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Electrochemical Production of High-Concentration Ozone-Water Using Freestanding Perforated Diamond Electrodes

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High-concentration ozone-water can be directly produced with a zero-gap electrolytic cell containing a freestanding perforated boron-doped diamond electrode. For the sake of improving current efficiency for electrochemical ozone-water production, optimization of the electrode configuration was performed. It was proven that the number of holes, hole size, and electrode thickness affect current efficiency. In particular, increasing the number of holes per unit area was the most effective method for improving current efficiency. In regard to hole size, 1 mm diameter was more appropriate than 1.5 mm diameter. Electrode thickness affected the current efficiency, and maximum values were found to be around 0.5–0.6 mm. Based on these results, an electrode optimal for electrochemical ozone-water production was prepared and achieved a maximum current efficiency of 47% in moderate conditions thus far.

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Ozone dissolved in water is one of the most powerful chemicals used for disinfection and sterilization. The effectiveness is based on the generation of reactive oxygen species by reactions between ozone and water molecules as well as the strong oxidative ability of ozone. Furthermore, ozone-water is very environmentally friendly because the residual spontaneously decomposes to oxygen, rendering postwashing unnecessary. Due to these advantages, ozone-water has been employed for hand washing in hospitals and welfare institutions, vegetable washing in food factories and kitchens, and so on.

Water electrolysis with a solid polymer electrolyte (SPE) cell, or a zero-gap (ZG) electrolytic cell, is a unique technique suitable for ozone-water production.[1-7] The cell is divided into two compartments by a proton exchange membrane, to which a porous anode and a porous cathode are firmly attached. The system is so user-friendly that an electrolyte is unnecessary for electrochemical ozone production (EOP). The anode and cathode compartments are filled with pure water; water electrolysis at the anode evolves oxygen and ozone; protons electrogenerated at the porous anode move thorough the membrane toward the porous cathode; and, hydrogen evolution reaction occurs at the cathode surface. When pure water, or tap water, is continuously supplied to the electrolytic cell, electrolyte-free ozone-water can be continuously produced.

EOP systems available in Japan have employed a porous lead dioxide (PbO_2) plate or a platinum (Pt) mesh as an anode. Although they are effective in producing ozone gas or ozone-water, they have the drawbacks of being low in durability, costly, and environmentally harmful. Conductive diamonds have attracted much attention as a promising electrode material for EOP because of the large overpotential for oxygen evolution reaction (OER) as well as superior chemical and dimensional stability.[8-10] Recent progress for electrochemical ozone-water production (EOWP) with diamond electrodes has been reported by Kraft et al.[11] and our research group,[12] separately.

Kraft et al. employed a thin boron-doped diamond (BDD) electrode formed on a niobium expanded metal substrate (29 × 45 mm in size). An electrolytic cell was constructed by sandwiching a Nafion film between two flat BDD-coated expanded metal electrodes. They attained a relatively high current efficiency of 24% with an applied current of 2 A, a flow rate over 40 L h^{-1}, and water temperature of ca. 20°C.

In contrast, we employed a freestanding conductive diamond plate with holes of 1 mm diameter (15 × 50 mm in size). A ZG electrolytic cell was constructed by firmly pressing the freestanding perforated BDD anode and a Pt mesh cathode onto a proton exchange membrane. We attained high current efficiency of 29% with an applied current of 1 A, a flow rate of 2.0 L min^{-1} (120 L h^{-1}), and water temperature of ca. 25°C, although this value was somewhat overestimated as is discussed later.

These findings urged us to advance the EOWP system with BDD electrodes. Even with a tentative electrode (hole diameter was 1 mm, with 2 mm intervals) we have achieved the highest current efficiency thus far.[12] It can be easily imagined that further improvement in current efficiency will be achieved by fine-tuning the electrode configuration in consideration of the number of holes, hole size, hole arrangement, and electrode thickness. This paper describes results of EOWP with various types of freestanding perforated BDD electrodes, and introduces the most appropriate electrode configuration for EOWP at present.

