

Plasma-induced liquid phase reaction in atmospheric pressure glow discharge electrolysis

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Abstract: We experimentally investigated some of initial reactions in liquid induced by electron or positive ion irradiation from atmospheric pressure dc glow discharge in contact with liquid. The local change of pH in the solution was visualized using pH indicator. OH radical generation yield in liquid was observed by chemical probe method. Possible reaction process was qualitatively discussed.

Keywords: plasma-assisted electrolysis, plasma-liquid interface, atmospheric glow discharge.

1. Introduction

Nonthermal atmospheric pressure plasmas in contact with liquid are widely studied expecting new plasma applications such as material processing, water treatment including sterilization, analytical chemistry and so on [1]. DC glow discharge with liquid electrode is one of easy methods to obtain stable electrical discharge in contact with liquid. It was studied to analyze the chemical composition of electrolyte by spectroscopic investigation [2]. Recently, advantage of dc glow discharge with liquid electrode is applied for synthesis of metallic nanoparticles (NPs) in liquid [3,4]. In our previous paper, we reported the characteristics of atmospheric dc glow discharges with liquid electrode [5]. When we focus attention on the liquid-phase reaction, the discharge system is considered as the electrolysis with plasma electrode. The plasma electrode will supply electrons or positive ions to the liquid surface with different chemical reaction scheme from the conventional electrolysis with metal electrodes. Although the electrolysis with plasma electrode is not the new technology [6], the interfacial phenomena between plasma and liquid have not been understood well.

In this work, we experimentally investigated some of initial reactions in various electrolytes induced by electron or positive ion irradiation from atmospheric pressure dc glow discharge with liquid electrode. Discussion is focused on the primary reactions in liquid initiated by electron or ion irradiation from plasma.

2. Experimental

Experimental setup used in this work is shown in Fig. 1. H-shaped glass reactor is used to separate the anodic and cathodic reactions. The reactor is filled with electrolyte solution. Aqueous solution of sodium chloride (NaCl) is used as electrolyte. A nozzle electrode made of stainless steel with inner and outer diameters of 500 and 800 μm is set about 2 mm above the solution surface. By injecting helium gas from the nozzle electrode with flow rate of 200 sccm, helium flow is formed between the nozzle electrode and liquid surface. We also used a platinum wire

electrode immersed in the solution. We prepared two types of reactors, single plasma reactor and dual plasma reactor as shown in Fig. 1. By applying a dc voltage between electrodes, electrolysis with single plasma electrode or dual plasma electrodes was operated. The applied voltage was measured by a high-voltage probe, and the discharge current was monitored by a voltage drop across a resistor of 100 Ω . In this paper, we use the terms “plasma anode” and “plasma cathode”. Plasma anode exposes positive ions from the cathode fall of glow discharge to liquid surface while plasma cathode exposes electrons from positive column to liquid surface. To visualize the local change of pH, small amount of bromothymol blue (BTB) was added in the solution. The pH change was also monitored by pH meter. Gas detector tube was used to detect Cl_2 , HCl and H_2 as a liquid-phase reaction product. The detection range is 0.1-2.0 ppm for Cl_2 , 2.0-20.0 ppm for HCl, and 0.05-0.8% for H_2 .

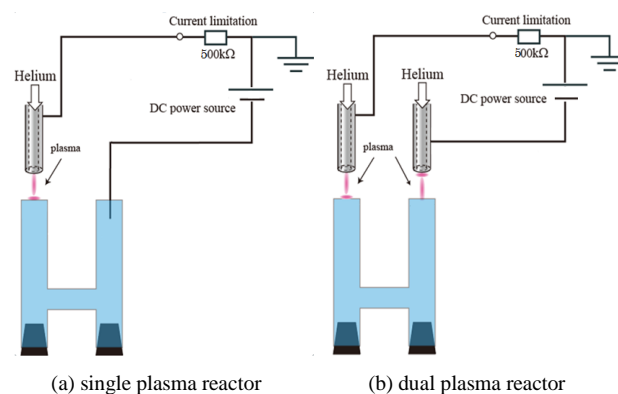


Fig.1 Reactors used for electrolysis with plasma electrode.

