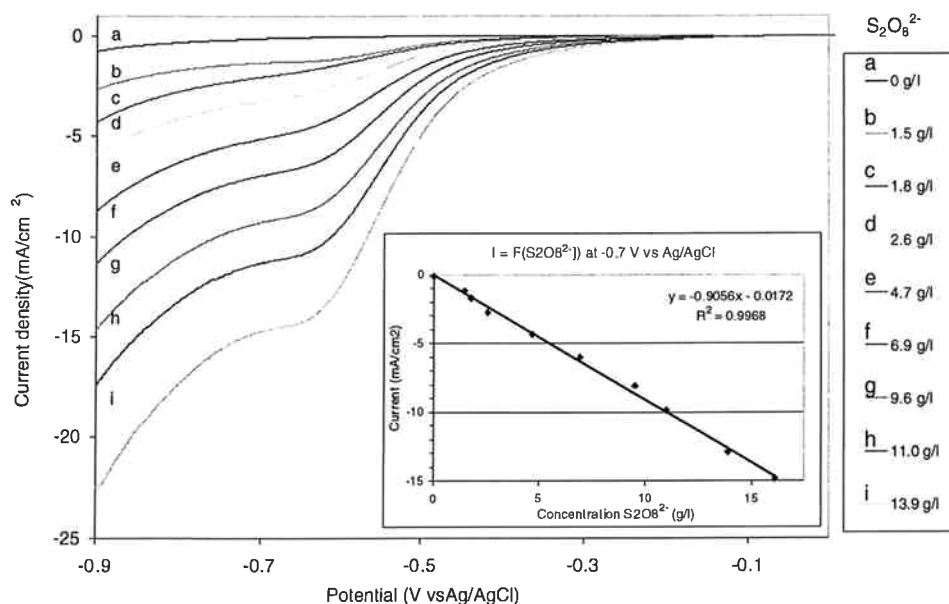*E-mail address:* pry@csem.ch (P. Rychen).

Fig. 4. Voltametric curves and plot of the current density value for a potential of $-0.7\,V$ as a function of sodium peroxodisulfate concentration for solutions of sodium peroxodisulfate in 1 M sulfuric acid (BDD RDE 2000 rpm; scan rate 100 mV/s).

chart also shows the effect of rotation rate on the oxidation response.

The same cyclic voltametry measurements were performed with the microdisc array electrode shown in Fig. 1. As observed with the rotating disk electrode, the evolution of the current density as a function of the sulfuric acid concentration showed good linearity ($R^2 = 0.996$) (Fig. 3).

The detection limit observed with BDD electrodes for such measurement is in the gram per liter range and during these tests, no modification of the electrode response was observed. The measurements of sulfate could also be performed with other amperometric techniques, particularly if a monitoring application is targeted.

3.2. Peroxodisulfate measurement

Peroxodisulfate can be generated electrochemically from sulfuric acid and potassium, sodium or ammonium sulfate salts and it would be useful to be able to monitor its concentration during this process. In order to evaluate if such measurement is possible, peroxodisulfates were analyzed by cyclic voltametry in sulfuric acid (H_2SO_4) and sodium sulfate solutions (Na_2SO_4). These measurements were first performed at rather low concentrations compared to those observed in production reactors. These measurements were performed with the conventional three-electrode system, using the same electrodes (BDD rotating disk electrode and microdisc array electrode) as for sulfate detection. Fig. 4
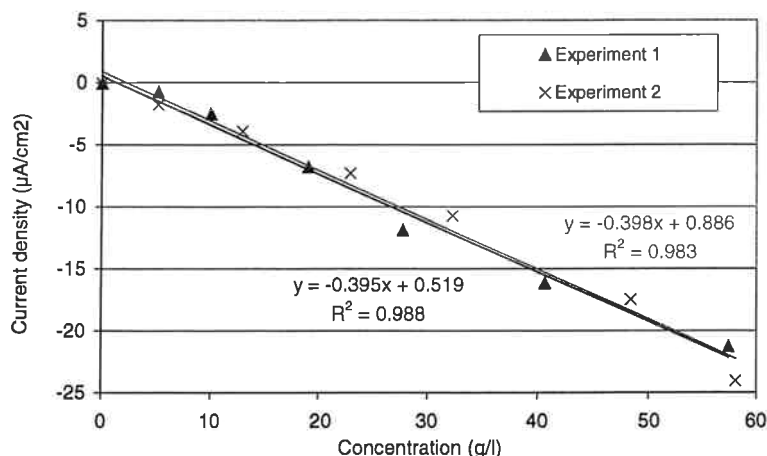

