Sensitive Detection of Hydroxyl Radical Production in Ultrasonic Field with an Electrochemiluminescence Optical Sensor

Jiye Jin,*[1] Hiroaki Kumeta,[1] Fumiki Takahashi,[1] and Yoshiyuki Asakura[2]
[1]*Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto 390-8621*
[2]*Honda Electronics Co., Ltd., 20 Oyamazuka, Oiwa-cho, Toyohashi 441-3193*

(Received September 12, 2008; CL-080875; E-mail: jin@shinshu-u.ac.jp)

A new method of cavitation diagnostics with an electrochemiluminescence (ECL) optical sensor is described for study of the hydroxyl radical production by ultrasonic cavitation. Because of the high sensitivity of this method, it is possible to measure the sonochemical activity in situ, so as to obtain spatial distribution of the cavitation zone in the ultrasound field.

The generation of cavitation by ultrasonic waves can lead to the formation of reactive species such as OH•, H•, and H_2O_2 in aqueous liquids.[1] These short-lived species are capable of effecting secondary oxidation or reduction reactions, which are referred to as sonochemical reactions. For the purpose of optimizing sonochemical processes and allowing cavitation to be as a useful industrial and academic technique, a confident analytical approach is needed to ascertain the importance of the quantification of •OH radical so as to evaluate the cavitation activity.[2–4]

Although electron spin resonance coupled with spin trapping has proven to be promising for measurement of •OH radicals,[5] it is restricted by short-term reproducibility and the complicated measurement procedure. Recently, the chemical dosimetry based upon the Weissler reaction has been widely used for the characterization of the cavitation activity for a sonochemical reactor.[3,4] In the Weissler reaction, iodide was oxidized to triiodide (I_3^-) by •OH radicals or H_2O_2 produced during cavitation. This reaction constitutes a standard dosimeter in sonochemistry since the rate of I_3^- formation can be determined spectrophotometrically.[6] These methods, however, do not provide enough sensitivity for the determination of sonochemical activity in situ. In the study, an alternative approach with an electrochemiluminescence (ECL) optical sensor was proposed for the determination of sonochemical product with high sensitivity. The spatial distribution of cavitation activity within an ultrasonic reactor was primarily studied.

A schematic experimental setup and the ECL optical sensor are represented in Figure 1. A platinum wire (ϕ 0.2 mm) was used as working electrode which was coiled around an optical fiber (core size: 1 mm). A platinum wire and a silver (Ag) wire were employed as a counter electrode (CE) and a quasi-reference electrode (QRE), respectively. These elements are housed in a Teflon rod (ϕ 4 mm). The light emitting from the working electrode was collected by an optical fiber and was measured with a H5784 photomultiplier tube module (Hamamatsu Photonics, Japan). The sonochemical reactor for in situ measurement was made of a cylindrical acrylic chamber with an inner diameter of 60 mm and a height of 200 mm. A vibration plate made from a 0.1-mm thick stainless steel was fixed at the bottom of the acrylic pipe, under which a piezoelectric ceramic transducer (ϕ 50 PZT, Honda Electronics) was mounted. The transducer

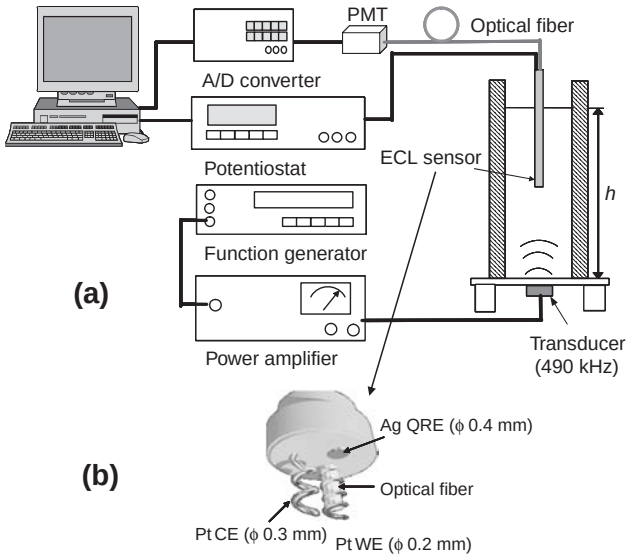

Figure 1. Schematic diagrams of an experimental setup (a) and an ECL optical sensor used for the measurement (b).

was connected to a function generator, which generated sine waves through a high frequency amplifier (Model 4015, NF Electric Co., Ltd.). The ECL experiments were conducted in a light proof box.

ECL is the production of light from an electrolytic system.[7] It is known that blue chemiluminescence with an emission peak at 430 nm can be generated by electrochemical oxidation of luminol in the presence of an amount of H_2O_2. ECL has advantages over the conventional chemiluminescence protocols because the luminescence is localized on the electrode surface and can be performed in neutral or weak alkaline solution. In this study, the ECL signal from the sensor was confirmed to be proportional to the concentration of H_2O_2, ranging from 0 to 50 μmol dm^{-3} in 0.1 M phosphate buffer solution (pH 8.0) containing 50 μmol dm^{-3} luminol, with a detection limit of 20 nmol dm^{-3}. The sensor was thus applied to the determination of H_2O_2 yield in an ultrasound reactor. In this case, 250 cm^3 of pH 8.0 phosphate buffer was irradiated with four different frequencies (28, 45, 100, and 490 kHz). After a period of irradiation time, 5 cm^3 of sonicated solution was added in 50 μmol dm^{-3} luminol, and the ECL signal was recorded with a potential sweep mode from 0 to 0.8 V vs. AgQRE with potential scan rate of 50 mV s^{-1}. It was found that the yield of H_2O_2 was linearly proportional to the irradiation time. Under a fixed electric output power (50 W), the rates of H_2O_2 production (d[H_2O_2]/dt), 4.8, 6.1, 19.3, and 44.4 nmol dm^{-3} s^{-1} were determined when 28, 45, 100, and 490 kHz waves were used for irradiation.

