

Liquid-phase reactions induced by atmospheric pressure glow discharge with liquid electrode

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Abstract. We experimentally investigated some of the initial reactions in a liquid induced by electron or positive-ion irradiation from an atmospheric-pressure dc glow discharge in contact with the liquid. We used an H-shaped glass reactor to observe the effects of electron irradiation and positive-ion irradiation on the liquid-phase reaction separately and simultaneously. Aqueous solutions of NaCl, AgNO₃, HAuCl₄, and FeCl₂ are used as the electrolyte. Solutions of AgNO₃ and HAuCl₄ are used for the generation of Ag and Au nanoparticles, respectively. Solution of FeCl₂ is used for the generation of ferromagnetic particles. Experimental results showed that electron irradiation of the liquid surface generates OH⁻ in water and that positive-ion irradiation of the liquid surface generates H⁺ in water even without the dissolution of gas-phase nitrogen oxide. A possible reaction process is qualitatively discussed. We also showed that the control of reductive and oxidative environment in the liquid is possible not only by the gas composition for the plasma generation but also by the liquid composition.

1. Introduction

Nonthermal atmospheric-pressure plasmas in contact with liquids have been widely studied for realizing a variety of plasma applications such as material processing, water treatment including sterilization, analytical chemistry, and so forth[1, 2]. DC glow discharge with a liquid electrode is one of the simplest methods to obtain a stable gas discharge plasma in contact with a liquid. In our previous paper, we reported the characteristics of atmospheric-pressure dc glow discharge with a liquid cathode[3] and liquid anode[4]. A dc glow discharge with a liquid electrode was studied to analyze the composition of the electrolyte by spectroscopic investigation[5, 6]. The surface treatment of polypropylene and polyethylene in a liquid was demonstrated using an atmospheric-pressure air glow discharge with an electrolyte cathode[7]. A dc glow discharge with a liquid electrode has also been applied for the synthesis of metallic nanoparticles in a liquid[8, 9, 10, 11, 12, 13, 14]. A dc glow discharge with a liquid electrode is considered as electrolysis with a plasma electrode. The plasma electrode supplies electrons or positive ions to the liquid surface via a different chemical reaction from that in conventional electrolysis with metal electrodes. Although electrolysis with a plasma electrode is not a new technology[15], the interfacial phenomena between the plasma and the liquid are not yet understood well.

In this work, we experimentally investigated some of the initial reactions in a liquid induced by electron or positive-ion irradiation from an atmospheric-pressure dc glow discharge in contact with a liquid electrode by using Hoffman electrolysis apparatus. A possible reaction process is qualitatively discussed on the basis of the experimental results.



2. Experimental method

Figure 1 shows the experimental setup used in this work. An H-shaped Hoffman electrolysis reactor is used to separate the anodic and cathodic reactions. The reactor is filled with an electrolyte, the solution surface of which is roughly 1 cm below the top mouth of the H-shaped reactor. Aqueous solutions of sodium chloride (NaCl), silver nitrate (AgNO₃), chlorauric acid (HAuCl₄), and ferrous chloride (FeCl₂) are used as the electrolyte. Solutions of AgNO₃ and HAuCl₄ are used for the generation of Ag and Au nanoparticles, respectively[14]. Solution of FeCl₂ is used for the generation of ferromagnetic particles.

A nozzle electrode made of stainless steel with inner and outer diameters of 500 and 800 μm, respectively, is set about 2 mm above the solution surface in each mouth of the H-shaped reactor. Helium gas with a flow rate of 200 sccm is injected from the nozzle electrode. We refer to this electrode configuration as the normal-type electrode [see Fig. 1(b)]. We also use a sheath-flow-type electrode, in which the core helium flow is surrounded by a sheath flow of nitrogen or oxygen [see Fig. 1(c)]. The nozzle electrode for the core helium flow is the same as that of the normal-type electrode. The typical flow rate of the sheath flow is 1000 sccm while that of the helium core flow is kept at 200 sccm. We expected to change the reductive and oxidative environment by changing the sheath-flow gas. By applying a dc voltage between the two nozzle electrodes, two glow discharges as an anode and a cathode for the plasma-assisted electrolysis are formed in contact with the solution along the helium flows. Let us use the terms “plasma anode” and “plasma cathode” in this paper. Positive ions enter the solution at the plasma anode while electrons enter the solution at the plasma cathode. For comparison, conventional electrolysis was also observed with two platinum electrodes immersed in the solution.

