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Evaluation of chemical species in liquid induced by atmospheric glow discharge in contact with liquid

液体と接する大気圧グロ-放電によって誘起される液中化学種の評価

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Atmospheric pressure glow discharge in contact with a liquid is considered as electrolysis with a plasma electrode. We studied liquid phase reaction in plasma-assisted electrolysis using atmospheric DC glow discharge as a plasma electrode instead of conventional metal electrode. In this work, we measured the quantity of free residual chlorine, nitrite ion, and hydrogen peroxide by using reagents as a parameter of discharge condition comparing with those in the normal electrolysis reaction.

1. Introduction

Nonthermal atmospheric pressure plasmas in contact with liquid are widely studied aiming variety of plasma applications [1]. DC glow discharge with liquid electrode is an easy method to obtain simple and stable plasma-liquid interface. When we focus attention on liquid-phase reaction, the discharge system is considered as electrolysis with plasma electrode. The plasma electrode will supply electrons and positive ions to the liquid surface in a different way from the conventional metal electrode. However, the phenomena at plasma-liquid interface have not been understood completely. In this work, we measured the concentrations of residual chlorine, nitrite ion and hydrogen peroxide in the liquid using reagents as a parameter of discharge condition comparing with those in the normal electrolysis reaction.

2. Experimental procedure

Figure 1 shows basic experimental setup. Petri dish (70 mL) is filled with an electrolyte of NaCl or Na_2SO_4 solution with a concentration of 1 %. A platinum wire is immersed in the liquid as a metal electrode. A stainless steel nozzle, from which helium gas is injected into air with a rate of 200 sccm, is set about 1 mm above the liquid surface. By applying a dc voltage between the nozzle and the Pt electrode, atmospheric-pressure glow discharge as a plasma electrode is generated along the helium flow between the nozzle and the liquid surface. By changing the polarity of the applied voltage, the plasma electrode works as both anode and cathode. Let us refer each system as “plasma cathode system”, and “plasma cathode system”, respectively. We also used “dual plasma system”, in which plasma anode and plasma cathode are simultaneously places without Pt electrode. A sheath-flow-type electrode shown in Fig. 1 is also used to control the gas composition around the discharge. The typical rate of the sheath flow is 600 sccm while that of the helium core flow is kept 200 sccm. For comparison, normal electrolysis was also observed with two platinum electrodes immersed in the solution. Experiment was carried out typically at a constant current of 3 mA for 5 minutes.

In this work, we measured the concentrations of free residual chlorine, NO_2^-, and H_2O_2 using chemical reagents. The concentration of free residual chlorine, which mainly consists of HClO, was measured by DPD(N,N-diethyl-p-phenylenediamine) color comparison method. The concentrations of NO_2^-, H_2O_2 are measured by naphthylethylenediamine absorptiometry and 4-aminoantipyrine absorptiometry with enzyme, respectively.

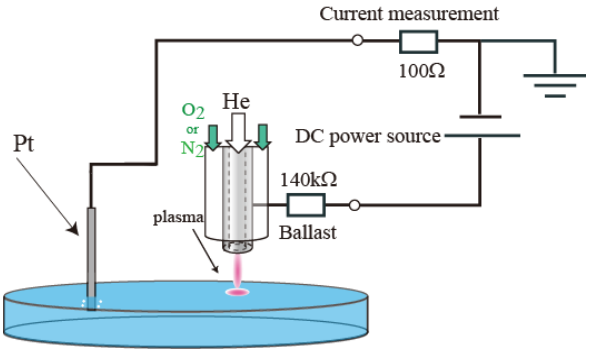

Fig.1.Experimental setup of anode plasma system

3. Results and discussion

3.1 *Measurement of free residual chlorine*

The concentration of free residual chlorine in NaCl solution was 2-5 mg/L after normal electrolysis while it was below the detection limit after positive ion irradiation of liquid surface with plasma anode system. The free residual chlorine is considered to be HClO in the present experiment. The major reaction for HClO generation in liquid is

$$Cl_2+H_2O \Leftrightarrow HClO+HCl \quad (1)$$

The HClO concentration estimate from electric current in the present normal electrolysis is 3.14 mg/L. Thus the measured concentration is reasonable within the margin of error. The experimental results show that the generation of Cl_2 gas is not active in positive ion irradiation of liquid surface as predicted in our previous paper [2].

