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Study on Plasma-Liquid Interaction by Numerical Simulation
計算科学によるプラズマ-液相相互作用

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We mainly present the results of numerical simulation on dc glow discharge with liquid electrode to reveal a part of plasma-liquid interactions. The results were compared with that of conventional electrolysis to discuss the liquid phase structure such as electric double layer formation. Charge injection from plasma to liquid largely affects not only the potential distribution in liquid but also the local pH near the plasma-liquid interface.

1. Introduction

Nonthermal atmospheric-pressure plasmas (APP) in contact with liquids have been studied energetically for material processing, environmental and biomedical applications [1,2]. There are many kinds of APPs in contact with liquids such as dielectric barrier discharge, plasma jet with noble gas flow, and electrical discharges in bubbles. In any types of APPs, the plasma-liquid interaction is very important for determining the physical and chemical processes in liquid. Although liquid-phase reactions induced by high-energy particles have been investigated in radiation chemistry, the plasma-liquid interactions with APPs are too complicated because many kinds of charged and neutral particles are irradiated on the liquid surface simultaneously. Recently, numerical simulations are attempted to understand the plasma-liquid interaction with APPs on the basis of simplified model. In this paper, we mainly show the simulation results of electrical discharge with liquid electrode, and discuss the plasma-liquid interaction.

2. Physical Quantities in Plasma and Liquid

It is worthy to compare the physical quantities in plasma and liquid, and they are shown in Table I. The plasma density in liquid depends on the electrolyte concentration, and is high even in the deionized water. This means that small unbalance of charged species causes the strong electric field such as electric double layer (EDL) in front of metal electrode. Diffusion coefficient of both ionic and neutral species in liquid is on the order of 10^{-5} cm^2s^{-1}, thus, the diffusion is not the dominant process for transport of chemical species in liquid. When the electrolyte concentration is approximately less than 10 mM, the conductivity in liquid becomes lower than that in APP. In such case, the electric field in the liquid becomes relatively large.

Table I. Comparison of physical quantities in atmospheric pressure plasma and in liquid.

	In APP	In liquid
Medium density (cm^{-3})	2.45×10^{19}	3.34×10^{22}
Plasma density (cm^{-3})	$10^{12}\sim10^{15}$	6.02×10^{20} (1M electrolyte) 6.02×10^{13} (deionized water)
Diffusion coefficient (cm^2s^{-1})	$\sim10^3$ (electron)	$\sim10^{-5}$
Mobility ($cm^2V^{-1}s^{-1}$)	$\sim10^3$ (electron)	$\sim10^{-3}$
Conductivity ($S\cdot cm^{-1}$)	0.01 (@10^{14} cm^{-3})	0.1 (1M electrolyte) 5.48×10^{-8} (deionized water)

3. Electrical discharges with liquid electrode

3.1 *Conventional electrolysis*

When dc voltage is applied between two metal electrodes in the liquid, EDLs are formed in front of electrodes due to the drift motion of ionic species as shown in Fig. 1. The EDL is similar to the Debye shielding, and the Debye length λ_D is written as

$$\lambda_D = 0.304M^{-1/2}\ \text{nm}, \qquad (1)$$

where *M* is the concentration of electrolyte in mol/L. The Debye length becomes in the range of nm. The strong electric field at the EDL promotes the electrode reaction. Morrow et al. calculated the EDL formation process in NaCl solution using continuity equations for ionic species coupled with Poisson's equation [3]. For example, with 0.01 M NaCl solution, the concentrations of $Cl^-$and Na^+ in front of the anode were 3×10^{20} cm^{-3} and 10^{17} cm^{-3}, respectively. The electric field reaches 55 MVm^{-1}. Since the concentrations of OH^- and

H^+ also drastically change in front of electrodes, local pH value changes from 7. This suggests that local reactivity varies with location considerably.

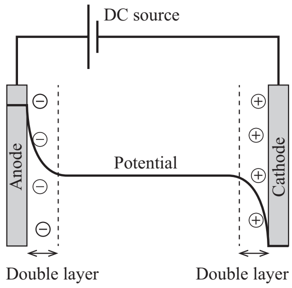

Fig.1. Schematics of electric double layer formation and potential distribution in conventional electrolysis.

3.2 *Barrier discharge in contact with liquid*

When one of the metal electrodes is replaced with APP, the charge injection mechanism into liquid changes from the conventional electrolysis. Shirafuji et al. performed numerical simulation of dielectric barrier discharge (DBD) in atmospheric pressure Ar in contact with a liquid by one-dimensional fluid model considering continuity equations for both gas-phase and liquid-phase species coupled with Poisson's equation [4]. The results predict the formation of EDL-like structure, where concentrations of anion and cation have their peaks alternately coincident with the applied ac voltage. They also predict that unipolar EDL-like structure is possible to form by tuning the ion transport parameters. Since the EDL-like structure is formed by the injection of electrons or positive ions from the DBD to the liquid surface, its formation mechanism is different from that in conventional electrolysis.

3.3 *DC glow discharge in contact with liquid*

DC glow discharge with a liquid electrode is an easy method to obtain a stable gas discharge plasma in contact with liquid. It can be applied for the synthesis of metallic nanoparticles in a liquid [5]. We performed numerical simulation of dc glow discharge in atmospheric pressure He in contact with a liquid by one-dimensional simulation. Both gas gap and liquid depth are set to be 1 mm. The liquid is a NaCl solution. The simulation method is essentially the same as that by Shirafuji et al [4]. Figure 2 is the potential distribution with 6 mM NaCl solution. Typical glow discharge structure with cathode fall and positive column is formed in the gas. Because the conductivity of the liquid is not so high, the voltage drop in the liquid is large. In Fig. 3, the spatial distribution of ionic species in liquid is shown. EDL is formed in front of the metal electrode. However, the concentration of Na^+ and Cl^- are almost same near the plasma-liquid interface, and therefore, EDL-like structure is not formed. Higher H^+ concentration near the plasma-liquid interface is caused from the positive ion injection from plasma, similar to the case of DBD in contact with the liquid.

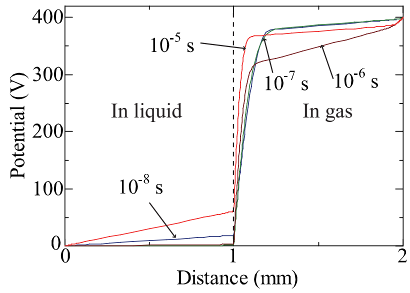

Fig.2. Potential distribution in dc glow discharge in atmospheric pressure He in contact with liquid. Liquid is 6 mM NaCl solution.

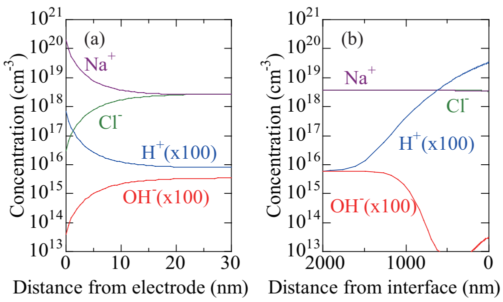

Fig.3. Spatial distribution of ionic species in liquid near (a) metal electrode and (b) plasma-liquid interface.

4. Summary

Simulation results of electrical discharge with liquid electrode are shown to reveal a part of plasma-liquid interactions. The charge injection from plasma to liquid determines the electrical characteristics such as EDL-like structure.

Acknowledgments

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