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Detection of free radicals produced by a pulsed electrohydraulic discharge using electron spin resonance

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ABSTRACT

The detection of free radicals such as hydroxyl radical and hydrogen radical for plasma in solution induced by a pulsed electrohydraulic discharge are successfully performed using electron spin resonance measurement. The plasma reactor is a barrier-type and consists of a stainless needle high-voltage (+35 to 65 kV) electrode partially immersed in the solution and a Pyrex glass solution container around which an aluminum film grounded electrode is wrapped. Streamers are induced in the solution. After adding iron (II) sulfate or radical trapping agent before the plasma application, the spectrum for radicals is clearly detected. A reactive dye solution is dramatically decolorized.

1. Introduction

Recently, it has become clear that a pulsed power technology which can easily generate extremely high voltage in a very short time (a nanosecond), is very effective for the treatment of hazardous gases [1–3], and plasma treatment for NO_x, SO_x, PM (particulate matter) [1], VOC (volatile organic compounds) [2], odorous substances and dioxin [3] have been investigated. On the other hand, as it is also possible to generate plasma stably in water or electrohydraulic discharge plasma using pulsed power, research of applications such as solution purification [4], sterilization [5,6], and decolorization [7–9] using the technology have been extended [4–14]. However compared with research of gas-phase plasma, plasma in liquids has a relatively short history. Therefore, we cannot say that basic phenomena such as the decomposition reaction mechanism in solution, type of generated gas by discharge in solution, difference between electrolysis reaction and plasma reactions, and phase-change inside the plasma are have been completely understood. There is especially a few researches on radical identification in electrohydraulic discharge induced plasma although chemical probes [10,11], and optical analysis [12] can be applied to this end.

In the present paper, we report experimental results on the decolorization of a reactive dye solution, which is a relatively strong dye and cannot be decomposed only by plasma. Free radicals produced by a pulsed electrohydraulic discharge are detected using electron spin resonance (ESR) measurement.

2. Experimental apparatus and method

A schematic diagram for the experimental setup is shown in Fig. 1. A Pyrex glass beaker (inner diameter = 6.24 cm, glass thickness = 1.8 mm, liquid volume = 200 mL) is filled with pure water or a dye solution. A stainless steel needle electrode (diameter = 1 mm) is completely covered in PTFE plastic, except for the tip, which is immersed in water to a depth of 3 cm and used as a positive electrode. Aluminum foil is wrapped around the outside and bottom surfaces of the beaker as a grounded electrode. A high voltage pulse is applied between the electrodes using a sphere gap type direct-current pulse high-voltage electric power source (gap = 4–6 mm, Masuda Research Inc., Japan) with an applied output voltage of 10–65 kV, a pulse width of 540 ns and a pulse frequency of 120 pps (pulses per second, 120 Hz). The circuit consists of, a protection resistance (3 MΩ), a load resistance (50 kΩ), capacitor (1 nF), and an inductor (4.7 mH). A photograph of the

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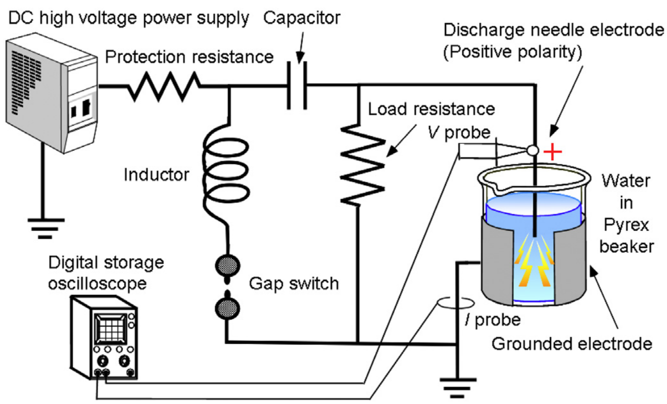
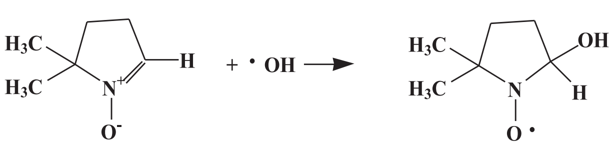


Fig. 1. Schematic diagram of experimental setup for liquid-phase plasma.

pulse generating circuit for high-voltage power supply is shown in Fig. 2. The voltage and current waveforms are measured with a digital storage oscilloscope (Yokogawa Electric Co., DL1740) through a high voltage divider (Nissin Pulse Electronics Co., Ltd., 5000:1 high voltage probe, EP-100K) and a current probe (Pearson Electronics Inc., 2878). The plasma reactor is a barrier-type electrohydraulic discharge plasma reactor, and stable discharge can be realized with a dielectric barrier between the electrodes.