To verify if the rates of H_2O_2 determined by ECL were indeed accurate, the Weissler method was carried out under the same output power. When 0.1 mol dm^{-3} KI solution was irradiated with ultrasonic waves, iodide was oxidized to triiodide (I_3^-) by •OH radicals or H_2O_2 produced during cavitation.

$$H_2O \xrightarrow{)))} \bullet OH + H\bullet \quad (1)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (2)$$

$$2I^- + H_2O_2 \rightarrow I_2 + 2OH^- \quad (3)$$

$$I^- + I_2 \rightarrow I_3^- \quad (4)$$

The produced I_3^- concentration was determined by measuring the absorbance at 355 nm ($\varepsilon = 26303$ dm^3 mol^{-1} cm^{-1}). The rates of I_3^- production (d[I_3^-]/dt) were determined to be 4.0, 5.7, 19.4, and 45.0 nmol dm^{-3} s^{-1} under 28, 45, 100, and 490 kHz ultrasound irradiations, respectively. The results were in excellent agreement with those of the ECL experiment. In eq 1, the OH radicals were generated in the sonochemical process. However, they were short-lived. Since the recombination between primary radicals is very fast with a second-order rate constant of 5×10^9 cm mol^{-1} s^{-1}, it resulted in the formation of stable H_2O_2 at the final step, as shown in eq 2. According to eqs 1 to 4, the production of H_2O_2 should be equivalent to the amount of I_3^- in the Weissler system. We thus suggest that the yield of H_2O_2 can be considered to be a direct indicator of the sonochemical activity.

In the next experiment, the measurements were carried out by placing the ECL optical sensor directly into a 490 kHz cylindrical sonochemical reactor, which was filled with phosphate buffer solution (pH 8.0) containing 50 μmol dm^{-3} luminol with solution height of 16 cm. It can be seen in Figure 2a that significant ECL signal was observed upon ultrasound irradiation. Since the magnitude of ECL intensity could not be observed in a stirred solution, it should be due to the chemical effect of cavitation rather than the effect of mass transport enhancement. The role of ECL induced by cavitation has not been fully clarified yet but has been suggested to be raised from the reactive species including H_2O_2.

Because the ECL optical sensor is sufficiently sensitive to determine the sonochemical activity in situ, the spatial distribution of the cavitation intensity in an ultrasound field was measured by placing the sensor in different sites during irradiation. Two types of waveform generation mode were employed. One was 490-kHz continuous wave (CW), and the other was a pulsed wave (PW) which was achieved by modulation of 490-kHz ultrasound with a 100 Hz square-wave pulse. As can be seen in Figure 2b, the highest ECL intensity was not in the region near the transducer but in the vicinity of the solution surface ($h =$ 16 cm, where h refers to the distance from the transducer) in the CW experiment. This phenomenon was also observed by other investigators.[6] The cavitational bubbles might be trapped near the reflection surface owing to the formation of standing waves. On the other hand, the cavitation zone appeared at $h =$ 12 cm in PW experiments, but the reason is not clear now. The spatial resolution of the measurement is dependent on the size of ECL probe. In this experiment, the optical fiber exposing into the solution was 3 mm in length, and the spatial resolution was less than 5 mm. The cavitation intensity in a transparent vessel

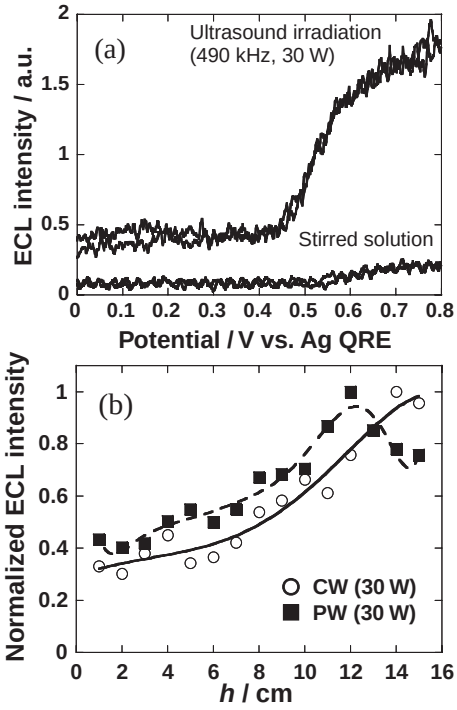

Figure 2. (a) ECL responses under ultrasonic irradiation and the stirred conditions, respectively. (b) Dependence of ECL intensity on the distance from the transducer (h) under CW and PW irradiations.

can be visualized based on sonochemiluminescence of luminol in an alkaline solution. It was confirmed that the distributions of the cavition intensity by ECL sensor were coincident with results in sonochemiluminescence experiments.[8]

In summary, a luminol-based ECL sensor has been shown to be an appropriate and reliable tool for the determination of hydroxyl radical production in aqueous solution. It is sufficiently sensitive for in situ measurement of sonochemical activity as well as the cavitation distribution within an ultrasound field.

References and Notes

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