

Investigation of Simple Electrochemical Conditions for Generation of Ozonized Water

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(Received April 11, 2008 : Accepted May 27, 2008)

Abstract : An electrochemical generation of ozonized water was investigated by using β -PbO₂ as an anode and tap water as an anolyte. According to the potentiometric ozone detection which utilizes potential differences arisen from a chemical reaction of ozone and iodide, increasing tendency of ozone concentration on electrolysis time could be observed to show the maximum value of 8 ppm at an electrolysis time of 10 min. Ozone could be generated promptly even at an electrolysis time of 10 sec., suggesting great advantages of this electrochemical process in terms of simplicity and readiness that might be applied directly to practical uses including medical and/or food industries. Influences of electrolysis on the properties and surface conditions of a PbO₂ electrode were also discussed from the results of cyclic voltammetry, scanning electron microscope, and X-ray diffractometer.

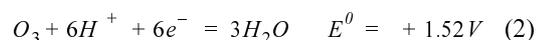
Keywords : Ozonized water, Tap water, Potentiometric detection.

1. Introduction

Ozone, as the second strongest oxidant in natural world, is expected to play more important roles than ever before. Due to the environmentally-friendly characteristics of ozone that it naturally decomposes into oxygen at room temperature without leaving toxic residues, its application area ranges widely from domestic to industrial fields such as waste water treatment including sterilization and deodorization, bleaching, chemical syntheses, semi-conductor cleansing, and so on. Especially the usability of ozone dissolved in water (*i.e.*, ozonized water) is good enough to be applied to practical uses directly from an ozone generating system. In terms of generation of ozonized water, an electrochemical process should be more advantageous than the conventional corona process which requires two main steps; generating ozone in the air and dissolving the generated ozone into a reagent, which implicates a significant loss of the generated ozone. Besides, an electrochemical process needs only a simple system with relatively lower applied voltage

(< 2 V) to show far higher concentration of generated ozone compared with a corona process.^{1,2)} Experimental conditions which can be easily controlled is also one of the merits of an electrochemical process.

Theoretically, ozone generation occurs at a higher potential than competing and thermodynamically favorable oxygen evolution as below.



And the anolyte is usually a strong acid such as H₂SO₄, H₂SO₄ with NaF, H₂SO₄ with KPF₆, H₃PO₄, or HClO₄, regardless of the kinds of anode material.³⁻⁵⁾ These severe electrochemical conditions put high demand on electrode materials to have toughness to endure the conditions as well as to have high overpotential to suppress an oxygen evolution. And this has limited the usage of various electrode materials. Although several anode materials such as boron-doped diamond,^{6,7)} Pt-TaO_x composite,^{8,9)} IrO₂-NbO₃ composite⁵⁾ have been reported, lead dioxide (β -PbO₂) seems to be the only practical material as an anode due to its high oxygen evolution overpotential, high resis-

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tance to corrosion, high electric conductivity, and an economical vantage.^{3,10-11)}

Therefore, we have investigated simple and less demanding electrochemical conditions for generation of ozonized water by using a β - PbO_2 electrode. The generation of ozonized water from simple reactants (ex. H_2O) with simple electrochemical conditions should be a promising method in the light of industry-scale ozone production in future as well as the possibility of direct usage of resultant ozonized water from a generation system. Since decomposition of ozone in water into oxygen occurs in no time,⁹⁾ an investigation of a prompt detection method for generated ozone within the time range of several minutes is also required. In this study, detection of ozone contents by using the potentiometric method¹¹⁾ was also studied.

2. Experimentals

2.1 Electrolysis performance

An electrolysis cell used for generation of ozone in this study was assembled as shown in Fig. 1. Electrodes of a commercialized β - PbO_2/Ti (Permelec Electrode Ltd.) and a laboratory-prepared Pt/Ti were used as an anode and a cathode, respectively. The PbO_2 electrode consists of β and α -structured PbO_2 layers deposited on a Ti substrate. The platinum cathode layer was electrochemically deposited by using a Pt precursors of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$.⁴⁾ Tap water and 10 mM of NaCl