Fig. 5. Evolution of the current density measured at $-0.6\,V$ as a function of the peroxodisulfate concentration in 1 M sulfuric acid. Both measurements were performed with the same BDD MDA.
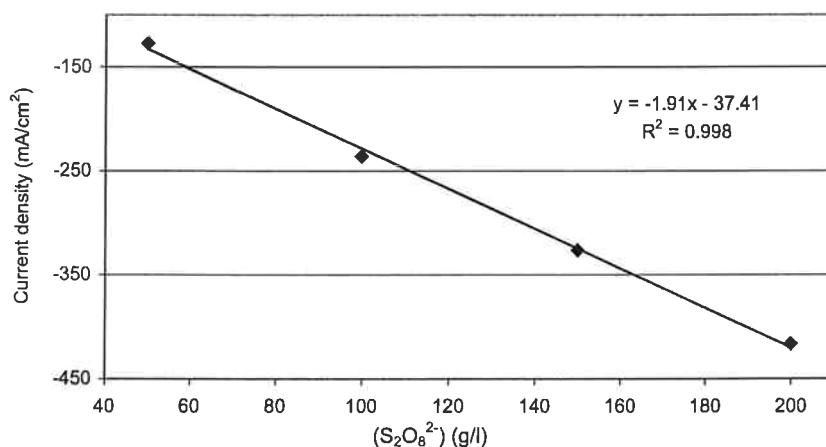
Fig. 6. Current density measured at -1.3 V as a function of $[S_2O_8{}^{2-}]$ in a H_2SO_4 (160 g/l)/Na_2SO_4 (240 g/l) solution (RDE 2000 rpm).

shows the voltametric curves obtained by measuring solutions of concentrations between 0 and 14 g/l of sodium peroxodisulfate in 1 M sulfuric acid with a rotating disc BDD electrode. In this medium, the limiting current for the reduction of peroxodisulfate into sulfate is observed between -0.6 and -0.8 V versus Ag/AgCl/KCl 3 M and the chart inset in Fig. 4 shows the linearity of the current density for a potential of -0.7 V as a function of the peroxodisulfate concentration. Fig. 5 shows the results of two measurements performed under the same conditions with a microdisc array of electrodes. The two almost identical trend-lines illustrate the good reproducibility observed with such arrays of microelectrodes when measuring peroxodisulfate in sulfuric acid.

The objective of this study is to evaluate the possibilities for monitoring industrial processes. This means that the measurement has to be performed in very concentrated solutions.

For example, peroxodisulfate production in acidic solutions or recycling of peroxodisulfate microetchant baths are interesting issues 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 these highly concentrated solutions, amperometric measurements achieved by cyclic voltametry with diamond electrodes, under high cathodic potential (-1.3 V versus Ag/AgCl/KCl 3 M), showed good linearity (Fig. 6).

When recycling peroxodisulfate microetchants, the typical composition of the regenerated solution to be analysed, is: sodium peroxodisulfate (120 g/l,) sulfuric acid (150 g/l), sodium sulfate (200 g/l) and Cu ($\sim$1 g/l). Copper is a highly electro-active specie and it was interesting to evaluate its ef-
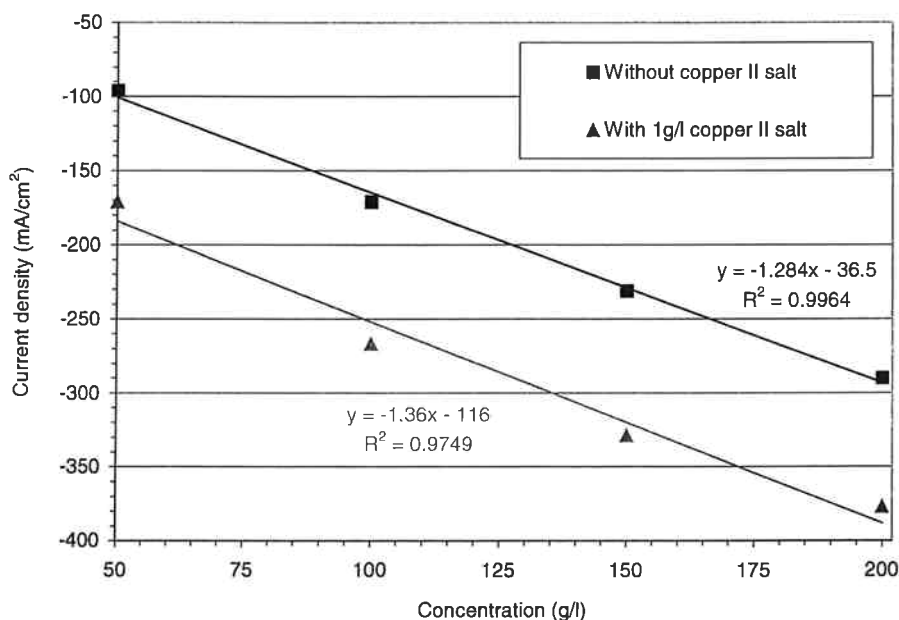