Since OH radical is important chemical species in liquid, the generation yield of OH radical was measured by a chemical probe method using terephthalic acid (TA) [7]. In this method, TA reacts with OH radical to form hydroxyterephthalic acid (HTA), which absorbs the light at 310 nm. In this experiment, we used a quartz cell with 10 mm length, 10 mm width and 45 mm height as an

electrolysis cell. The cell was filled with TA solution. The plasma anode/cathode is the same as that shown in Fig. 1(a). As a metal electrode, Pt wire was immersed in the solution. Light at 310 nm from semiconductor laser was introduced in the cell, and absolute HTA concentration was measured from the light transmission characteristics based on Beer-Lambert law.

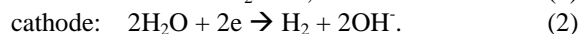
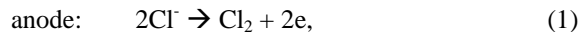
Metallic NPs synthesis was also carried out using the dual plasma electrolysis reactor in Fig. 1(b) to find the effect of electron and positive ion irradiation on NPs synthesis at same current condition simultaneously. We prepared silver nitrate (AgNO_3) solution with concentration of 0.1 mM for Ag NPs generation and tetrachloroauric acid (HAuCl_4) solution with concentration of 0.24 mM for Au NPs generation, in both of which sodium dodecyl sulfate (SDS) was added with concentration of 1.73 mM as surfactant to reduce the particles' agglomeration. The morphology and composition of the NPs generated was observed by transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX), respectively.

3. Experimental results

3.1 pH change by electron and ion irradiation

The experiment was performed at current of 3 mA in 3%-NaCl solution for 15 minutes. The initial pH was 7.4.

Let us first confirm the reaction in conventional electrolysis in NaCl solution between two metal electrodes. The electrolytic reaction is wellknown as



Thus Cl_2 gas is generated at anode while H_2 gas is generated at cathode and the liquid around cathode is slightly alkalinized. In our experiment, the pH around the cathode increased from 7.4 to 10.3. We observed H_2 generation at cathode, Cl_2 and HCl generation at anode by gas tube detector. The generated Cl_2 gas is partly dissolved in water and generates HClO as



Since HClO with high oxidizability easily decomposes BTB as pH indicator, the solution around anode was decolorized. That is, decolorization of solution is the evidence of Cl_2 generation in liquid. The pH around anode decreased from 7.4 to 3.0.

Next, we show the experimental result of electrolysis in dual plasma reactor. The solution in contact with plasma cathode, which exposes electrons to liquid surface, was alkalinized; the pH increased from 7.4 to 9.6. This means that the electrons from the plasma contribute OH^- generation in the solution directly or indirectly. The generation of H_2 gas was below the detection limit of the present gas tube detector.

The solution in contact with plasma anode, which exposes positive ions to liquid surface, was acidified; the pH decreased from 7.4 to 3.2. That is, the positive ion irradiation to the solution surface generates H^+ in liquid directly or indirectly. Decolorization of BTB was not clearly observed. In the conventional electrolysis, Cl_2 generation caused the acidification of solution. Although the generation of Cl_2 and HCl was below the detection limit in electrolysis with plasma anode, it is premature to conclude that positive ion irradiation does not generate Cl_2 without detailed gas analysis. However, we confirmed similar solution acidification in electrolysis with plasma anode in Na_2SO_4 solution, which never generates Cl_2 gas. In the series of experiment, we reduced NO_x dissolution into liquid, which often becomes dominant for liquid acidification. Therefore, the liquid acidification will result from the reaction induced by positive ion at liquid surface.

3.2 Estimation of OH generation yield

The experiment was performed at constant current of 1 mA. By reacting with OH radical, TA is transformed into HTA, which absorbs the light at around 310 nm. Measuring the temporal decay of transmitted light of 310 nm enables us to estimate the absolute concentration of HTA; ideally the HTA concentration equals to time integral of net OH yield in liquid. Fig. 2 shows the example of temporal decay of transmitted light during the positive ion irradiation to liquid surface.