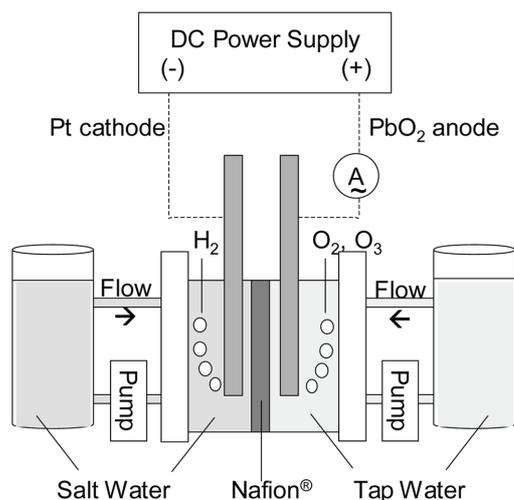


Fig. 1. Schematic diagrams of the cell assembly for generation of ozonized water.

Table 1. Electrolysis conditions

Conditions	Value
Applied voltage [V]	2.0
Electrolysis Duration [S]	0~1800
Cell system temperature [°C]	r.t.
Electrolyte Flow Rate [mL/s]	10

salt water were used as an anolyte and a catholyte, and Nafion[®] 324 (DuPont) was used as a proton-exchange membrane. Salt water acted as an electric conductor, and tap water was chosen in hope of a direct application to practical uses in future. There is also a report which uses imitation tap water with a Pt-TaO_x composite electrode [8], and the main chemical reactions at the interface between a β - PbO_2 electrode and an electrolyte can be expressed as in Eqs. (1) and (2).

The electrolysis conditions are shown in Table 1. Voltage of 2.0 was applied while both electrolytes were circulated by pump throughout the electrolysis. The electrolysis duration was varied from 0 to 1800 seconds. Experiments were done under room temperature and the flow rate of both electrolyses was 10 mL/s.

2.2 Ozone detection by electrochemical method

Potentiometric measurements were performed at room temperature by using a potentiostat (IviumStat, Ivium Technologies Co.). Platinum wires were used as working and counter electrodes, and an Ag/AgCl_2 (sat. KCl) electrode was used as a reference electrode. These three electrodes were well separated by a three-neck flask and a salt bridge. A potential buffer solution was prepared to have known-concentrations with 10 mM of I^- and 1 mM of I_3^- ¹¹⁾ by adding a potassium iodine (KI) and an iodine (I_2) volumetric solution into a standard buffer solution (pH = 4.0). An open circuit potential of the working electrode put into the prepared buffer solution was recorded in order to obtain the potential difference of before and after the introduction of generated ozonized water into the buffer solution. All detections of generated ozone were performed within a minute after the completion of the electrolysis.

According to the T. Ohsaka,¹¹⁾ the introduction of ozonized water into the buffer solution with I^- and I_3^- promotes the oxidation of the iodide ion, resulting in potential differences. The potential change on the working electrode measured by an open circuit potential could be used for the calculation of ozone

contents as follows.

From the Nernst equation at 25°C, the following simplified equation was proposed for the calculation of oxidant concentration when $[I^-]_o \gg [Ox]$ and $[I_3^-]_o [Ox]$.¹¹⁾

$$\Delta E = 13.0 ([Ox] / [I_3^-]_o) \quad (3)$$

Where $[I^-]_o$ and $[I_3^-]_o$ are initial concentrations of I^- and I_3^- ions and $[Ox]$ is the concentration of generated ozone. Although there are three kinds of calculation equations depending on the value of $[I^-]_o$, $[I_3^-]_o$, and $[Ox]$, the Eq. (3) was chosen in this study since the concentration of each iodide ion is projected to be 10 mM of I^- and 1 mM of I_3^- , respectively while that of ozone is speculated to be in the range of 0.02~0.2 mM (1~10 ppm) from our past investigations using an ozone detector equipment.

2.3 Cyclic Voltammetry

Cyclic Voltammetry was performed by using a potentiostat (Ivium Technologies Co.) to observe redox reactions on a β -PbO₂/Ti electrode. A Pt electrode put into 0.5 M-H₂SO₄ aq. was used as a working electrode, An Ag/AgCl₂ (sat. KCl) as a reference electrode, and a Pt/Ti meshed plate as a counter electrode, respectively. Scanning was performed in the range of 0 to 3 V at a scanning rate of 50 mV/s and a scanning step of 10 mV.