Experimental

Diamond electrodes.— Freestanding BDD electrodes with various patterns of perforated holes, which were prepared according to our specifications, were purchased from Element Six, Ltd. Perforation on a conductive diamond plate was performed by means of laser beam machining that can create perfectly circular holes with sheer edges.[12] Electrical resistivity of the electrodes was sufficiently low, from 0.04 to 0.01 Ω cm.

Table I contains some basic parameters of freestanding perforated BDD electrodes used in this work. The identifications (IDs) were defined from their hole diameter (D) and the total hole number (HN) as D**HN***. Basic patterns were put on freestanding conductive diamond plates 15 × 50 mm in size. The electrode thickness

Table I. Basic parameters of freestanding perforated BDD electrodes 15 × 50 mm in size.

ID[a]	Diameter (mm)	Hole number	Thickness (mm)	Total edge length (cm)[b]
D10HN166	1.0	166	0.77	65.78
D10HN288	1.0	288	0.92	103.48
D10HN312	1.0	312	0.3, 0.54, 0.90	111.01
D10HN410	1.0	410	0.54, 0.94	141.80
D15HN144	1.5	144	0.82	80.86
D15HN196	1.5	196	0.90	105.36

[a] ID was defined from hole diameter (D) and total hole number (HN) as D**HN***.

[b] Total edge length corresponds to the sum of the periphery of all of the holes and the four edge lines of a diamond plate.

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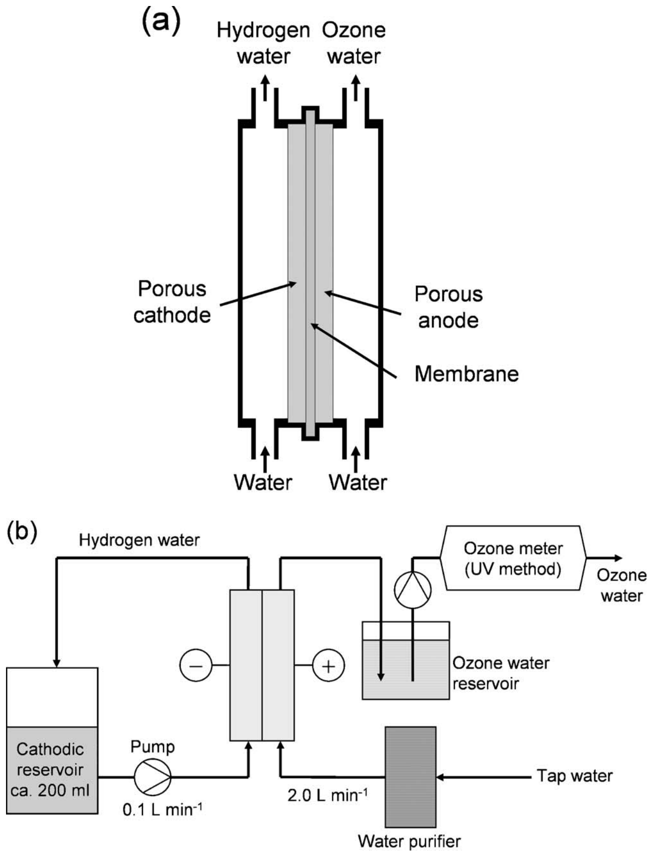

Figure 1. Schematic diagrams of (a) a ZG electrolytic cell and (b) a flow system for electrochemical ozone-water production and measurements of dissolved ozone concentration.

was in a range of 0.77–0.94 mm. For D10HN312, three kinds of the electrodes, 0.30, 0.54, and 0.90 mm in thickness, were prepared. D10HN410 has two kinds of electrodes in different thicknesses, and the thinner one was the most appropriate configuration, as is shown later. Total edge length corresponds to the sum of the periphery of all of the holes and four edge lines of a diamond plate.

