

Diagnostics and modelling of plasma and liquid interfacial phenomena

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Abstract: In this work, we discussed the plasma-liquid interfacial phenomena in atmospheric-pressure dc glow discharge in contact with liquid. Experiments were carried out to find some phenomena related to plasma-induced liquid-phase reaction. Numerical simulation was carried out to discuss the detailed structure of dc glow discharge with liquid electrode, especially the structure and the chemical reaction processes near the plasma-liquid interface in the liquid.

Keywords: plasma-liquid interface, glow discharge electrolysis

1. Introduction

Atmospheric-pressure nonequilibrium plasmas in contact with liquid are widely drawing attention for their various potentials in material science, medicine, agriculture, environmental protection and so on. In many cases, active species such as electrons, ions and neutral radicals in the plasma are transported into the liquid through the plasma-liquid interface, and the liquid-phase reactions are induced as shown in Fig. 1. Liquid has equal amounts of anions and cations which determine the liquid conductivity, and charged layer called as double layer is formed at heterogeneous surface in the liquid. Therefore, liquid, especially electrolyte has similar characteristics to gas discharge plasma. Comparison of physical properties of charged species in gas plasma and liquid water is shown in Table 1. Most important point is the large difference of transport coefficient such as mobility and diffusion coefficient. Consequently, the charged and neutral species from the plasma will accumulate near the plasma-liquid interface in the liquid. Although this thin active layer must be important in plasma-induced liquid-phase reaction, it is difficult to observe the physical and chemical properties of this thin layer experimentally.

There are many kinds of atmospheric-pressure non-equilibrium plasma in contact with the liquid. For the discussion of phenomena at plasma-liquid interface, dc glow discharge with liquid electrode is an effective tool since the plasma-liquid interface is temporally more stable

compared with other methods, the reaction rate can be controlled by changing the discharge current, and the liquid surface can be exposed to electrons or positive ions from the dc glow discharge selectively by changing the polarity of applied voltage [1,2]. This type of discharge is also considered as glow discharge electrolysis (GDE) at atmospheric pressure.

In this work, we show some of experimental results focusing on plasma-liquid interfacial phenomena using atmospheric-pressure dc glow discharge in contact with liquid. To investigate the detailed structure and the reaction processes in the dc glow discharge with liquid electrode, numerical simulation was also carried out.

Table 1. Comparison of physical properties in gas plasma and liquid water.

	In gas plasma @ 1 atm	In liquid water
Medium density	$2.45 \times 10^{19} \text{ cm}^{-3}$ @ 300 K	$3.34 \times 10^{22} \text{ cm}^{-3}$
Plasma density	$10^{11} \sim 10^{15} \text{ cm}^{-3}$	$6.02 \times 10^{20} \text{ cm}^{-3}$ @ 1M $6.02 \times 10^{13} \text{ cm}^{-3}$ in DI
Diffusion coefficient	electron $\sim 10^3 \text{ cm}^2/\text{s}$ ion $\sim 1 \text{ cm}^2/\text{s}$	$\sim 10^{-5} \text{ cm}^2/\text{s}$
Mobility	electron $\sim 10^3 \text{ cm}^2/\text{V} \cdot \text{s}$	$\sim 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$
Drift velocity	electron $10^6 \sim 10^8 \text{ cm/s}$ ion $10^3 \sim 10^5 \text{ cm/s}$	10^{-2} cm/s @ 10V/s
Conductivity	0.01 S/cm @ 10^{14} cm^{-3}	0.1 S/cm @ 1M ($5.48 \times 10^{-8} \text{ S/cm}$ in DI)

DI: deionized water.

2. Experiment

2.1. Setup of dc glow discharge with liquid electrode

Typical experimental setup and the picture of the dc glow discharge are shown in Fig. 2. A nozzle electrode made of stainless-steel with inner and outer diameters of 500 and 800 μm is set above the liquid surface with gap length of 0.5-2.0 mm. A working gas, helium, is fed through the nozzle electrode in open air. The typical flow rate is 200 sccm. Pt wire is immersed in the liquid as the counter electrode. By applying a dc voltage between the electrodes through the resistor for current limitation, a stable atmospheric-pressure dc glow discharge is generated along a helium flow as shown in Fig. 2(b) since the breakdown voltage of helium is much lower than that of air. We also

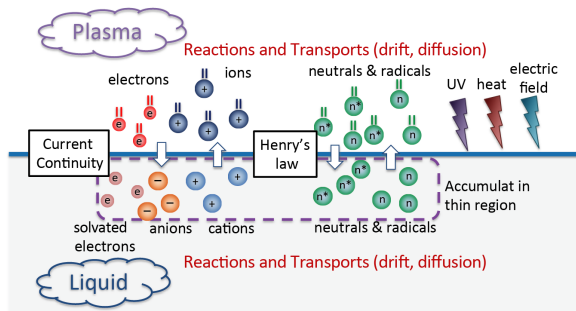


Fig. 1. Image of particle transport at plasma-liquid interface.