Fig. 7. Evolution of the current density measured at -0.9 V as a function of peroxodisulfate concentration, without and with 1 g/l CuSO$_4$ salt in a H$_2$SO$_4$ (150 g/l)/Na$_2$SO$_4$ (200 g/l); (BDD RDE 2000 rpm; scan rate 100 mV/s).
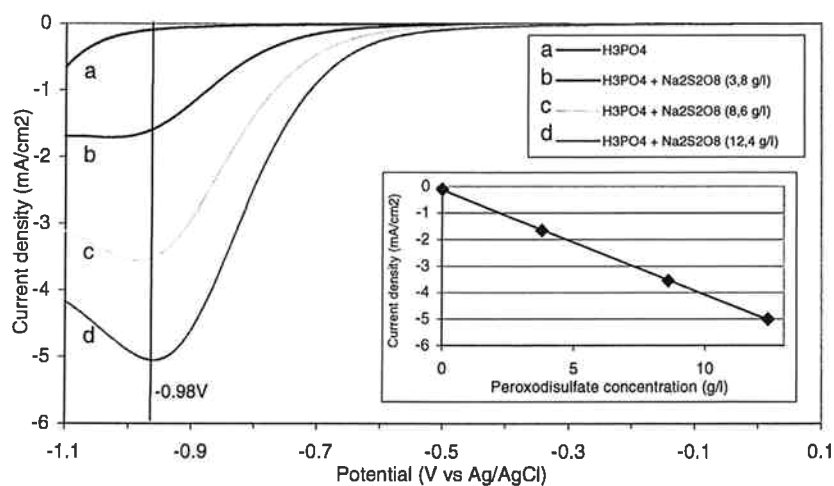
Fig. 8. Voltametric curves and current evolution as a function of concentration for solutions of sodium peroxodisulfate in 7 M phosphoric acid (BDD RDE 2000 rpm; scan rate 100 mV/s).
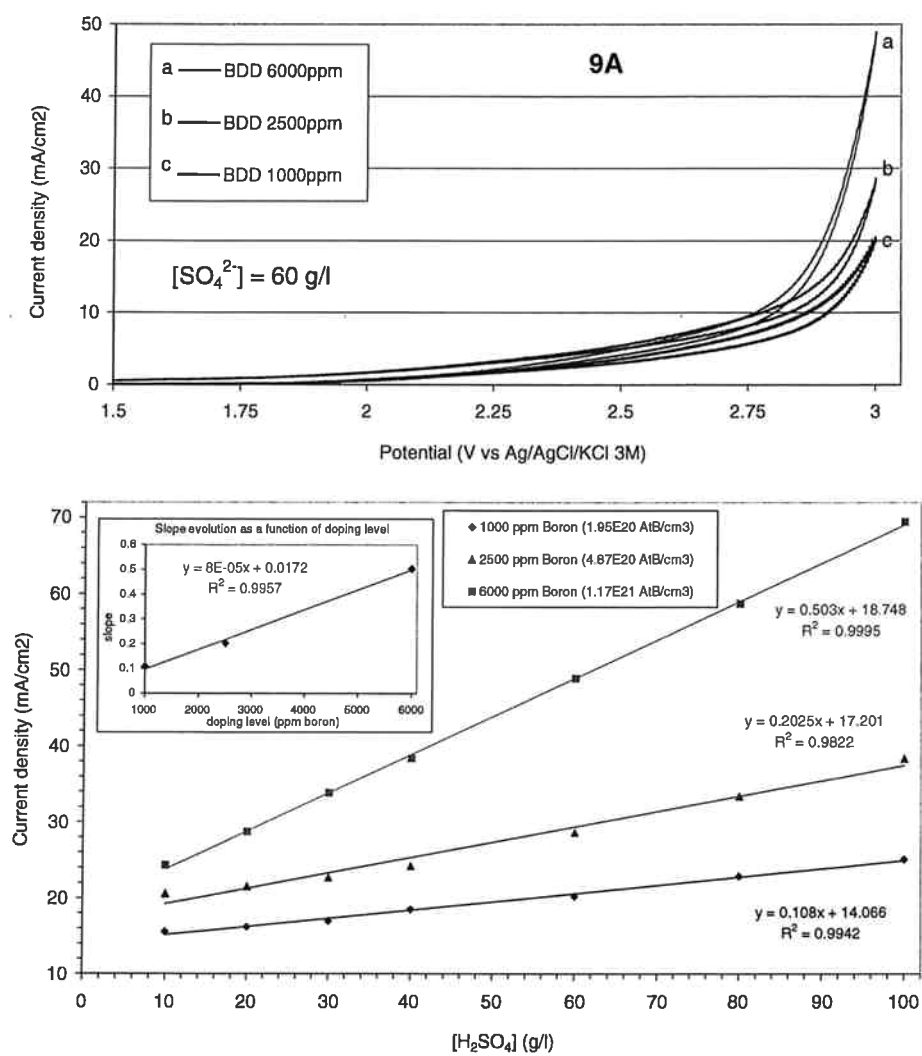

