Simulation of glow discharge electrolysis for material processing in liquid

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In glow discharge electrolysis, the liquid-phase reactions are induced by electrons/ions irradiation of the liquid surface from the plasma. In this work, we carried out numerical simulation of glow discharge electrolysis, which consists of atmospheric-pressure dc glow discharge and electrolyte solution connected in series between parallel plate metal electrodes, based on fluid simulation. The calculated glow discharge facing the liquid is essentially the same as that generated between metal electrodes. In the liquid, electric double layer with approximately 10 nm width was reproduced in front of metal electrode while no electric double layer was observed at plasma-liquid interface. We found that the liquid-phase chemistry is strongly affected by the electron/positive ion irradiation of the liquid surface from the glow discharge, especially in the thin region from the liquid surface.

1. Introduction

Atmospheric-pressure dc glow discharge with liquid electrode is applied for material processing such as metallic nanoparticles generation [1-2]. This system is considered as glow discharge electrolysis (GDE) at atmospheric pressure. In this system, the reactions in liquid are induced by the electrons/ions irradiation of the liquid surface from the liquid-phase thin layer at the plasma-liquid interface. Therefore, it is necessary to clarify the transport of charged and neutral species both in gas and liquid. In this work, we carried out one-dimensional numerical simulation of atmospheric-pressure GDE.

2. Simulation model

The simulation model for GDE is shown in Fig. 1. A glow discharge in atmospheric-pressure helium with 1 mm gas-gap is connected with NaCl solution with 1 mm depth in series. Both the glow discharge and the liquid regions were calculated based on fluid model using continuity equations for charged/neutral species coupled with Poisson equation. Boundary conditions at plasma-liquid interface is important to determine the characteristics of GDE. However, the information on the reactions at plasma-liquid interface is very limited, therefore, we assumed the following simple model: electron irradiation of the liquid surface from the plasma generates hydrated electrons: negative ion irradiation also generates hydrated electrons: any positive ion irradiation causes the generation of H^+ and OH through charge transfer collision: neutrals dissolve in the solution.

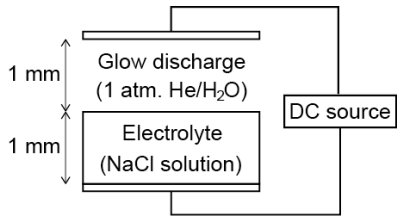

Fig.1. Model for glow discharge electrolysis.

3. Simulation results

The structure of atmospheric-pressure dc glow discharge is essentially the same as that calculated between two metal electrodes. Fig. 2 shows the ion distributions in liquid with glow discharge cathode. Very narrow negative charge layer with strong electric field is formed in the region of roughly 10 nm from metal anode. In front of the glow discharge cathode, we could not find the large difference in the concentrations between Na^+ and Cl^-. The incident electrons become hydrated electrons in the liquid, and react with other species. In the present case, hydrated electrons generate OH^- by the reaction with H_2O. Therefore, plenty of OH^- is generated close to the liquid surface, and local pH becomes approximately 10. The hydrated electron works as reductant. For example, hydrated electrons reduce the metal ions such as Ag^+ to synthesize Ag nanoparticles in liquid.

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References

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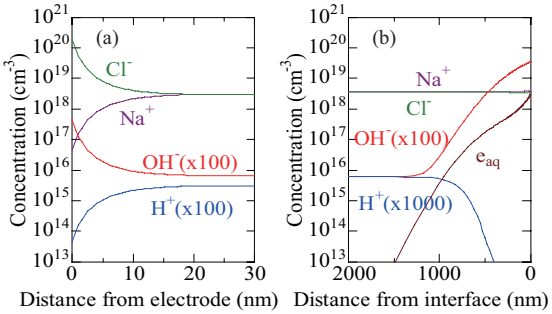

Fig. 2. Spatial distribution of ion species in the liquid in front of (a) metal anode and (b) glow discharge cathode.