We measure the pH value of the solution at approximately 10 mm below the solution surface using a pH meter. To visualize the local changes in the pH value, a small amount of bromothymol blue (BTB) is added as a pH indicator. The color of BTB changes to yellow at a pH value of less than 6.0 while it becomes blue at a pH value of larger than 7.6. A gas detector tube is used to detect Cl₂, HCl, and H₂ above the liquid surface resulting from the liquid-phase reaction. The detection limit of the gas detector tube is 0.1 ppm for Cl₂, 2 ppm for HCl, and 0.05% for H₂. We also measure HClO concentration in the liquid by DPD color comparison method. DPD stands for N,N-diethyl-p-phenylenediamine, a chemical reagent. The DPD color changes into pink when DPD is oxidized by HClO. Nanoparticles generated in liquid are analyzed by transmission electron microscopy (TEM) and an energy dispersive X-ray spectroscopy (EDX).

3. Experimental results

3.1. Comparison between conventional and plasma-assisted electrolysis

Figure 2 shows photographs of conventional and plasma-assisted electrolysis in NaCl solution with a concentration of 0.5 M taken 15 min after starting electrolysis at a constant current of 3 mA. A small amount of BTB was added to the solution. The initial pH of the solution was 7.4. In the conventional electrolysis in Fig. 2(a), the liquid color around the cathode became blue, alkalified, and that around the anode was decolorized. The pH values measured by the pH meter were 10.3 near the Pt cathode and 3.0 near the Pt anode. We detected Cl₂ and HCl from the anode side and H₂ from the cathode side using the gas tube detector although we could not measure their generation yields quantitatively. The reaction of conventional electrolysis in NaCl solution is well known to be



Thus, Cl₂ gas is generated at the anode while H₂ gas is generated at the cathode. Hydroxide ion (OH⁻) generation causes the alkalification of the liquid around the cathode. The Cl₂ gas

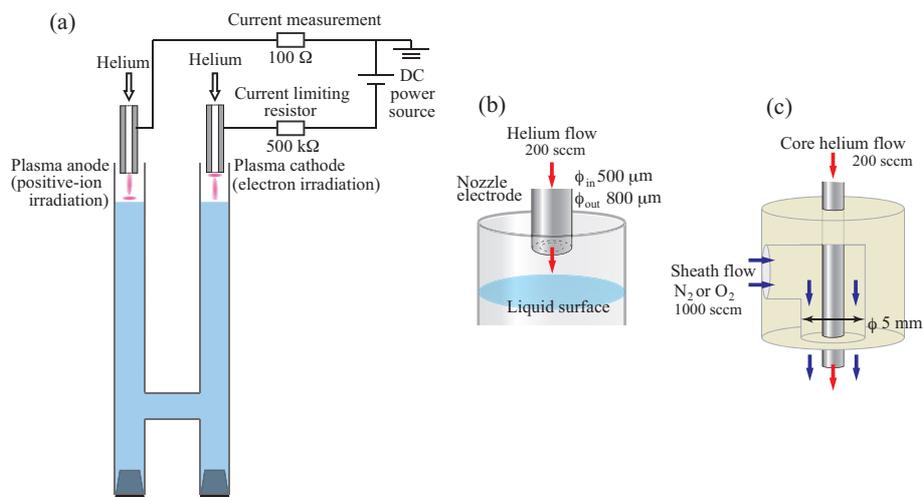


Figure 1. Experimental setup for plasma-assisted electrolysis using H-shaped Hoffman electrolysis apparatus, (a) overall arrangement of apparatus, (b) normal-type electrode, and (c) sheath-flow-type electrode.