Fig. 9. Effect of diamond doping level on the measurement of sulfate. CVs (A) and evolution of the current density as function of concentration (B).

$y = -0.0153x - 0.1004$
$R^2 = 0.9964$

$y = -0.055x + 0.108$
$R^2 = 0.9694$

$y = -0.3005x + 0.5986$
$R^2 = 0.9907$

◆ 1000 ppm Boron (1.95E20 AtB/cm3)

▲ 2500 ppm Boron (4.87E20 AtB/cm3)

■ 6000 ppm Boron (1.17E21 AtB/cm3)

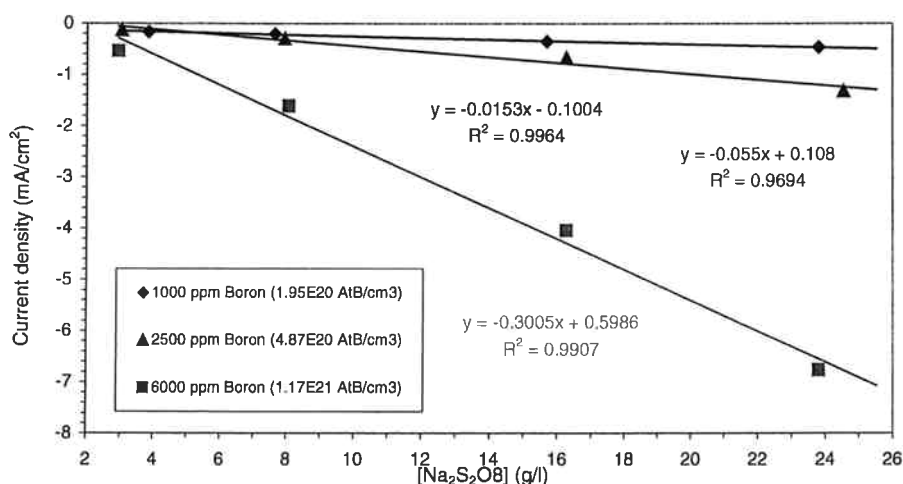Current density (mA/cm²)

[Na₂S₂O₈] (g/l)

Fig. 10. Effect of diamond doping level on the measurement of peroxodisulfate. Evolution of the current density as function of concentration.

fect on the current density. Fig. 7 shows the linearity of the current density as a function of the peroxodisulfate concentration in such media and the effect of the addition of 1 g/l of copper II. As foreseen, the reduction of copper, which takes place at a potential lower than −1 V, interferes with that of the peroxodisulfate. Nevertheless, the fact that for a given peroxodisulfate concentration, the current density was proportional to the copper concentration means that the development of an peroxodisulfate measurement method in the presence of copper salts should be possible if the concentration range of the latter is well known.