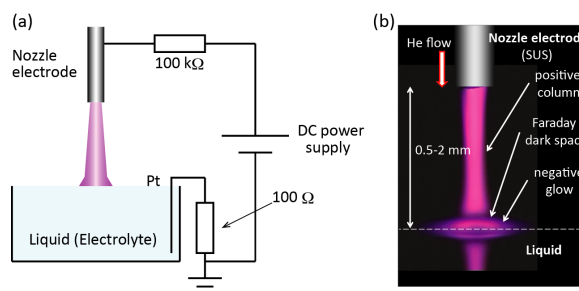


Fig. 2. Experimental setup, (a) electrical circuit and (b) picture of typical glow discharge.

used Hoffman electrolysis apparatus, the H-shape glass reactor, to separate the anodic and cathodic reactions. The typical electrolyte in this work is NaCl solution, Na₂SO₄ solution, AgNO₃ solution and HAuCl₄ solution. The glow discharge is observed by a digital camera or high-speed camera. The spatial optical emission is also observed by a monochromator. The fluctuation of refraction index caused by the gas/liquid heating or gas flow was monitored by schlieren method.

2.2. Plasma irradiation changes the solution pH

It is well known that the plasma irradiation of liquid surface in air acidifies the liquid because of the dissolution of nitrogen oxides. However, even in the environment without nitrogen oxides, the plasma irradiation changes the local pH of the solution. We separated the anodic and cathodic reactions by using the H-shaped reactor [2]. The liquid surface was exposed to electrons or positive ions from the dc glow discharge independently, and the local change of solution pH was visualized by adding bromothymol blue or phenolphthalein in the solution. The results showed that the electron irradiation of liquid surface alkalinized the solution locally and the positive ion irradiation acidified the solution. The incident electron impact dissociation or ionization of water molecules at liquid surface is less effective. The incident electron on the solution surface will be stabilized as hydrated electron by electron-dipole interactions, and the hydrated electron is changed into OH⁻ through the reaction with water molecule. It is difficult for low-energy positive ions at atmospheric pressure to ionize the water molecule at the liquid surface although they are accelerated in the cathode fall region. It is reasonable to consider that the irradiation of low-energy positive ions from the glow discharge to the liquid surface effectively generates H⁺ and OH via charge transfer collision, which effectively occurs at low energy condition.

2.3. Reaction of plasma-induced active species

The GDE is studied for material processing in liquid such as metal nanoparticles (NPs) synthesis [3,4] and surface modification [5]. In the synthesis of metal NPs, metal ions in the liquid are considered to be reduced by short-lived active species such as hydrated electrons or H atoms, which are expected to be generated in the liquid near plasma-

liquid interface by the electron irradiation of liquid surface. This type of reaction at plasma-liquid interface will be the distinctive one in plasma-induced liquid-phase reaction, and it is not replaceable by other methods.

The surface modification of polymer materials was achieved by GDE with electrolyte cathode using KCl, KBr or KI solutions [5]. We tried the surface modification of polypropylene (PP) in the liquid by GDE with electrolyte cathode. However, the hydrophilicity of PP was not improved. It was improved by advanced oxidation process using H₂O₂ and UV, and Fenton method using Fe₂⁺ and H₂O₂. We could modify the PP surface by the combination of GDE and iron electrolysis, which supply H₂O₂ and Fe₂⁺, respectively. This fact implies that the OH radical is necessary for surface modification of PP, but GDE cannot directly supply OH radical in the liquid bulk if there are no chain reactions. This type of reaction can be sometimes replaced by other methods very effectively.

2.4. Plasma-induced liquid flow

Plasma-induced liquid-phase reactions starts in the liquid near the plasma-liquid interface. Since the diffusion in a liquid is very slow, the surface-layer reaction is diffusion-limited. Therefore, some sort of liquid flow is necessary to exchange the chemicals in the thin surface layer of a liquid for the promotion of efficient reactions.

We found the appearance of specific downward liquid flow immediately below the dc glow discharge in GDE [6]. The downward liquid flow started to become strong from the plasma-liquid interface just after the initiation of the dc glow discharge, but gradually weakened with time, and finally disappeared at approximately 10 s. The direction of the downward liquid flow was not changed by the current direction in the liquid. The downward liquid flow becomes stronger with increasing liquid conductivity because the Joule heating of liquid is suppressed. These observations clearly show that the plasma-induced downward force at the plasma-liquid interface generates the downward liquid flow, while other factors such as liquid heating and gas-flow-induced liquid flow prevent the downward liquid flow.