2.4 Surface characterization

Surface morphology of a β -PbO₂ electrode before and after the electrolysis was observed by using a scanning electron microscope (SEM, HITACHI S-2500C). The magnitude was 15.00 K, the extra high tension (EHT) was 5 kV, and the working distance (WD) was 3 mm. Microstructure of the PbO₂ electrode surface was analyzed by using a X-ray diffractometer (XRD, Bruker AXS, D8 DISCOVER) with Cu-K α radiation.

3. Results and Discussion

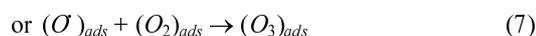
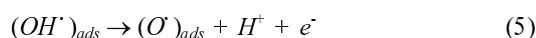
3.1 Generation of ozonized water

By utilizing the electrolysis cell shown in Fig. 1, the possibility of ozone generation was checked with a commercialized ozone detector (Ai denshi kogyo Co. AOM-05). As seen in Table 2, ozone was successfully generated from drinking tap water. Although the detectable concentration of ozone by the detector is rough with the minimum scale of

Table 2. Ozone concentrations of ozonized water

Electrolysis time [S]	Concentration [ppm]
30	ca. 2.5
60	> 5.0
600	> 5.0

0.5 ppm, high concentration of more than 5 ppm could be obtained when the electrolysis duration is over 1 min. Remarkably, relatively high concentration of ca. 2.5 ppm was also obtained even with the electrolysis duration of as short as 30 sec. This readiness of ozone generation as well as the usage of tap water should be noted as great advantages of this electrochemical process for future application, revealing the resultant of ozonized water can be applied to a practical use directly from a generator. Although the mechanism of ozone generation on a PbO₂ electrode has yet to be clarified, it has been reported that the existence of an adsorbed radical oxygen (O^{\cdot}) acts as an active part.¹⁰⁾



According to this mechanism, the adsorbed oxygen ($(O_2)_{ads}$) seems to be required while only the evolution to oxygen gas (Eq. (8)) should be blocked for an effective ozone generation.

3.2 Potentiometric detection of generated ozone

In the light of prompt and accurate detection of the generated ozonized water, an electrochemical process should be advantageous because chemical reactions occur in no time and gap of the electrochemical potential from the reaction is minute in unit of mV. The reaction between ozone and iodine is well known as written in the past patent [12], and they react in compliance with the Eq. (10).



And the reaction of I₂/I⁻ redox electrode was reported to show the following equation (Eq. (11))

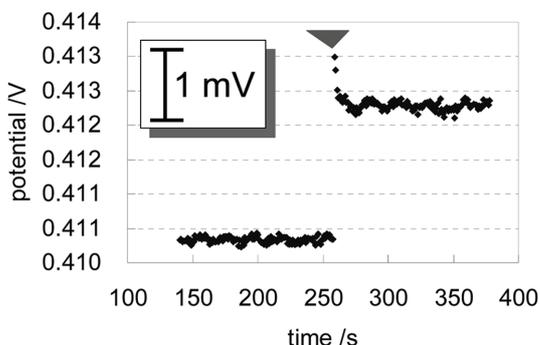


Fig. 2. Example of the potential gap from an open circuit potential obtained by introduction of generated ozonized water into the buffer solution (electrolysis duration = 30 s. at r.t.). A triangle mark indicates the timing when the ozonized water was added.

in the presence of an excess of I^- to I_2 .¹¹⁾



Fig. 2 shows an example of the potential gap obtained from an open circuit potential measurement. The potential gap arisen from an addition of the ozonized water into the iodine buffer solution was seen regardless of electrolysis duration in the range of 10–1800 sec. Fig. 3 is the tendency of ozone concentration which was calculated from the Eq. (3) and the potential gap in Fig. 2. Ozone could be detected even at short electrolysis duration of 10 sec and its concentration increased slightly as the electrolysis continued. The value of maximum concentration we could obtain was 8.8 ppm at 10 min

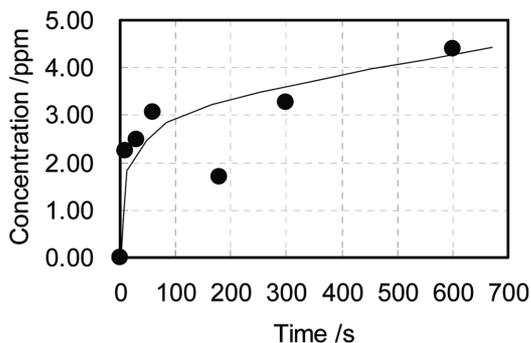


Fig. 3. Tendency of ozone concentration on the electrolysis duration at r.t. and flow rate of 8 mL/s, ozone was detected by a potentiometric analysis. All data were corrected by subtracting the value at where electrolysis time equals to 0.

of the electrolysis. By comparing the ozone concentration directly obtained from the potentiometric method (not shown in this paper) with that from an ozone detector (Table 2), the concentration were loosely accordant to show the value of over 5 ppm when the electrolysis duration was over 1 min.

