

## Electrochemical Reduction of Ozone Dissolved in Perchloric Acid Solutions at Boron-doped Diamond Electrodes

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With boron-doped diamond electrodes, an apparent cathodic peak was observed at 0 V in cyclic voltammograms obtained in 0.1 M HClO<sub>4</sub> solution containing ozone. This peak was attributed to the reduction of dissolved ozone. A calibration curve obtained from the cathodic peak current, which has a slope of 6.7 μA cm<sup>-2</sup> (mg L<sup>-1</sup>)<sup>-1</sup>, can be applied to determining the dissolved ozone concentration. This result will lead to the development of an electrochemical ozone sensor employing a diamond electrode.

Ozone is a strong oxidant, close to fluorine in strength, and has been applied to sterilization, deodorization, and decolorization.<sup>1</sup> Additionally, the activity is remarkably enhanced in water owing to the generation of reactive oxygen species. However, in order to gain satisfactory effects, ozone concentration in water must be monitored and controlled strictly, usually in a range of 0.1–20 mg L<sup>-1</sup>. Electrochemical detection of dissolved ozone provides some advantages in producing more compact device and lowering cost. However, since the measuring atmosphere is extremely oxidative due to the presence of ozone, the detecting electrodes have been limited to a few noble metals.<sup>2,3</sup>

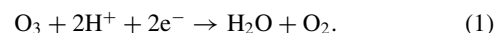
Recently, conductive diamond has attracted increasing attention as a promising electrode material for electrochemical sensors due to chemical inertness, dimensional stability, low residual current, and wide potential window.<sup>4</sup> Many research works have been mainly dedicated to developing biosensors and dissolved trace-metal detectors.<sup>4,5</sup> On the other hand, Yano and co-workers reported that an ideal diamond electrode inhibited the oxygen-reduction reaction and retained a relatively wide potential window even in the presence of dissolved oxygen.<sup>6</sup> This character is tremendously advantageous in the applications to practical analysis under normal atmospheric conditions. Accordingly, we have tried for the first time to apply the diamond electrodes to the electrochemical detection of dissolved ozone.

A polycrystalline boron-doped diamond (BDD) thin film was synthesized on an *n*-Si(111) substrate with a high-pressure microwave plasma-assisted chemical vapor deposition (CVD) system (AX6500, Seki Technotron Corp). The substrate was pre-treated by polishing with 0.5–1.0 μm diamond powder, followed by ultrasonication in acetone. The carbon source was an acetone/methanol mixture (9:1, v/v) containing B<sub>2</sub>O<sub>3</sub> as the boron source (B/C atomic ratio 10<sup>4</sup> ppm). Deposition for 6 h at a microwave power of 8 kW produced a diamond electrode with a thickness of ca. 5 μm, resistivity of 8.3 mΩ cm, and a typical doping level of ca. 2 × 10<sup>21</sup> atoms cm<sup>-3</sup> that was confirmed by SIMS. The diamond electrode was characterized by SEM observation and Raman spectroscopy.

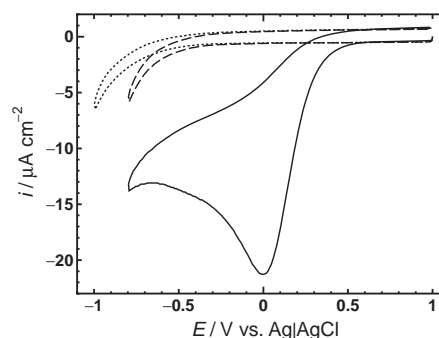
A 0.1 M HClO<sub>4</sub> solution was prepared with an analytical grade reagent and ultra pure water. Ozone solutions were prepared by bubbling ozone gas generated by a silent electric discharge system (ED-OG-R3Lt, EcoDesign Inc.) into the electrolyte solution. The concentration of dissolved ozone was calculated from UV absorbance at 258 nm with the molar absorption coefficient of 2900 M<sup>-1</sup> cm<sup>-1</sup>.<sup>7</sup>

Electrochemical measurements were performed in a two-compartment glass cell. Geometric area of the working electrode was 0.38 cm<sup>2</sup>. Pt wire was employed as the counter electrode, which was settled in a compartment separated by a glass-filter. A KCl saturated Ag|AgCl electrode was employed as the reference. Before each experiment, the BDD electrode was electrochemically oxidized at +3.2 V in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution in order to normalize the electrode condition.

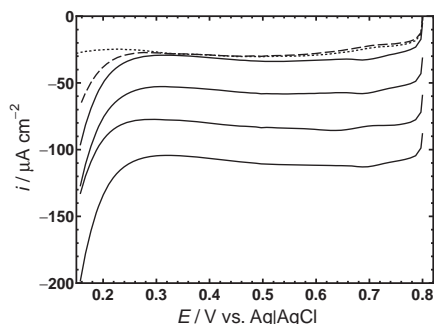
Cyclic voltammetry with BDD electrodes was performed in the presence of ozone in electrolyte solutions. Cyclic voltammograms (CVs) in Figure 1 demonstrate that ozone dissolved in a 0.1 M HClO<sub>4</sub> solution can be detected as a clear cathodic wave at 0 V, through the following reaction:<sup>2,3</sup>