3. Simulation

Experimental results suggest that plasma-induced liquid-phase reactions are initiated in the surface layer by electron or positive ion irradiation of liquid surface. Numerical simulation of GDE at atmospheric pressure was carried out to investigate the detailed structure and the reaction processes.

3.1. Modelling of glow discharge electrolysis

Assuming the radial uniformity of the glow discharge in Fig. 2(b), one-dimensional simulation of GDE was carried out. The model consists of atmospheric-pressure dc glow discharge in helium and electrolyte solution connected in series between parallel plate metal electrodes based on fluid simulation. Thus, continuity equations of species in gas and liquid are calculated simultaneously coupled with

Poisson's equation. Both the gas-gap length and electrolyte solution depth are set to be 1 mm. The electrolyte solution is assumed to be NaCl solution or AgNO₃ solution. The boundary condition at plasma-liquid interface is important for the prediction of the liquid-phase reaction in GDE, and is assumed based on the discussion in ref. [2]. That is, the electrons impinging on the liquid surface from the glow discharge were transformed into hydrated electron, and the positive ions impinging on the liquid surface were changed into H⁺ and OH due to charge transfer and the dissociation.

Electron irradiation: $e \rightarrow e_{aq}$ (1)

Positive ion irradiation: $\begin{cases} A^+ + H_2O \rightarrow A + H_2O^+ \\ H_2O^+ \rightarrow H^+ + OH \end{cases}$ (2)

Fig. 3 shows the spatial distributions of electrons and ions in the gas gap of GDE with 6 mM NaCl solution at applied voltage of 400 V. The current density is 440 mA/cm², which is higher than that of typical electrolysis. Since the cathode fall region faces the liquid surface, positive ions impinge on the liquid surface. Fig. 4 shows the liquid-phase ion distributions near the interface. In front of the metal cathode, cations are attracted while anions are repelled, thus the positive charge layer with strong electric field is formed within the thin region of approximately 10 nm from the metal cathode. This is so-called double layer. Cation concentration in the double layer is two orders of magnitude greater than that at bulk, and the pH close to the metal cathode decreases. On the other hand, double layer is not formed in front of plasma-liquid interface. Anions could be electrostatically attracted toward the anode. However, the positive ions from the glow discharge neutralized the negative charge layer. Since the assumption of eq. (2) causes plenty of H⁺ generation near the liquid surface, the solution pH in the thin region of a few 100 nm from the plasma-liquid interface ranges from 3 to 4. OH radicals are transported from the plasma or are generated at plasma-liquid interface, and again concentrate in the very thin region from the plasma-liquid interface. In the present case, OH radicals are transformed into H₂O₂, which will become a major oxidant in the liquid.

Similar simulation was carried out for AgNO₃ solution with applied voltage of -500 V aiming Ag nanoparticle synthesis with electron irradiation of the liquid surface. Spatial distributions of chemical species in liquid near the plasma-liquid interface is shown in Fig. 5. The hydrated electrons, which are transformed from incident electrons, react with other species. Thus, the hydrated electrons exist in very thin region from the liquid surface. This result qualitatively supports the experimental observation by Rumbach et al [7]. The fastest reaction of hydrated electrons is the reduction of Ag⁺, with reaction time of approximately 35 ns, and thus Ag has higher concentration with thinner profile near the plasma-liquid interface. This profile will influence the nucleation and growth for Ag particle synthesis. Another interesting property is the pH of the solution. The hydrated electrons react with H₂O to form

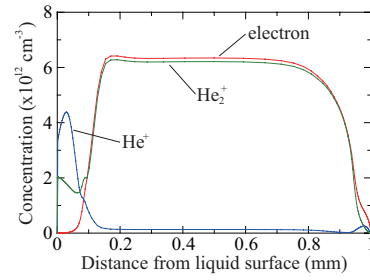


Fig. 3. Spatial distribution of charged species in the gas region of GDE with 6 mM NaCl solution.

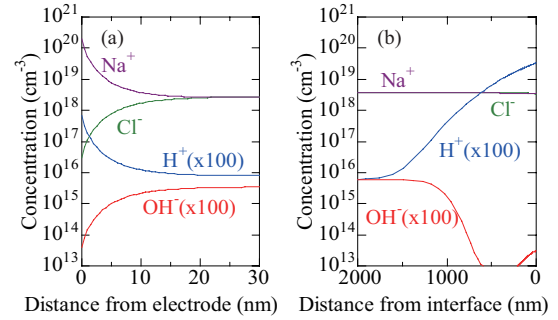


Fig. 4. Spatial distribution of ion species in the liquid of GDE in front of (a) metal cathode and (b) liquid surface at 40 μs.