However, as can be seen in Fig. 3, the fluctuation of the potential graph which is relatively large compared with the measurement scale undermines the accuracy of this electrochemical measurement. Furthermore, the potential gap of ca. 0.8 mV was obtained with addition of tap water, which is not negligible. According to Eq. (10), the evolution of oxygen and hydroxide ion (OH^-) occurs as a result of oxidation by ozone. However, this reaction seems to be able to happen when whatever the oxidant was introduced. The cause of the potential gap with introduction of tap water is yet to be cleared, but instead of ozone, chloride ion (Cl^-) which naturally exists in drinking water might act as an oxidant.



Therefore, the value of potential gap at where no electrolysis was operated should always be subtracted from each datum in order to obtain reliable plots.

One thing to be noticed is that all potentiometric detections in this study were performed within a minute, indicating that this electrochemical measurement is suitable for ozone detection in terms of readiness.

3.3 Cyclic Voltammetry

Cyclic voltammograms of a β - PbO_2 electrode were shown in Fig. 4 in the applied potential range

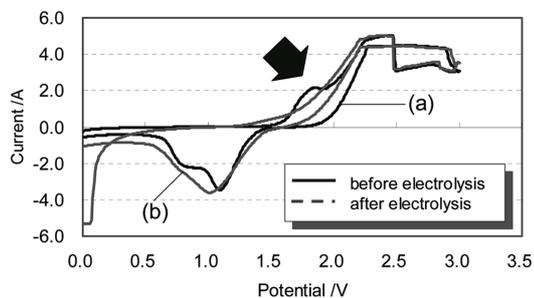
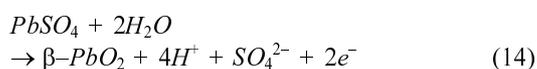
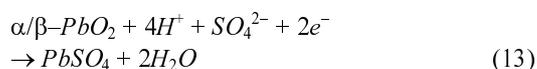


Fig. 4. Cyclic voltammograms obtained with a PbO_2 electrode in 0.5 M- H_2SO_4 aq., (a) before electrolysis and (b) after ca. 30 hours of electrolysis, respectively. An arrow shows a peak attributes to O_2 and O_3 evolutions.

of 0 to 3 V in order to observe the change in redox reactions on a PbO₂ electrode before and after several electrolysis operations. In both Fig. 4 (a) and (b), large cathodic peaks are seen at ca. +1.2 V indicating the reduction of PbO₂(IV) to PbSO₄(II) (Eq. (13)) as well as large anodic peaks at over ca. +2.0 V indicating the recovery of PbO₂ by the oxidation of PbSO₄ formed during the cyclic voltammogram performance (Eq. (14)). It was reported that when cycled in a sulfuric acid, PbSO₄ was oxidized to give preferably β-PbO₂ according to Eq. (14) rather than α-PbO₂, changing the composition of α/β-PbO₂.¹³⁾



Another remarkable point is that the broad peak at ca. +1.8 V which attributes to the oxygen and ozone evolutions (see the arrow in Fig. 4 (a)) has disappeared after about 30 hours of electrolysis in total, suggesting that the surface of PbO₂ has lost its catalytic characterization for ozone generation.

3.4 Surface characterization

In order to investigate the cause of the deterioration of a PbO₂ electrode observed in the cyclic voltammogram, a plane image of SEM was taken. Fig. 5 shows plane images of the surface of the PbO₂ electrode before (a) and after (b) the 30 hours of electrolysis in total. From SEM images, a drastic change in the surface morphology after the electrolysis can be seen with apparently higher surface roughness, larger agglomerates (size of > 1 μm), and acicular materials. Therefore, the deterioration of a PbO₂ electrode on the