Electrolytic system.— Direct EOWP was performed with a ZG cell made of an acrylic frame, which included a porous anode, a porous cathode, and a proton exchange membrane, as shown in Fig. 1a. The details of a ZG cell are described in Ref. 13. One of the freestanding perforated BDD plates was employed as the anode, and a Pt mesh (55 mesh, 99.99%) as the cathode, and they were firmly pressed onto the membrane (Nafion film, N324, DuPont). A Pt mesh was also adopted as the anode for comparison purposes. The membrane was immersed in pure water for at least 24 h. Titanium meshes were used as a current collector.

Figure 1b is a diagram of an experimental setup. Pure water of ca. 12°C with electrical conductivity of less than 1 μS cm^{-1} was continuously supplied into the anodic compartment at a flow rate of 2.0 L min^{-1} (120 L h^{-1}). Cathodic water was pure water cycled at a flow rate of 0.1 L min^{-1}. Electrogenerated hydrogen was spontaneously released as gas. Water electrolysis was performed under galvanostatic conditions. A ZG cell newly constructed was pre-electrolyzed at 10 A for 2–5 h to normalize the cell conditions. Then, ozone concentration and cell voltage were recorded at a steady state attained after the application of a constant current to the cell.

Ozone-water produced at the anodic compartment drained into a reservoir and was then introduced into an ozone meter by a pump. This prevented gas interfusion, thereby providing more reliable data compared with that reported in Ref. 12. Ozone-water concentration was measured with a dissolved ozone meter (SOZ-8000, Ozone System Co., Japan) based on the UV absorption method. The data were calibrated with a molar absorption coefficient of 2900 M^{-1} cm^{-1} at 258 nm.[1,2]

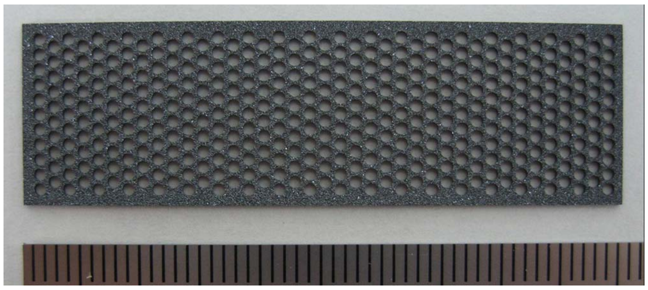

Figure 2. A photograph of the representative freestanding perforated BDD electrode (D10HN410).

Theoretical calculations.— Theoretical electric charge for EOP was calculated by assuming 6-electron transfer reaction[14,15]

$$Q_0(\mathrm{Ah\ g^{-1}}) = nF/M = 3.35$$

where n was the stoichiometric number of electrons transferred, F (C mol^{-1}) was the Faraday constant, and M was molecular weight (g mol^{-1}). The ozone amount dissolved in electrolyzed water was defined as $V_w C_{O3}$ (g h^{-1}), where V_w (L h^{-1}) was a flow rate of water, and C_{O3} (g L^{-1}) was ozone concentration. Electric charge passed to produce specific amount of ozone was obtained from applied current, I(A), by using the following equation

$$Q(\mathrm{Ah\ g^{-1}}) = I/V_w C_{O3}$$

Current efficiency for EOWP, ε_{O3}, was obtained by ε_{O3} (%) = $Q_0/Q \times 100$. Specific power consumption of an electrolytic cell, P, was defined as $P(\mathrm{Wh\ g^{-1}}) = Q \times U$, where $U(V)$ corresponded to cell voltage.

Results and Discussion

Figure 2 is a photograph of the representative freestanding perforated BDD electrode, D10HN410, on which 410 holes 1 mm in diameter were perforated. Scanning electron microscope (SEM) investigation demonstrated that an average size of diamond microcrystals was ca. 100 μm, and perfectly circular holes with sheer edges were formed by means of laser beam machining.[12] Microscopic Raman spectroscopy provided evidence that laser beam machining had no discernible effect on the crystallinity of the diamond sp^3 structure.[12] Accordingly, we can say that the perforated freestanding diamond plates used here are entirely ideal diamond electrodes.

