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Attempt of Controlling Chemical Reactions by Ion-Exchange Membrane in Plasma-Assisted Electrolysis Using Atmospheric-Pressure DC Glow Discharge with Liquid Electrode

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1. Introduction

Recently, atmospheric-pressure plasmas in contact with liquid are energetically studied. We have studied the gas-phase and liquid-phase reactions in atmospheric-pressure dc glow discharge with liquid electrode [1]. The dc glow discharge with liquid electrode is considered as electrolysis with plasma electrode, which irradiates liquid surface with electrons or positive ions. Therefore, different reaction pathway from the conventional electrolysis with two metal electrodes is expected in the plasma-assisted electrolysis. In the conventional electrolysis, ion-exchange membrane enables us to use different solutions at anode side and cathode side and to control the ion migration in the liquid. In this work, we applied the ion-exchange membrane to control the plasma-assisted electrolysis as a new attempt. As an example, we show the metal nanoparticles synthesis with ion-exchange membrane.

2. Experimental method

Experimental setup is shown in Fig. 1. A rectangular vessel made of acrylic resin is divided into two regions, which are filled with 0.2 mM $AgNO_3$ solution and 0.125 mM $HAuCl_4$ solution. The volume of each solution is 50 mL. Grounded Pt wire is immersed in one of the solutions as a metal anode. A stainless-steel nozzle with inner and outer diameters of 500 μm and 800 μm, respectively, is placed at 1 mm above the other solution. From the nozzle, He gas is injected with flow rate of 200 sccm. By applying a dc voltage between the nozzle and Pt wire, a stable dc glow discharge as a plasma cathode is formed in contact with liquid along the He flow. The plasma cathode irradiates the liquid surface with electrons. The current is kept to be 8 mA in this work. We used both cation-exchange membrane and anion-exchange membrane. To prevent the agglomeration of nanoparticles, sodium dodecyl sulfate (SDS) of 0.05 % is added to the solution.

3. Experimental results

As a first attempt, the vessel of metal anode side was filled with $AgNO_3$ solution while that of plasma cathode side was filled with $HAuCl_4$ solution with SDS addition. Figure 2 shows the temporal evolution of nanoparticles synthesis with cation-exchange membrane. Ag^+ can penetrate the cation-exchange membrane. Before starting the plasma-assisted electrolysis, the colors of both solutions were colorless and transparent. At 10 minutes after starting the plasma-assisted electrolysis, the color of the solution at plasma cathode side became red. This color change results from the surface plasmon resonance of Au nanoparticles, which were generated by the reductive reaction in $HAuCl_4$ solution. At 20 minutes, the color of the solution at plasma cathode side became yellow, which shows the synthesis of Ag nanoparticles. In our previous work, similar color change was observed in the plasma-assisted electrolysis in the mixed solution of $HAuCl_4$ and $AgNO_3$, and we found the synthesis of nanoparticles with Au-core/Ag-shell structure [2]. At that time, the concentration of the mixed solution has to be very low and the quantity of the generated nanoparticles were small, because high concentration of the mixed solution immediately results in the generation of suspended solids, which will be AgCl. In the present system, the cation-exchange membrane gradually and selectively supplies Ag^+ for Ag-shell after synthesizing Au nanoparticles without leading unnecessary reactions. Therefore, the use of highly-concentrated solutions without mixing enables us faster synthesis of Au-core/Ag-shell nanoparticles. Maybe, the change of pH is also the important effect in using the ion-exchange membrane.

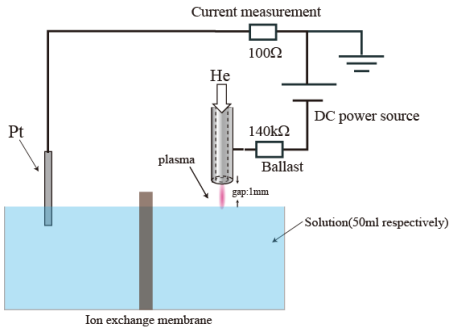

Fig.1 Experimental setup

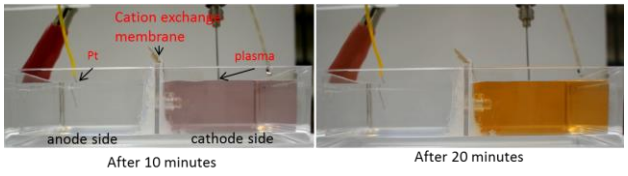

Fig. 2 Temporal evolution of nanoparticles synthesis with cation-exchange membrane.

Acknowledgements

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References

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