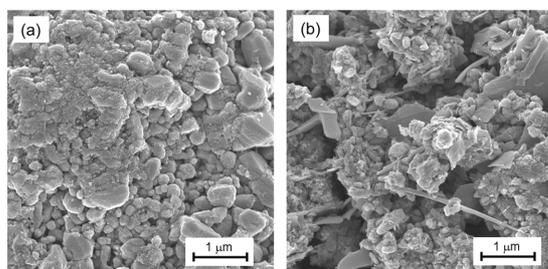


Fig. 5. Plane SEM images of a PbO₂ electrode surface, (a) before electrolysis and (b) after ca. 30 hours of electrolysis, respectively.

electrolysis seemed to attribute to the formation of impurities which interferes the catalytic property of a PbO₂ electrode. The color of the PbO₂ electrode surface has also changed apparently from dark grey to a mixture of brown and white. It was impossible to completely clean up the changed color by using 0.1 M-HCl aq. together with ultrasonication for several times. Although further investigation to identify the impurities is needed, the natural reduction of PbO₂ to α-PbO of red color (Eq. (15)), the formation of Pb₄(OH)₄(ClO₄)₄(H₂O)₂ of grey color from Cl⁻ ion in tap water, and the formation of PbSO₄ of white color (Eq. (13)) are among strong possibilities of the impurities.

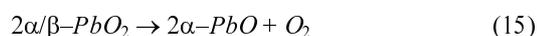


Fig. 6 shows XRD patterns of a PbO₂ electrode before (a) and after (b) the hours of electrolysis. As seen in Fig. 6, most of peaks are attributed to α or β-structured lead dioxide in accordance with the composition of the commercialized PbO₂ electrode. However, there are some peaks (indicated as circle marks) observed for the PbO₂ electrode only after hours of the electrolysis. From the JCPDS data, these peaks are well in agreement with those of lead sulfate (PbSO₄, where strong peaks appear at 2θ = 29.6°, 43.6°, 44.4°, and 45.8°). It is possible to assume that considerable amount of PbSO₄ was formed onto the PbO₂ electrode when H₂SO₄ solution was utilized as an anolyte for the electrolysis (data are not shown in this paper) and/or as an electrolyte for

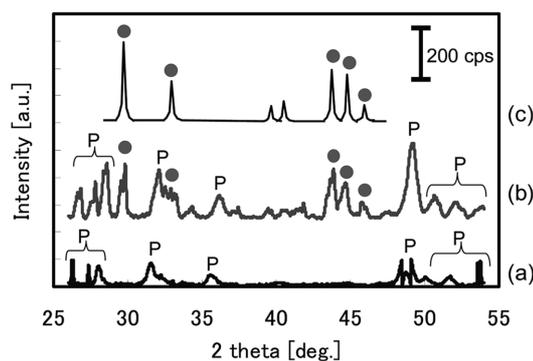


Fig. 6. XRD Patterns of a PbO₂ anode (a) before and (b) after hours of electrolysis, where P is attributed to either α-PbO₂ or β-PbO₂, and circle marks (●) to PbSO₄, respectively. The image patterns of PbSO₄ (c) was also included.

a cyclic voltammetry experiment. Therefore, the cause of the deterioration in the overpotential characteristics of the PbO₂ electrode seems to be due to the existence of PbSO₄ on the electrode surface and it is essential to remove this impurity for achieving more stable ozone generation.

4. Conclusions

Ozonized water was successfully generated from drinking tap water and salt water with a β-PbO₂ electrode. From the potentiometric ozone detection which uses the potential gap arisen from a chemical reaction of ozone and iodide ion, increasing tendency of the ozone concentration on the electrolysis duration was observed to give the maximum value of 8.8 ppm when the electrolysis duration was 10 min. And also, ozone could be readily generated even at the electrolysis duration of 10 sec. This readiness of ozone generation as well as the simplicity of using tap water and salt water is a great advantage of the electrochemical process in this study, suggesting the resultant ozonized water could be applied to the future practical use directly from a generator.

It should be noticed that the potentiometric analysis in this study could detect ozone contents within a minute, revealing the method to be suitable for ozone detection. However, relatively high fluctuation of the calculated ozone concentration and the existence of potential gap with addition of just tap water undermined the accuracy of this electrochemical measurement. Cyclic voltammograms indicated the vulnerable catalytic property of a β-PbO₂ electrode with showing no oxidation peak contributing to ozone generation after about 30 hours of electrolysis. The cause of the degradation seems to be the existence of PbSO₄ formed onto the electrode surface.

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