Figure 3 shows (a) ozone concentration, (b) current efficiency, and (c) cell voltage for EOWP as a function of applied current. The perforated freestanding BDD electrodes with holes 1 mm in diameter exhibited great performance for EOWP compared to the Pt mesh electrode. Figure 3a demonstrates that, accompanied with an increase in the applied current at the BDD electrodes, ozone-water is gradually concentrated to a maximum of about 9 mg L^{-1} at 10 A. Although applying higher current was not performed due to limitations of the power source, we believe that more concentrated ozone-water could be available. In contrast, at the Pt mesh electrode, ozone concentration was negligibly less than 0.5 mg L^{-1} maximum. The low catalytic activity is attributed to a lower overpotential toward OER and the absence of anions in pure water which adsorb on a Pt surface and inhibit OER processes.[12,16]

The current efficiency reached a maximum at 3–4 A, as shown in Fig. 3b. This tendency is rather different from that reported in the previous paper, in which the current efficiency monotonically dropped depending on applied current.[12] The difference is partly

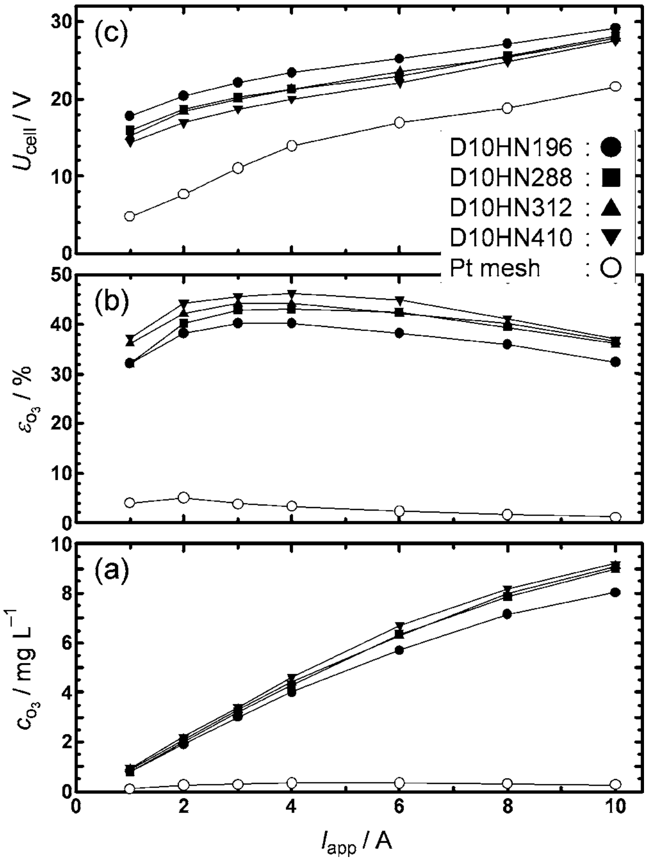

Figure 3. Plots of (a) ozone concentration, (b) current efficiency, and (c) cell voltage with respect to applied current. Ozone-water was produced by electrolysis of pure water with freestanding perforated BDD electrodes and a Pt mesh electrode.

attributed to the employment of a flow system in which electrolyzed ozone-water was directly introduced into an ozone meter. The direct injection accompanied small bubbles of ozone and oxygen gases that caused UV light scattering, resulting in an overestimation of ozone-water concentration. In the present system, however, ozone-water was drained into a reservoir and then introduced into an ozone meter by a pump, which inhibited gas interfusion. Because excess gaseous ozone dispersed at the reservoir, the current efficiency was probably underestimated. However, in view of the estimation of the current efficiency for ozone-water production, we think the present results are more practical.