Peroxodisulfate measurements were also performed in phosphoric acid. The voltametric curves, shown in Fig. 8, were obtained by measuring solutions with concentrations between 0 and 10 g/l of sodium peroxodisulfate in 7 M phosphoric acid. As shown on the chart, in phosphoric acid the reduction of peroxodisulfate to sulfate took place at approximately −1.0 V versus Ag/AgCl/KCl 3 M. Fig. 8 shows that, once again, the peroxodisulfate concentration is proportional to the current density at a potential of −0.98 V.

3.3. Effect of the diamond doping level

The effect of boron doping of diamond on the measurement of both sulfate and peroxodisulfate was evaluated. Three films prepared according to the same experimental procedure but with different doping gas concentrations were tested. Their boron contents, evaluated by GDOS technique (Glow Discharge Optical Spectroscopy), were 1000, 2500 and 6000 ppm boron, which respectively correspond to 1.95E20, 4.87E20 and 1.17E21 boron atoms per cubic centimeter of diamond. Fig. 9 shows the results obtained for the sulfate measurements. On the voltametric curves and on the graph of current density as function of concentration, it can be seen that the higher boron concentration gives metallic conduction and is more sensitive to sulfate. Moreover, Fig. 9b shows that the slopes of the lines representing the current as function of the concentration

are directly proportional to the boron concentration in the diamond films. Fig. 10 shows equivalent evaluation for the peroxodisulfate measurements. As observed for the sulfate measurement, the more highly doped diamond is clearly the most sensitive. However, in this case, the difference between the highly doped diamond (6000 ppm) and the two others (2500 and 1000 ppm) is very pronounced and the slope of the lines which represent the current as function of concentration are not proportional to the boron concentration of the diamond films. The effect of the boron-doping level on the reduction response could have several origins. It could be due to a reduced electronic state density at the negative potentials while the doping level is reduced, or to a reduced electrochemically active area linked to an increase of the impurity concentration in films. To date, no evidence for either model has been obtained.
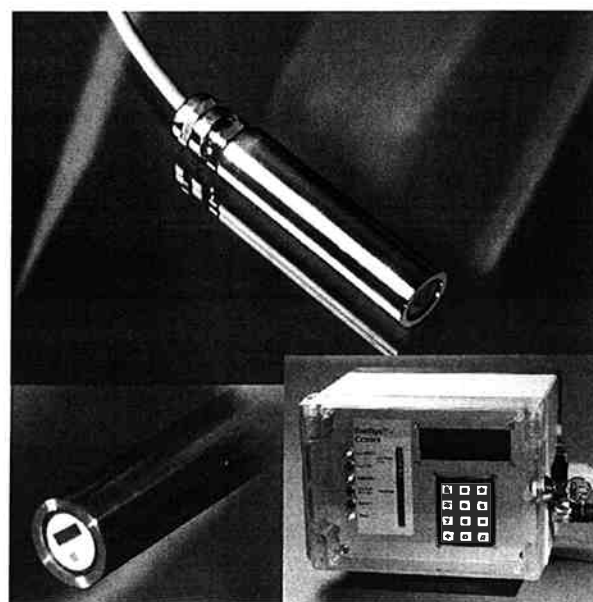

Fig. 11. Electrochemical monitoring system, which includes the SenSys™ sensor and the SenSys™-Control electronic interface.

These results show that for analytical applications a relatively high concentration of boron in the film is an asset, because it leads to increased conductivity and sensitivity. However, it must be kept in mind that higher doping means more impurities. In fact, in diamond films, boron atoms increase to the heterogeneity of the films and films which have a high doping level generally exhibits an increase of the Csp2/Csp3 (graphitic carbon/diamond carbon) ratio [26]. Raman spectroscopy studies are currently underway to identify how these impurities are generated and to limit them in thin diamond films.

4. Conclusion

The results presented here are a good basis for the development of laboratory measurement methods of sulfates and peroxodisulfates, and their adaptation for the development of on-line monitoring systems dedicated to process control applications.

Such systems have already been developed at CSEM for other applications. They consist of a sensor (Fig. 11) that integrates the three-electrode system (Au-SenSys^{TM} or BDD-SenSys^{TM}) and of an electronic interface (Fig. 11), which includes a miniaturized potentiostat (SenSys^{TM}-Control). The systems, which remain under development, are dedicated to the measurement of oxidizing species (chlorine, ozone, hydrogen peroxide), dissolved oxygen and heavy metals in water. Other developments related to micro-disc array electrodes are currently under way. These are both linked to development of new designs of electrode and to the on-line monitoring of CrVI, organic compounds and other analytes in aqueous media.

Acknowledgements

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