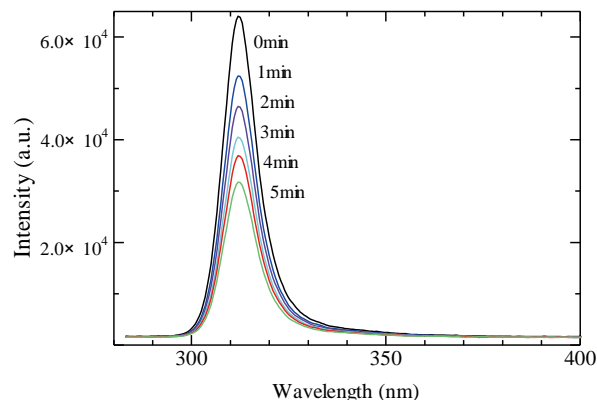


Fig.2 Temporal decay of transmitted light of 310 nm during the positive ion irradiation to liquid surface.

Fig. 3 shows the temporal evolution of HTA concentration. The HTA concentration increases almost linearly with time because OH radical in liquid is supplied at constant rate. The measured HTA concentration depends on the initial TA concentration. The reason will be the depletion of TA close to gas-liquid interface in liquid or rapid reaction of OH radical with other species. Another interesting point is that HTA generation yield is higher with plasma anode than with plasma cathode. Using the experimental result at TA concentration of 0.04 mol/L, the OH radical generation ratio per one impinging positive

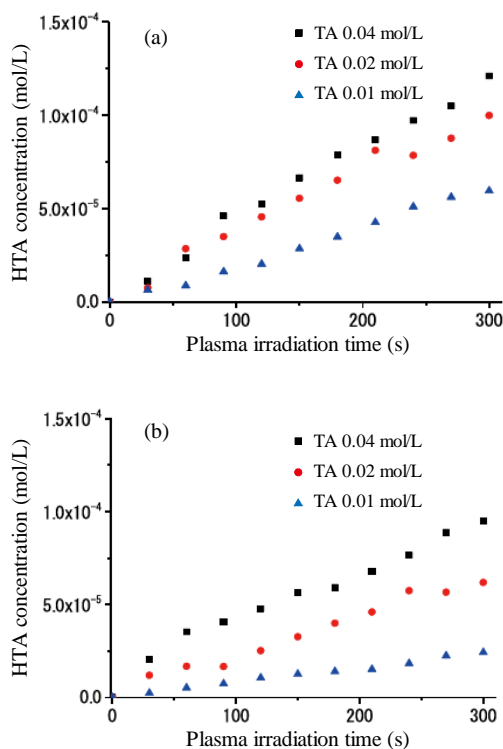


Fig.3 Measured HTA concentration at discharge current of 1 mA with (a) plasma anode (positive ion irradiation) and (b) plasma cathode (electron irradiation).

ion is at least 0.15, and that per one impinging electron is at least 0.11, based on Faraday's 1st law of electrolysis.

3.3 Reduction of metallic ions for NPs generation

Experiment for Ag and Au NPs generation was carried out at constant current of 3 mA for 5 min. Fig. 4 shows the picture of the dual plasma reactor with AgNO₃ solution before and after the plasma operation. After the discharge operation, the color of the solution below plasma cathode changed to yellow, which resulted from surface plasmon resonance due to Ag NPs, while that below plasma anode unchanged visually. From the observation using TEM, we confirmed the size of Ag NPs below plasma cathode ranged from 50 to 80 nm.

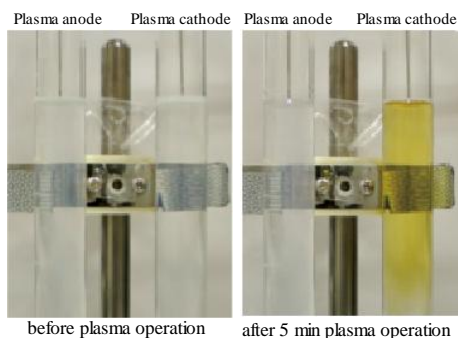


Fig. 4. Pictures of Ag NPs synthesis by means of electrolysis with dual plasma reactor.

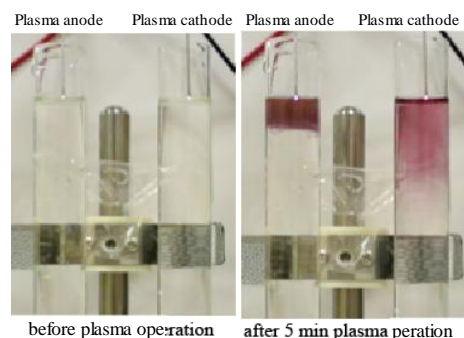


Fig. 5. Pictures of Au NPs synthesis by means of electrolysis with dual plasma reactor.