ESR measurement is conducted with a free radical monitoring apparatus using electron spin resonance under a magnetic field (JEOL Ltd., Japan, JES-FR30). Measurements are mainly carried out under the following conditions: microwave output power of 4 mW, resonance frequency of 9.425 GHz, magnetic field strength of 336.5 mT, and sweep width and sweep time of the magnetic field of 5.000 mT, and sweep time of 2.0 min, respectively. All data are averaged three times. After the plasma application, 0.13 mL of solution is sampled from the beaker and put into a measurement container. The sample is placed inside the resonator cavity of the ESR apparatus for measurement. The period between the end of the plasma application and the beginning of the ESR measurement is less than 3 min. Manganese (Mn) is used as a marker to calibrate the measured data. DMPO (5.5-Dimethyl-1-pyrroline N-oxide, $C_6H_{11}NO$) is used as a radical (spin) trapping agent, or, radical stabilizer, because the lifetime of radicals is generally very short ($\sim\mu s$). The concentration of added DMPO is 2 g to 200 mL liquid throughout the experiments. When DMPO reacts with a hydroxyl radical, a spin adduct of DMPO-OH with a longer lifetime ($\sim$1 h) is generated according to the chemical reaction (1):



(1)

The treated liquids are as follows: pure water and solutions of reactive dye (C. I. Reactive RED 106, $C_{25}H_{18}O_8N_3S_4Na$) with concentrations of 0.1 g/L, 0.05 g/L, and 0.01 g/L. The electrical conductivity is measured with a conductivity meter (Hach Co., Japan, CO150). The optical absorption of the dye solution is measured with a spectrophotometer (Shimadzu Corporation, Japan, UV-1600PC).

3. Experimental results and discussion

3.1. Generation of plasma induced by electrohydraulic discharge

First, the minimum voltage to generate plasma in distilled water (electrical conductivity = 2.6 μS/cm) is determined. For instance, when the applied voltage is 50 kV (pulse width of 520 ns and pulse frequency of 120 pps), a series of electrohydraulic discharge streamers are observed as shown in Fig. 3. A significant amount of small bubbles is generated by the discharge. The composition of these bubbles is investigated using a gas detection tube (Gastec Corp.). As a result, ozone ($\sim$60 ppm) and hydrogen ($\sim$0.1%) are detected near the water surface.

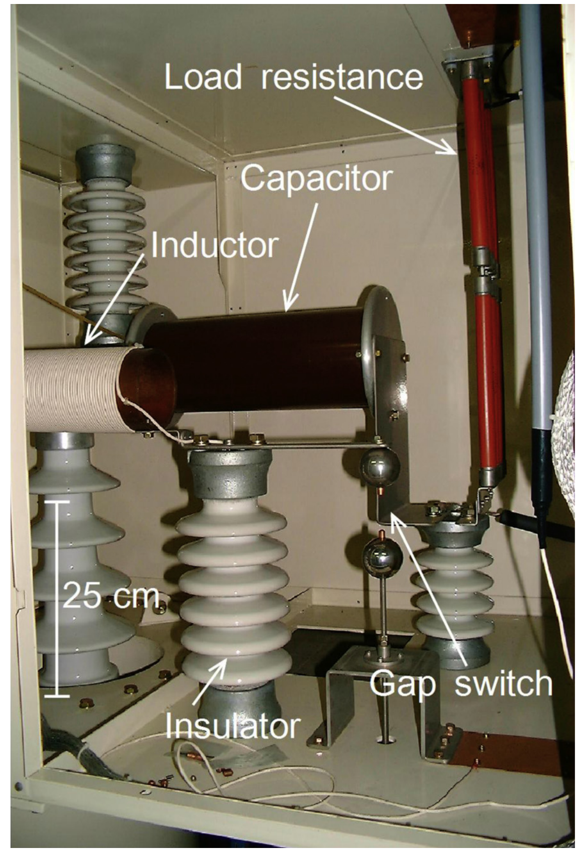


Fig. 2. Photograph of pulse generating circuit for high-voltage power supply.

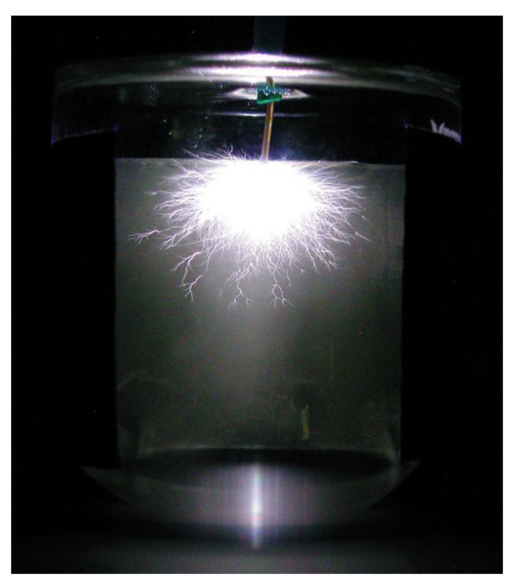


Fig. 3. Photograph of plasma induced by the electrohydraulic barrier discharge (exposure time = 1/3 s).