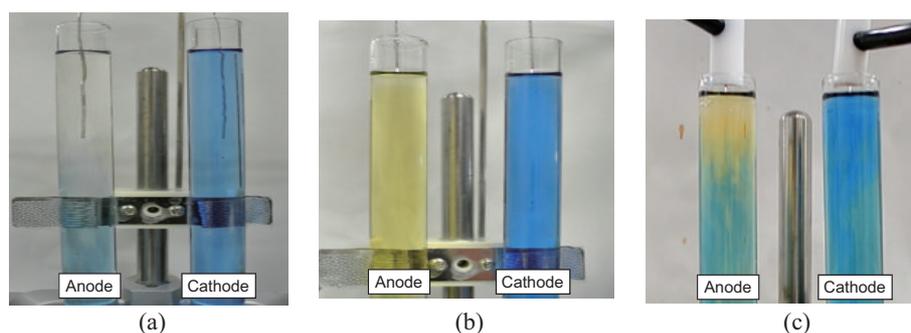


Figure 2. Photograph of electrolysis in 0.5 M NaCl solution with added BTB with a constant current of 3 mA at 15 min after starting electrolysis, (a) conventional electrolysis, (b) plasma-assisted electrolysis with the normal-type electrode, (c) plasma-assisted electrolysis with the sheath-flow-type electrode with O₂ sheath flow.

partly reacts with water molecule as



Therefore, the liquid around the anode is acidified. Since HClO has a high oxidation potential, it easily decomposes BTB, and the solution around the anode is decolorized. We confirmed the generation of HClO in liquid by DPD color comparison method.

In the plasma-assisted electrolysis with the normal-type electrode in Fig. 2(b), the liquid color below the plasma cathode became blue, and that below the plasma anode became yellow without the decoloration of BTB. The pH values measured by the pH meter were 9.0 below the plasma cathode and 3.0 below the plasma anode. We attempted to measure the generation of H₂, Cl₂, and HCl gases using the gas detector tube. These gases were below the detection limit although they were detected in conventional electrolysis. The concentration of HClO in the liquid was also below the detection limit of the DPD color comparison method. Therefore, we deduce that

Cl₂ gas generation is less active in plasma electrolysis than that in conventional electrolysis. It is reasonable to consider that the acidification of the solution below the plasma anode results from the dissolution of gaseous nitrogen oxides generated in the plasma. To evaluate this effect, same experiment was carried out using the sheath-flow-type electrode with O₂ sheath flow, which avoid contact between the discharge plasma and the surrounding air to reduce the generation of nitrogen oxides. The photograph of the plasma-assisted electrolysis with the sheath-flow-type electrode is shown in Fig. 2(c). The pH values measured by the pH meter were 9.3 below the plasma cathode and 3.4 below the plasma anode. These results imply that electron irradiation of the liquid surface generates OH⁻ in water and that positive-ion irradiation of the liquid surface generates H⁺ in water even without nitrogen oxide generation, although we did not measure the nitrate ion concentration in the liquid. A detailed discussion of the reaction process is given in section 4.

3.2. Plasma-assisted electrolysis using aqueous solutions of AgNO₃ and HAuCl₄

Plasma-assisted electrolysis was carried out using aqueous solutions of AgNO₃ for Ag nanoparticles generation and HAuCl₄ for Au nanopaticles generation. The concentrations of AgNO₃ and HAuCl₄ were typically on the order of 10⁻⁴ M. Sodium dodecyl sulfate (SDS) with a concentration of 0.05% (1.7 mM) was added to the solution as a surface active agent. Specimen photographs of the plasma-assisted electrolysis are shown in Fig. 3 with TEM images of nanoparticles generated in the liquid. In the plasma-assisted electrolysis with AgNO₃ solution, the solution color below the plasma cathode becomes yellow, the color of which results from the surface plasmon resonance of Ag nanoparticles. That is, Ag nanoparticles were only synthesized on the plasma cathode side via the reduction of Ag⁺. In the case of using HAuCl₄ solution, the solution colors below both the plasma anode and the plasma cathode become red as a result of surface plasmon resonance of Au nanoparticles. That is, Au nanoparticles were synthesized by both positive-ion irradiation and electron irradiation of the solution surface. Positive-ion irradiation with the plasma anode is more effective than electron irradiation for the synthesis of Au nanoparticles. The detail of the nanoparticle generation is shown in our previous paper[14].