Fig. 5 shows the pictures of the dual plasma reactor with HAuCl₄ solution before and after the plasma treatment. After the discharge treatment, the color of the solution below both plasma anode and plasma cathode changed to red as a result of surface plasmon resonance of Au NPs. The liquid color is darker below plasma anode. The diameter of Au NPs is about 100 nm below plasma anode and 30 nm below plasma cathode. This implies that Au NPs are generated more efficiently below plasma anode; the positive ion irradiation enhances the nucleation for Au NPs synthesis.

4. Discussion

Experimental results are summarized in Table 1. Let us discuss the liquid-phase reaction process.

Electrons are exposed from positive column of dc glow discharge to liquid surface below plasma cathode. The low energy electrons will be captured in liquid as hydrated electrons. The hydrated electrons react with H₂O to form OH⁻ (e_{aq}+H₂O→H+OH⁻, e_{aq}+e_{aq}→H₂+OH⁻). Therefore, the alkalization of solution by electron irradiation is reasonable. Although we did not detect H₂ gas, it can be generated from this reaction process. The mean electron energy in the positive column is several eV; the only high energy part of electron energy distribution function will contribute ionization and dissociation of H₂O at liquid surface. Since H₂O⁺ is unstable in liquid, it immediately dissociates into OH and H⁺. Thus OH radicals are generated by both electron impact dissociation and ionization. Of course OH radical can be transported from gas. H radical will be also generated via dissociation of H₂O. NPs will be generated through the reduction of metallic ions. Hydrated electrons and H radicals are candidate to reduce Ag⁺ and AuCl₄⁻.

In the field of radiochemistry, the liquid-phase reaction initiated by high-energy particle such as alpha particle and proton beam is well studied. Such high energy particle ionizes H₂O into hydrated electron and H₂O⁺, which automatically dissociated into H⁺ and OH, and the successive reactions are started. Although positive ions are exposed from cathode sheath to liquid surface, the impin-

Table 1. Summary of experimental results.

Solution (Concentration)	Conventional electrolysis		Glow discharge electrolysis	
	Anode	Cathode	Plasma anode (Positive ion irradiation)	Plasma cathode (Electron irradiation)
NaCl (0.51 M)	Acidification (pH 7.4 → 3.0) Cl ₂ & HCl gas	Alkalization (pH 7.4 → 10.3) H ₂ gas	Acidification (pH 7.4 → 3.2) H ⁺ generation Gas generation was below detection limit.	Alkalization (pH 7.4 → 9.6) OH ⁻ generation Gas generation was below detection limit.
Telephthalic acid (0.04 M)	OH was not detectable.	OH was not detectable.	OH radical in liquid	OH radical in liquid
AgNO ₃ (0.1 mM)	no visible change	no visible change	NPs were not observed. Conductivity increased.	Ag-NPs generation Ag ⁺ → Ag Constant conductivity
HAuCl ₄ (0.24 mM)	no visible change	no visible change	Au-NPs generation (more active in comparison to plasma cathode) AuCl ₄ ⁻ → Au + 4Cl ⁻ Conductivity increased.	Au-NPs generation AuCl ₄ ⁻ → Au + 4Cl ⁻ Constant conductivity

ging ion energy is not high because of frequent collisions at atmospheric pressure [8]. Therefore, it is not easy for low energy ions to initiate reactions from ionization or dissociation of H₂O. However, our experimental results suggest that positive ion irradiation generates H⁺. Leading hypothesis is the charge transfer collision between impinging positive ion and H₂O, which often has high cross section at low energy part [9]. Once H₂O⁺ is generated via charge transfer collision, H⁺ and OH radical are generated; both species are detected indirectly in our experiment.

5. Summary

We experimentally investigated the initial liquid-phase reaction induced by electron or positive ion irradiation from atmospheric pressure dc glow discharge. As application of electrolysis with plasma electrode, metallic NPs' synthesis was demonstrated, and the reduction process of metallic ions was discussed.

We found that electron irradiation generated OH⁻ and OH in liquid while positive ion irradiation generated H⁺ and OH. The contribution of charge transfer collision by low energy positive ion was introduced to explain the experimental results.

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