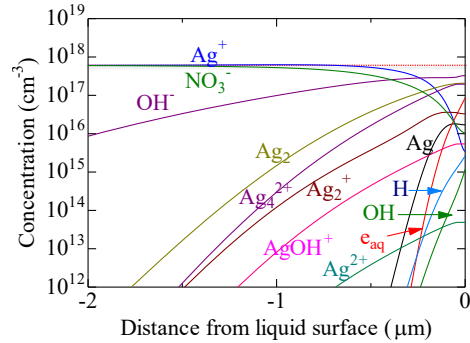


Fig. 5. Spatial distribution of chemical species near liquid surface in 1 mM AgNO₃ solution at 50 μs with applied voltage of -500 V.

OH⁻. Therefore, the solution near the plasma-liquid interface is alkalified, and the pH value locally exceeds 10.

Since the plasma-induced liquid-phase reaction depends on the current density, it is preferred to consider the radial distribution of the glow discharge. Besides the local electric field in the liquid is often effective against the gene transfection using plasma. Therefore, two-dimensional simulation was carried out under the condition similar to the experimental setup shown in Fig. 2. Both the gas-gap length and the liquid depth are set to be 1 mm. Helium gas is fed into atmospheric-pressure nitrogen with flow velocity of 10 m/s. Current continuity equation in the liquid was solved at given liquid conductivity. Fig. 6 is the potential distribution at applied voltage of ±500 V with

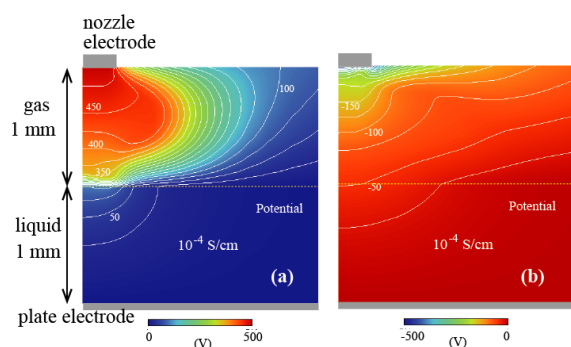


Fig. 6. Calculated potential distributions in GDE at liquid conductivity of 10^{-4} S/cm and applied voltage of (a) 500 V and (b) -500 V, respectively.

liquid conductivity of 10^{-4} S/cm, which roughly corresponds to 1 mM electrolyte. The potential drop in the liquid depends on the liquid conductivity. The electric field in the liquid is enhanced just below the glow discharge.

3.2. Monte Carlo simulation of incident electrons

Monte-Carlo modeling of the radiolysis of liquid water by high-energy electrons is carried out in the radiation chemistry [8]. Same method can be applied to consider the generation of hydrated electrons by the irradiation of liquid surface to low-energy electron from the glow discharge. We traced the trajectory of electrons by Monte-Carlo simulation. The electron energy distribution in the plasma is assumed to be Maxwellian distribution with 3 eV. Total number of incident electron is 100,000. Fig. 7 shows the distribution of hydrated electrons and OH radical generated

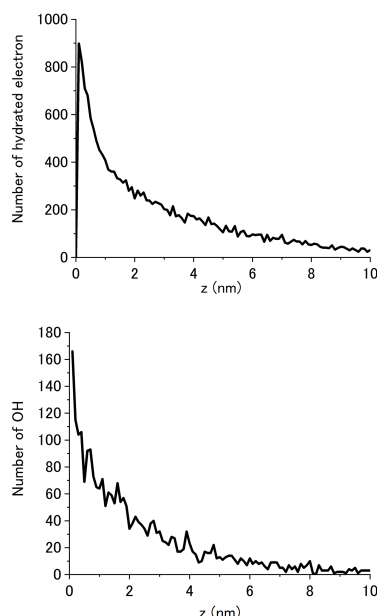


Fig. 7. Generation distributions of hydrated electron and OH radical in the liquid from the liquid surface obtained by Monte-Carlo simulation. The gas-phase initial electrons are Maxwellian distribution of 3 eV.

in the liquid. OH radical is generated by the electron impact dissociation. The averaged penetration depth of electron is 3.2 nm while the averaged position of OH generation is 2.5 nm from the liquid surface.

4. Summary

In this work, we discussed the plasma-liquid interfacial phenomena in atmospheric-pressure dc glow discharge in contact with liquid. Experiments were carried out to find some phenomena related to plasma-induced liquid-phase reactions. Numerical simulation was carried out to investigate the detailed structure of dc glow discharge with liquid electrode, especially the structure and chemical processes near plasma-liquid interface in the liquid. In the liquid, double layer with approximately 10 nm width was produced in front of metal electrode while no double layer formation was observed at plasma-liquid interface. Plasma-induced liquid-phase reaction starts from very thin layer less than 100 nm from the liquid surface since the active species from gas phase accumulate in this layer. The solution pH is also locally changed by the irradiation of liquid surface to electrons or positive ions.

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