3.3. Plasma-assisted electrolysis using aqueous solutions of FeCl₂

FeCl₂ is ionized into Fe²⁺ and Cl⁻ in the liquid. When Fe²⁺ is reduced by reductant such as hydrated electrons, ferromagnetic Fe particles can be generated[13]. When oxidative reaction is dominant, Fe²⁺ is oxidized to Fe³⁺, which shows yellow color in the liquid. If Fe²⁺ and Fe³⁺ are simultaneously oxidized in the liquid with reasonable molar ratio, ferromagnetic particles of magnetite, Fe₃O₄, will be generated, otherwise paramagnetic particles of hematite, Fe₂O₃, will be mainly generated. Figure 4(a) shows the photograph of the plasma-assisted electrolysis in aqueous solution of 0.01 M FeCl₂ with 1.7 mM SDS using normal-type electrode for both plasma anode and plasma cathode. Brown red particles, which are not attracted by a magnet, are generated below both plasma anode and plasma cathode. The particle generation is more active by the positive-ion irradiation below plasma anode. We confirmed that the generated particles consist of Fe and O by the EDX analysis. Therefore, the generated particles are deduced to be hematite. This result suggests that Fe²⁺ is considerably oxidized to Fe³⁺ even in the reductive environment by electron irradiation of the liquid surface below plasma cathode. To achieve further reductive environment at the liquid surface, the sheath-flow-type electrode with N₂ sheath flow is used as the plasma cathode, and its result is shown in Fig. 4(b). Black particles, which are easily attracted by a magnet, are generated in addition to the brown red particles below plasma cathode. The magnetic property of the paricles generated below plasma cathode was analyzed by a superconducting quantum interference device (SQUID), and is shown in Fig. 5. The magnetization curve has hysteresis characteristics with saturated magnetization value of 23 emu/g. The saturated magnetization of magnetite is 80 emu/g. Therefore, roughly

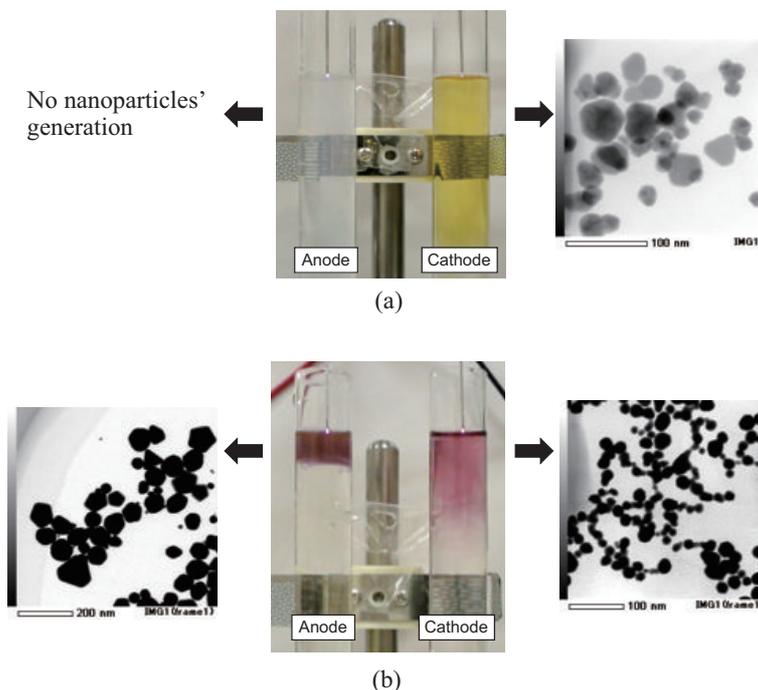
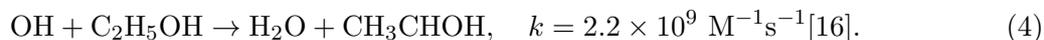


Figure 3. Photographs of plasma-assisted electrolysis taken 5 min after starting electrolysis at a constant current of 3 mA. TEM images of the generated nanoparticles are also shown. (a) 0.1 mM AgNO_3 solution with 1.7 mM SDS, and (b) 0.24 mM HAuCl_4 with 1.7 mM SDS.

a quarter of the generated particle is considered to be magnetite. It will be possible to increase the ratio of magnetite by optimizing the experimental condition such as FeCl_2 concentration and current density.