Another reason for the difference can be attributed to the temperature of the water supplied, which may largely affect catalytic activity of a diamond surface, solubility of ozone electrogenerated, and autolysis of dissolved ozone. In opposition to a downward slide by changing the measuring system, low water temperature contributed to the enhancement of ozone concentration and current efficiency. Accordingly, D10HN196 employed both for the previous (water temperature was about 25°C) and present (12°C) measurements represented a considerably high current efficiency in the latter case of up to 40% max. Lowering water temperature is an appropriate strategy for efficiently producing ozone-water and will be discussed in detail in a separate paper.

The current efficiency advanced depending on the number of holes. The order of D10HN166 < D10HN288 < D10HN312 < D10HN410 was consistent with the order of the total edge length. The maximum of ca. 46% was attained with D10HN410 at 4 A, which was tremendously larger than 20% obtained at a porous PbO_2 electrode.[2] At applied current lower than 4 A, strict potential applied to the electrode surface was not high enough and water could not be converted to ozone effectively. Much OER reaction in this region consumed about 60–70% of the applied current. The amount of electrogenerated ozone was small to completely dissolve into electrolyzed pure water. This was confirmed by the absence of bubbles in the line and the weak smell of ozone above the reservoir. Accordingly, the total amount of electrogenerated ozone was completely incorporated into the current efficiency.

Increasing applied current over 4 A slightly reduced the current efficiency as shown in Fig. 3b. Larger current would induce gasification and autolysis of dissolved ozone, as well as competitive current consumption by side reactions including hydrogen peroxide production and oxidative dissolution of the membrane. In fact, gasification was confirmed by the presence of large gaseous bubbles flowing through the line and strong smells of ozone here and there. Because the current efficiency here was estimated only from ozone dissolved in water and excludes scattered gaseous ozone, such a gibbous shape was observed for the current efficiency.

In spite of the high current efficiency, BDD electrodes in contrast have the drawback of requiring high cell voltage. Figure 3c shows that the cell voltage at the BDD electrodes was higher by ca. 6 V than that of Pt, and further in comparison with the case of a porous PbO_2 electrode.[1,2] The high cell voltage is partly attributed to a smaller electrode area active for water electrolysis. In fact, the cell voltage lowered depending on the hole number in the order of D10HN166 > D10HN288 > D10HN312 > D10HN410. Although porous structure is suitable to form a larger electroactive area as with a PbO_2 electrode, it is hard to form such a structure with diamonds due to low workability.

Another reason for the high cell voltage is a larger overpotential, even compared to Pt and PbO_2, which commonly have a large overpotential to OER. Babak et al.[5] and Da Silva et al.[14,15] proposed an EOP mechanism at a PbO_2 electrode as follows

$$H_2O \rightarrow (OH^{\cdot})_{ads} + H^+ + e^- \qquad [1]$$

$$(OH^{\cdot})_{ads} \rightarrow (O^{\cdot})_{ads} + H^+ + e^- \qquad [2]$$

$$2(O^{\cdot})_{ads} \rightarrow (O_2)_{ads} \rightarrow O_2 \qquad [3]$$

$$(O^{\cdot})_{ads} + (O_2)_{ads} \rightarrow (O_3)_{ads} \rightarrow O_3 \qquad [4]$$

OER process 3 competes with EOP process 4. The large overpotential toward OER at a BDD electrode would contribute to the production of many $OH^{\cdot}$ intermediates, and the inertness of the diamond surface would permit the stable presence of $OH^{\cdot}$ and $O^{\cdot}$. Comninellis's group has verified $OH^{\cdot}$ formation by means of spin-trapping.[17] They have proposed a mechanism similar to that mentioned above for ozone production at an electrode surface.[10] Accordingly, ozone can be produced predominantly at a BDD electrode, under the trade-off relationship between higher ozone production efficiency and higher cell voltage.