3.2 *Measurement of NO_2^-*

NO_2^- was not detected in the normal electrolysis with Na_2SO_4 solution. In the dual plasma system with Na_2SO_4 solution, the concentration of NO_2^- was 1.0 mg/L. This is inevitable result because nitrogen oxides generated in gas-phase dissolve in the liquid. The plasma anode system generated more NO_2^- than the plasma cathode system.

The influence of discharge condition on NO_2^- concentration in liquid was investigated. Figure 2 shows the discharge gap versus NO_2^- concentration using plasma anode system with Na_2SO_4 solution, the concentration increases with increase of discharge gap because air mixture ratio into helium increases. To control the gas composition around the discharge, a sheath-flow-type electrode was used and NO_2^- concentration was measured. As shown in Fig. 3, the NO_2^- concentration is higher with sheath flow of N_2 than with normal type electrode, and NO_2^- is below detection limit with sheath flow of O_2. The relationship between pH and NO_2^- concentration is shown in Fig. 4. Higher NO_2^- concentration causes the lower pH.

The concentration of NO_2^- was also measured using NaCl solution. Very few NO_2^- was detected with both plasma anode system and plasma cathode system. In dual plasma system, the concentration of NO_2^- was 0.05 mg/L. That is, the concentration of NO_2^- is lower than that with Na_2SO_4 solution. We deduce that very small amount of free residual chlorine affects the reaction of NO_2^- in the liquid.

3.3 *Measurement of H_2O_2*

The concentration of H_2O_2 in the liquid linearly increased with the discharge current and the plasma irradiation time. Figure 5 shows the dependence of H_2O_2 concentration on helium flow rate at current of 10 mA and gap distance of 5 mm. Increase of flow rate results in the decrease of H_2O_2 concentration. This will be explained by the gas composition for optimum generation of OH and H_2O_2 in the gas.

Acknowledgments

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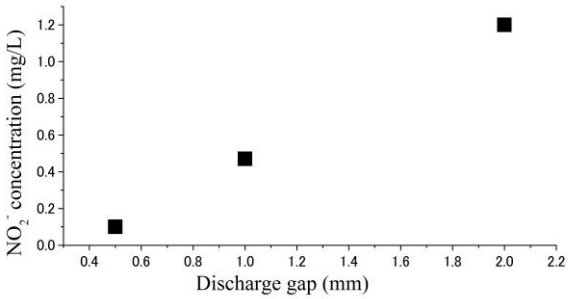

Fig. 2 Influence of discharge gap on NO_2^- concentration

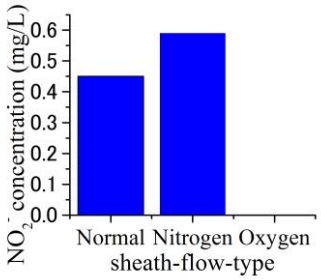

Fig. 3 Influence of sheath-flow-type on NO_2^- concentration

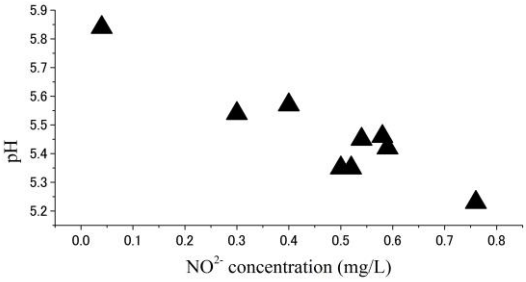

Fig. 4 The relationship between pH and NO_2^- concentration

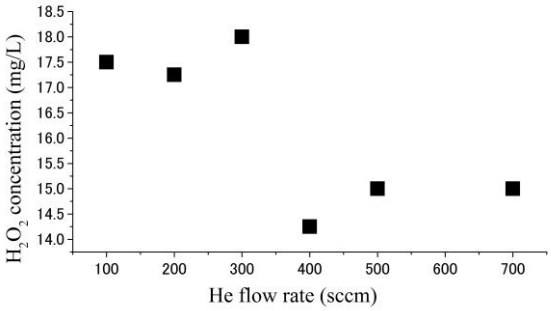

Fig. 5 Dependence of H_2O_2 concentration on helium flow rate

References

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[2] F. Tochikubo Y. Shimokawa, N. Shirai, and S. Uchida accepted in Jpn. J. Appl. Phys.