Surface active agent such as SDS is added in the solution to prevent the agglomeration of particles. Therefore, larger particles are often generated without adding the surface active agent. However, magnetite particles were not generated but hematite particles without adding the surface active agent. This result suggests that the main role of SDS in the present experiment is not to prevent the agglomeration of particles but to suppress the excess oxidation of Fe^{2+} to Fe^{3+} . To verify this hypothesis, ethanol is added in the solution of FeCl_2 instead of SDS. The amount of the added ethanol is the same as that of SDS. Ethanol is known to trap OH radical as



Magnetite particles were generated below plasma cathode by the plasma-assisted electrolysis using FeCl_2 solution with adding ethanol. It is confirmed that the role of SDS and ethanol is to suppress the excess oxidation of Fe^{2+} in liquid. That is, the control of reduction and oxidation in the liquid is possible not only by the gas composition for plasma generation but also by the liquid composition in the plasma-assisted electrolysis.

4. Discussion

In this work, we investigated the liquid-phase reactions induced by electron and positive-ion irradiation separately from atmospheric-pressure glow discharges. The results are summarized in Table 1. In this section, we discuss the reactions in a liquid induced by electron irradiation and positive-ion irradiation.

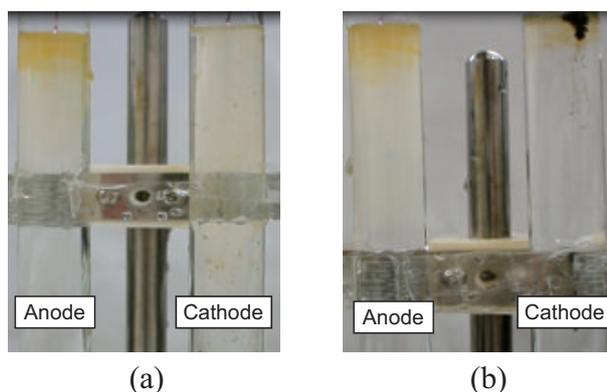


Figure 4. Photographs of plasma-assisted electrolysis using 0.01 M FeCl₂ solution with 1.7 mM SDS taken 5 min after starting electrolysis at a constant current of 2 mA. (a) normal-type electrode is used for both plasma anode and plasma cathode, and (b) sheath-flow-type electrode with N₂ sheath flow is used for plasma cathode while normal-type electrode is used for plasma anode.

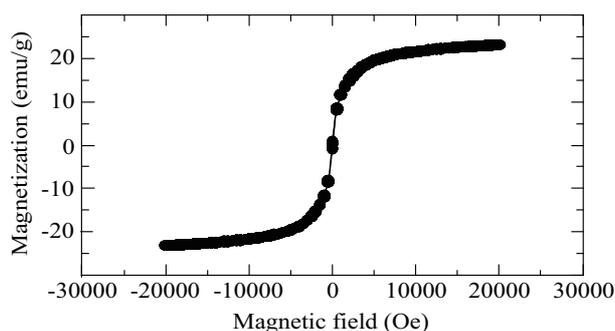


Figure 5. Magnetic property of the particles generated in FeCl₂ solution below plasma cathode using sheath-flow-type electrode with N₂ sheath flow.

4.1. Reactions in liquid induced by electron irradiation

In the present case, electrons in the positive column of the atmospheric-pressure glow discharges are exposed to the liquid surface. Thus, the electron impact dissociation or ionization of water molecules at the liquid surface is not very effective judging from electron impact cross-section data[17]. The electrons exposed to the solution surface will be stabilized as hydrated electrons. The important reactions involving hydrated electrons are listed in Table 2. The reaction path of the hydrated electrons depends on the concentration of the reaction partners. In reactions (R1) and (R2) in Table 2, hydrated electrons react with water molecules to form OH⁻. Reaction (R3) is also one of the dominant reactions, the frequency of which depends on the pH of the solution. At a solution pH of 3.0, the reaction time constant of hydrated electrons for (R3) is 42 ns, and even at a neutral pH of 7.0, it is 0.42 ms. Since reaction (R3) neutralizes H⁺ to form H atoms in the solution, the OH⁻ concentration is increased by the ionization equilibrium of water molecules. Therefore, it is reasonable to consider that electron irradiation of the water surface alkalifies the solution.