Before referring to optimization of the electrode configuration structure we consider the reaction mechanism. For the electrolysis of pure water, protons electrogenerated at a BDD anode should be transferred to a Pt cathode through a proton exchange membrane. This implies that water decomposition to ozone and oxygen occurs near the membrane surface. In other words, the reactions occur at the three-phase interface as well as SPE water electrolysis where a diamond surface, a proton-exchange membrane surface, and a water phase intersect with each other. However, at the interior surface of the holes a part available for anodic reactions is not evident. If we assume that the height active for electrolysis is constant at every electrode, then the active area is proportional to the total edge length.

Figure 4 plots the maximum current efficiency with respect to total edge length. The current efficiency apparently improved as the total edge length was increased and the hole diameter was reduced. In other words, the size of the three-phase interface is one of the basic factors affecting EOWP, which supports the assumption mentioned above. In the case of BDD electrodes with holes of 1 mm in

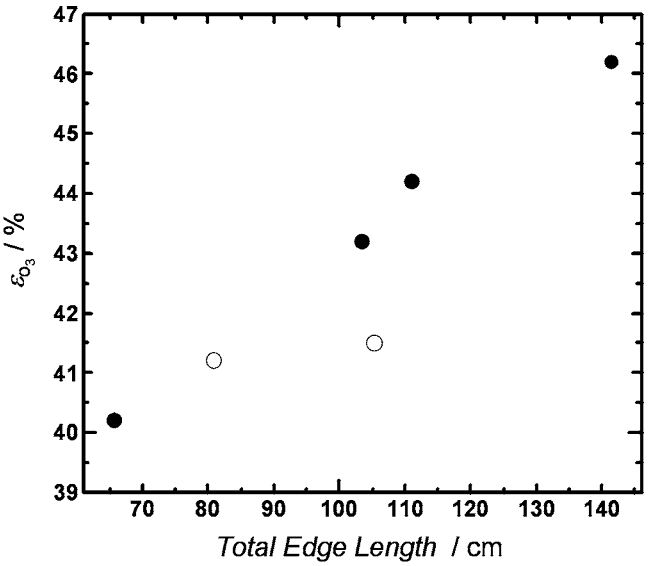

Figure 4. Plots of maximum current efficiency with respect to the total edge length of freestanding perforated BDD electrodes. Hole diameter was 1.0 mm (filled circle) and 1.5 mm (open circle).

diameter, current efficiency increased almost linearly depending on the total edge length. When the number of holes was increased, the current density was lowered even at the same applied current, resulting in a decrease in the amount of ozone produced per hole. This amount of decrease would facilitate dissolution of ozone, and contribute to the improvement of current efficiency. In contrast, fewer holes led to an increase in current density per hole, and as a result, an increase in ozone-water concentration. In this case, autolysis and gasification of ozone would occur to some extent.

In regard to hole size, the current efficiency for EOWP declined as diameter was increased. This was apparent for the BDD electrodes of D10HN288 and D15HN196, which had comparable total edge length. Dependency of the same sort was observed for the BDD electrode with holes of 2 mm in diameter (not shown). Although it is unclear how the hole diameter affects the ozone production mechanism at present, increasing the hole number per unit area and decreasing the diameter is an appropriate approach to improving ozone-water production efficiency. However, this is restricted by laser beam machining technology and electrode strength.

For the estimation of an effect of an electrode thickness, three kinds of D10HN312 of 0.3, 0.54, and 0.9 mm in thickness were prepared. Figure 5 plots the current efficiency with respect to the electrode thickness. Interestingly enough, the maximum was observed to be around 0.5–0.6 mm. The thinner one represented lower current efficiency of about 42% max, at 3 A. Improvement in current efficiency exceeded 45% as the electrode was thickened up to 0.54 mm, demonstrating that the inner wall surface of a hole up to this height contributes to electrochemical ozone generation. In addition, a fall of 0.5–1.0 V in cell voltage against the thinner one (not shown) supports the idea that applied current is dispersed over the surface up to this region, and that current density declines. Nevertheless, the difference of the current efficiency between the thinner and middle electrodes is relatively low at around 3%. This indicates that the great majority of ozone evolution reactions occurs at the inner wall surface of less than 0.3 mm in height. The thickened part of the middle electrode contributed to a mere 7% of the total ozone generation reaction.