No discernable cathodic responses were observed in the potential range from +1.0 to -0.5 V under the Ar and O<sub>2</sub> atmosphere. Ideal BDD electrodes generally represent a considerably high overpotential toward the hydrogen evolution reaction, up to -1.0 V, as well as the low and flat background response.<sup>6,8</sup> In addition, the O<sub>2</sub>-reduction reaction is inhibited in the positive potential region from -0.4 V. Defining the potential inducing the current density of 5 μA cm<sup>-2</sup> as the negative limit of the potential window, those under Ar and O<sub>2</sub> atmosphere were -0.97 and -0.8 V, respectively. Such a wide and flat potential



**Figure 1.** CVs obtained at an BDD electrode in 0.1 M HClO<sub>4</sub> under Ar (dotted line), O<sub>2</sub> (dashed line), and O<sub>3</sub> (2.6 mg L<sup>-1</sup>, solid line) atmosphere. Scan rate was 100 mV s<sup>-1</sup>.



**Figure 2.** LSVs obtained at an Au electrode in 0.1 M HClO<sub>4</sub> under Ar (dotted line), O<sub>2</sub> (dashed line), and O<sub>3</sub> (solid line) atmosphere. Dissolved ozone concentrations were 1.2, 7.4, 13.2, and 19.9 mg L<sup>-1</sup>. Scan rate was 100 mV s<sup>-1</sup>.

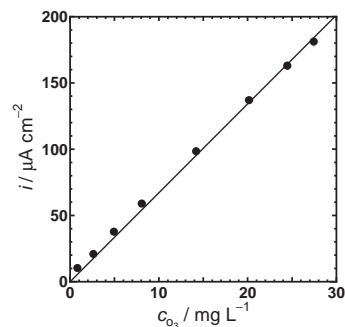
window is one of the reasons that clarify the cathodic peak attributed to dissolved ozone.

In general, the cathodic peak has been hardly observed at conventional metal electrodes including Au and Pt. In the potential region where the ozone reduction thermodynamically occurs (+2.07 V vs NHE<sup>3</sup>), the electrode surfaces are covered with an oxide layer which inhibits the reduction of dissolved ozone.<sup>5</sup> The ozone reduction occurs immediately after the reductive removal of the oxide layer, so that the cathodic peak can not be differentiated. Conveniently, a positive-direction scan beginning at a negative initial potential with a rotating disc electrode has been applied to clarify the ozone-reduction response as the steady-state current, which serves to investigate the reaction mechanism and the electrochemical parameters for the ozone-reduction reaction.<sup>2</sup>

Figure 2 shows linear sweep voltammograms (LSVs) obtained at an Au electrode in the presence of ozone under a static condition. The cathodic current increased depending on the ozone concentration. As mentioned above, the cathodic peak had never been observed, even when the LSVs beginning at more positive potential were attempted, because of oxide layer formation. Although we can estimate the dissolved ozone concentration from the cathodic current response at the Au electrode, the sensitivity is considerably advanced at the BDD electrode. The signal-to-background ratio (S/B) estimated from CVs for an ozone solution of 2.0 mg L<sup>-1</sup> (not shown) was 1.43 and 28.1 at the Au and BDD electrodes, respectively. Therefore, the cathodic responses at the former electrode would be readily influenced by the surface conditions including the molecular adsorption and the oxide formation. The low, flat, and reproducible residual current is essential for the improvement of the detection sensitivity with the diamond electrode system.

In addition to the physical and chemical stability, BDD electrodes are almost inert toward adsorption of ions and molecules,<sup>9</sup> which is advantageous over the conventional metal electrodes that can easily adsorb dissolved species. The inertness frequently induces slowness or hindrance of inner-sphere electron-transfer reactions, in which several intermediate adsorption steps are included.<sup>9</sup> Although the detailed mechanism is unclear at present, the reduction of ozone at the diamond electrode may include adsorption steps and be kinetically hindered, such that the reduction peak appeared shifted compared to the thermodynamic equilibrium potential.

Figure 3 shows a calibration curve for the ozone detection,



**Figure 3.** Plots of cathodic peak current density for ozone reduction observed at an BDD electrode in 0.1 M HClO<sub>4</sub> as a function of dissolved ozone concentration.

which was obtained from the cathodic peak current at the BDD electrode in 0.1 M HClO<sub>4</sub> solutions containing ozone of 0.9–27.5 mg L<sup>-1</sup>. The slope was 6.7 μA cm<sup>-2</sup> (mg L<sup>-1</sup>)<sup>-1</sup> with the correlation coefficient of 0.9986. The detection limit was 0.06 mg L<sup>-1</sup>, which was very lower, compared to the value of 0.3 mg L<sup>-1</sup> obtained at the Au electrode from the present CV results. Based on the linear relationship between ozone concentration and cathodic peak current density, we can utilize cyclic voltammetry or other electrochemical techniques to monitor dissolved ozone under static conditions.

In this short article, we demonstrated for the first time that diamond electrodes represent the reduction peak corresponding to the dissolved ozone in CVs. The calibration curve enable us to determine the dissolved ozone concentration by cyclic voltammetry. We believe that this result will lead to the development of an electrochemical ozone sensor employing a diamond electrode. In addition, the cathodic peaks at the BDD electrode are available to investigate the mechanism and kinetic parameters for the ozone reduction reaction more easily.

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