In AgNO₃ solution, reaction (R4) is considered to be the dominant reaction causing the trapping of hydrated electrons. A high concentration of neutral Ag in the liquid leads the

Table 1. Summary of experimental results. NP denotes a nanoparticle.

Solution (typical concentration)	Conventional electrolysis		Plasma-assisted electrolysis	
	Anode	Cathode	Plasma anode positive-ion irradiation	Plasma cathode electron irradiation
NaCl (0.5 M)	Acidified Cl ₂ , HCl gas decoloration	Alkalified H ₂ gas	Acidified H ⁺ generation	Alkalified OH ⁻ generation
AgNO ₃ (0.1 mM)	No visible change	No visible change	Ag-NPs not observed	Ag-NP generation
HAuCl ₄ (0.24 mM)	No visible change	No visible change	Au-NP generation (more effective)	Au-NP generation
FeCl ₂ (0.01 M)	Cl ₂ gas	Fe deposition	Fe ₂ O ₃ generation	Fe ₂ O ₃ generation, With N ₂ sheath flow Fe ₃ O ₄ generation

Table 2. Important reactions induced by electron irradiation. e_{aq} denotes a hydrated electron.

No.	Reaction	Rate coefficient	Ref.
(R1)	e _{aq} + H ₂ O → OH ⁻ + H	10 ³ s ⁻¹	[18]
(R2)	e _{aq} + e _{aq} → 2OH ⁻ + H ₂	6.0 × 10 ⁹ M ⁻¹ s ⁻¹	[19]
(R3)	e _{aq} + H ⁺ → H	2.4 × 10 ¹⁰ M ⁻¹ s ⁻¹	[20]
(R4)	e _{aq} + Ag ⁺ → Ag	4.8 × 10 ¹⁰ M ⁻¹ s ⁻¹	[21]
(R5)	H + Ag ⁺ → Ag + H ⁺	2.0 × 10 ¹⁰ M ⁻¹ s ⁻¹	[22]
(R6)	H + AuCl ₄ ⁻ → AuCl ₄ ²⁻ + H ⁺	5.7 × 10 ⁹ M ⁻¹ s ⁻¹	[23]
(R7)	e _{aq} + Fe ²⁺ → products	1.6 × 10 ⁸ M ⁻¹ s ⁻¹	[24]
(R8)	e _{aq} + Fe ³⁺ → Fe ²⁺	6.0 × 10 ¹⁰ M ⁻¹ s ⁻¹	[25]

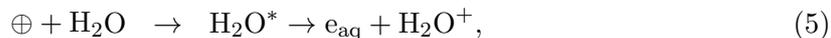
nuclear formation of Ag nanoparticles. H atoms in the liquid also reduce Ag⁺ via reaction (R5).

Since HAuCl₄ is a strong acid, the initial pH of the solution under the present experimental conditions was approximately 3.0. Thus, the dominant reaction path for hydrated electrons will be reaction (R3). H atoms in a liquid will reduce AuCl₄⁻ (Au³⁺) via reaction (R6). Although the elementary process for the reduction of Au ions in HAuCl₄ solution has not been clearly shown to the best of our knowledge, it is reasonable to consider that H atoms or hydrated electrons contribute to the successive reduction from Au³⁺ to Au by electron irradiation of the solution surface by the plasma.

Hydrated electrons have high reaction rate coefficient with Fe²⁺ and Fe³⁺ as shown in Table 2. However, the experimental results suggested that the oxidation of Fe²⁺ was more active than its reduction. It is difficult to identify what species is responsible for the oxidation of Fe²⁺. One possible answer is the oxidation of Fe²⁺ at plasma-liquid interface by OH radicals generated in the plasma. Adding SDS or ethanol in the liquid suppress the excess oxidation of Fe²⁺ for generating magnetite particles.