A further increase in the electrode thickness up to 0.9 mm reduced the current efficiency and elevated cell voltage. A deeper hole may retain electrogenerated ozone that is prone to autolysis or gasification, leading to lower current efficiency and higher cell voltage. Based on the results represented above, we concluded that the electrode configuration optimal for EOWP is the perforated BDD electrode of a thickness of 0.5–0.6 mm with a maximum number of holes with a diameter of 1 mm per unit area.

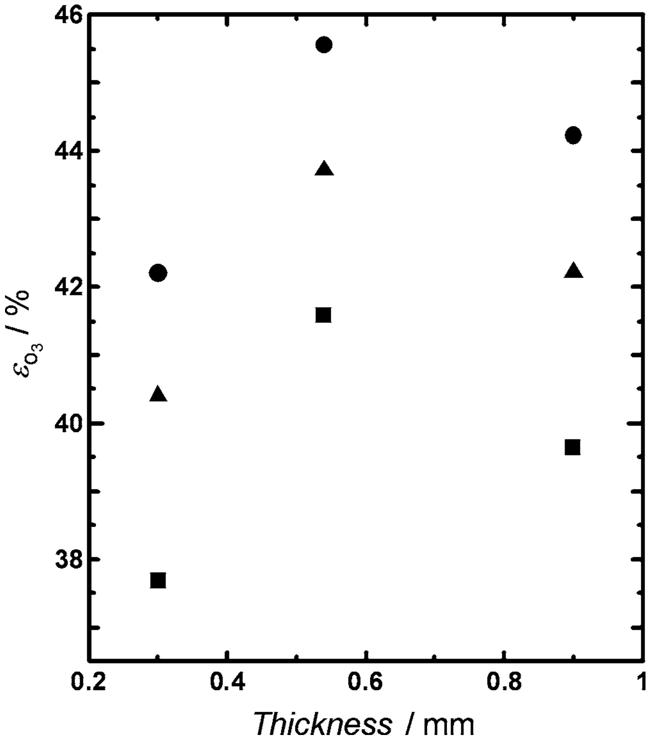

Figure 5. Plots of current efficiency with respect to electrode thickness. Water electrolysis was performed with D10HN312 (thickness 0.30, 0.54, 0.90 mm) at applied current of 2 A (filled triangle), 4 A (filled circle), and 10 A (filled square).

A photograph of the optimized electrode, D10HN410 with a thickness of 0.54 mm, is represented in Fig. 2. Figure 6 shows a series of results of (a) ozone concentration, (b) current efficiency, (c) cell voltage, and (d) specific power consumption, as a function of applied current with the optimized electrode. The ozone-water concentration attained about 9.5 mg L^{-1} at 10 A. The maximum current efficiency was improved up to ca. 47% around 3–4 A. Although Foller and Tobias reported higher current efficiency over 50%, the data were obtained in 7.3 M hexafluorophosphoric acid at 0°C with a β-PbO_2 anode.[16] We think that this condition is tremendously extreme and is not realistic for actual application. In contrast, the present system can be used in moderate conditions.

However, the cell voltage was still large compared with that obtained at the Pt mesh in Fig. 3a, especially with the case of a porous PbO_2 electrode by over 20 V.[1,2] This is due to the properties of BDD electrodes of a smaller surface area active for ozone evolution reactions and a larger overpotential for water decomposition as mentioned above. The large cell voltage leads to a severe disadvantage in specific power consumption for ozone generation. Stucki et al. reported the specific power consumption of 80–100 Wh g^{-1} for EOP at a porous PbO_2 electrode.[2] In addition, silent discharge apparatuses can produce gaseous ozone generally with a low power consumption of 10 Wh g^{-1}. Accordingly, in view of the energy efficiency for ozone production, the present system with the perforated BDD electrode seems to be fruitless.