4.2. Reactions induced by positive-ion irradiation

Our experimental results strongly suggested that positive-ion irradiation from the plasma to the liquid surface acidifies the solution even without the dissolution of nitrogen oxides from the gas phase. That is, positive-ion irradiation directly or indirectly results in H^+ generation. One hypothesis is the ionization of water molecules by energetic ions at the liquid surface as



However, the kinetic energy of positive ions impinging on the cathode is estimated to be of eV order in atmospheric-pressure glow discharge in helium because of the frequent energy loss due to collisions[26]. Although the ionization energy of a water cluster is lower than that of an isolated water molecule, it is still difficult for impinging low-energy positive ions to initiate reaction (5). If the same amounts of hydrated electrons and H^+ are generated via reactions (5) and (6), the solution pH does not change. In addition, Ag nanoparticles might be obtained by positive-ion irradiation to the surface of $AgNO_3$ solution if reaction (5) is dominant. Therefore, an other explanation is necessary for the generation of H^+ . A strong candidate for this reaction is charge transfer collision between an impinging ion X^+ and H_2O .



Gas-phase charge transfer collisions with water molecules have been experimentally investigated for Ar^+ and N_2^+ [27], for example. These ions have large collision cross sections for reaction (7) at low energies; the cross section is roughly 10^{-14} cm^{-2} at 0.1 eV and decreases with increasing ion energy. Similar reaction is expected between He^+ and H_2O , and it is reasonable to consider that the irradiation of low-energy positive ions from the plasma anode to the liquid surface effectively generates H^+ and OH via charge transfer collision.

Since positive-ion irradiation of the liquid surface essentially enhances the oxidation in the liquid, metallic particle generation by the reduction of metallic ion is difficult. However, Au nanoparticles are generated by positive-ion irradiation more effectively than by electron irradiation. We do not have clear answer for this problem at this moment.

5. Conclusion

We experimentally investigated the initial liquid-phase reaction induced by electron or positive-ion irradiation from an atmospheric-pressure dc glow discharge. We used an H-shaped glass reactor as an electrolysis apparatus with two atmospheric-pressure glow discharges as electrodes for plasma-assisted electrolysis. This apparatus enabled us to observe the effects of electron irradiation and positive-ion irradiation on the liquid-phase reaction separately and simultaneously. Aqueous solutions of NaCl, $AgNO_3$, $HAuCl_4$, and $FeCl_2$ are used as the electrolyte. Possible reaction processes induced in the liquid were qualitatively discussed. Following results are obtained.

- (i) At the plasma cathode, where electrons are exposed to the solution surface, the pH of the solution increased roughly from the initial value of 7 to 10 in NaCl solution. This result implies that electron irradiation of the liquid surface generates OH^- in water via neutralization of H^+ to form H atom or dissociative electron attachment of H_2O . Ag nanoparticles were synthesized with $AgNO_3$ solution and Au nanoparticles were synthesized with $HAuCl_4$ solution via the reduction of metallic ion by hydrated electron or H atom.
- (ii) At the plasma anode, where positive ions are exposed to the solution surface, the pH of the solution decreased roughly from 7 to 3 in NaCl solution even under the condition of preventing the dissolution of nitrogen oxides in the liquid. The generation of Cl_2 gas by the

plasma anode is negligible compared with that by the metal electrode in the conventional electrolysis. This result implies that positive-ion irradiation of the liquid surface generates H^+ in water. The contribution of charge transfer collision between low-energy incident positive ion and water molecule at liquid surface is introduced to explain the overall tendency of the experimental results.

- (iii) Although electron irradiation of the liquid surface essentially enhances the reductive reaction in the liquid, Fe^{2+} was not reasonably reduced but even oxidized in $FeCl_2$ solution, and hematite particles were generated. Ferromagnetic magnetite particles were synthesized in further reductive environment by adding chemical agent into the liquid to trap oxidizing agent and by changing the gas composition for plasma generation. In other words, the control of reductive and oxidative environment in the liquid is possible not only by the gas composition for plasma generation but also by the liquid composition in the plasma-assisted electrolysis.

Acknowledgments

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