However, if we consider the energy efficiency in terms of producing ozone-water, the freestanding perforated BDD electrode competes with other technologies because the electrolyzed water can be used as is. In the case of silent discharge methods, ozone gas generated should be dissolved in water to obtain ozone-water before use, which requires additional equipment. In regards to water elec-

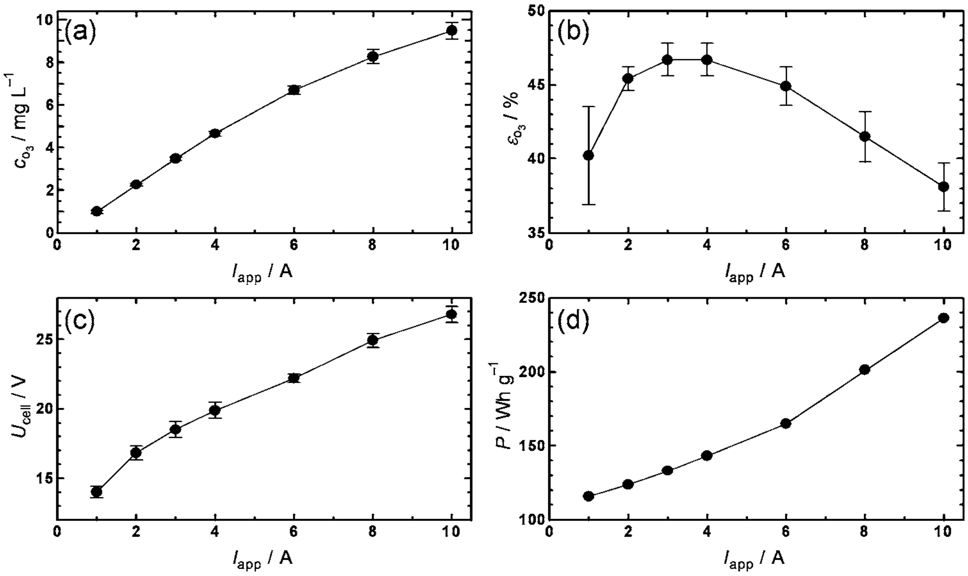

Figure 6. Plots of (a) ozone concentration, (b) current efficiency, (c) cell voltage, and (d) specific power consumption with respect to applied current. Ozone-water was produced by electrolysis of pure water with D10HN410 of 0.54 mm thickness.

trolysis at a porous PbO_2 electrode, ozone gas should be abstracted from electrolyzed water and then dissolved into water to obtain ozone-water due to the contact of electrolyzed water with hazardous lead compounds. Considering these aspects, the present system for the sake of ozone-water production has some advantages in terms of the total energy efficiency and can be realistically applied.

Conclusions

EOWP with freestanding perforated BDD electrodes was proven to be dependent on the number of holes, hole diameter, and electrode thickness. In particular, increasing the number of holes per unit area is the most effective method for improving current efficiency. The electrode configuration optimal for EOWP was D10HN410 of 0.54 mm in thickness, which offered a current efficiency of 47% in moderate conditions, the highest thus far.

The advantage of using freestanding diamond plates is obvious. The entire electrode surface retains an ideal diamond crystalline structure, and thus durability is considerably superior under high current conditions. The application of a diamond electrode formed on a mesh or a porous substrate is another option and has some merits, including low cost and high mechanical strength. However, diamond deposition onto complex substrates is a quite difficult task. Thinner areas of the diamond film tend to contain pinholes which lead to the erosion of the substrate after long-term usage under high current conditions. Accordingly, we believe that the present system is the most appropriate for EOWP in terms of high current efficiency as well as high durability.

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