Redox reactions on surface of water jet injected into low-pressure plasma

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Abstract: We observed reduction and oxidation reactions on the surface of a water jet injected into an inductively coupled helium plasma. The water jet was electrically floating. This means currentless redox reactions at plasma-liquid interface. We believe that the redox reactions are induced by electrons and ions transported from the plasma.

Keywords: currentless redox reactions, plasma-liquid interface, water jet

1. Introduction

It is widely understood that the interface between a plasma and water works for redox reactions. Many researchers report plasma-assisted electrolysis, where one or both of the electrodes in conventional electrolysis are replaced with atmospheric-pressure plasmas. Various nanoparticles of metals and oxides in a form of suspension are synthesized by plasma-assisted electrolysis. Note that all the experiments of plasma-assisted electrolysis keep the situations with the separated plasma-liquid interfaces for oxidation and reduction.

In this work, we observed oxidation and reduction on a water surface immersed in a low-pressure plasma. The reason for the use of a low-pressure plasma instead of an atmospheric-pressure plasma is that it is more suitable to quantitative experiment since the measurements of the plasma density and the composition of gas-phase species are easier. A point of this work is that we did not use the typical geometry of electrochemistry. We observed oxidation and reduction on the surface of the same water jet. The simultaneous oxidation and reduction did not need electrical current, which is another point of this work.

2. Experimental apparatus

Purified water with an electrical conductance less than 0.01 mS/cm was ejected from a plastic nozzle with a diameter of 50 μm at a flow rate of 1.6 mL/min. The inside pressure of the nozzle was so high that water was ejected from the nozzle in the form of a jet. The water jet system was installed at the top of a vacuum chamber, and the water passing through the chamber was caught at the bottom of the chamber using a tank at the temperature of liquid nitrogen. We employed a turbomolecular pump with a pumping speed of 2000 L/s. In addition to the high-speed pump, we installed a water vapor trap at the temperature of liquid nitrogen to reduce the pressure of water vapor in the chamber. By using this evacuation system, we realized 2 mTorr for the pressure of water vapor in the chamber. The potential of the water jet was floating and we did not have current through the water jet. We introduced helium into the vacuum chamber at a flow rate of 355 sccm, resulting in a helium pressure of 10 mTorr. The plasma was produced by inductively coupled discharge at 13.56 MHz. The composition of the gas in the plasma was analyzed using a quadrupole mass spectrometer (QMS). The chamber equipped with QMS was differentially pumped, and it was connected to the plasma chamber via an orifice with a diameter of 0.5 mm.

3. Results

We observed the productions of hydrogen and oxygen. Figure 1 shows the production rates of hydrogen and oxygen as a function of the plasma density. The plasma density was varied by changing the rf power with keeping the helium pressure. Figure 1(a) was obtained when we used the water jet, while in Fig. 1(b), the plasma jet was not used and only water vapor was injected into the chamber from a liquid water container. The partial pressure of water vapor at the latter experimental condition was also 2 mTorr. The production rates of molecular oxygen were almost the same in Figs. 1(a) and 1(b), whereas the production rate of molecular hydrogen when using the water jet was slightly higher than that using the water vapor injection. The most significant difference between Figs. 1(a) and 1(b) is found in the vaporization rates of water vapor. We observed the negative rate, i.e., the loss of water vapor in the experiment using the water vapor injection, as shown in Fig. 1(b). In contrast, in the experiment using the water jet, we observed the increase in the water vapor density as a function of the plasma density, as shown in Fig. 1(a).

The increase in the water vapor density in the water jet experiment was caused by the increase in the water temperature. We measured the temperature of the water nozzle using a thermocouple, and we estimated the increase in the flux of water vapor from the water jet. The estimated production rate of water vapor from the water jet is also plotted in Fig. 1(a). As shown in the figure, the estimated production rate was almost the same as that measured using QMS, indicating that almost all hydrogen and oxygen produced in the experiment using the water jet were not originated from the consumption of water vapor. Therefore, it is possible to set up a hypothesis that the productions of hydrogen and oxygen are attributed to the oxidation and reduction, which are induced by the irradiation of the plasma, on the surface of the water jet.

To confirm the redox reactions, we used silver nitrate solution instead of pure water, and examined the production rates of hydrogen and oxygen. As a result, we observed a lower production rate of hydrogen, and in contrast, the production rate of oxygen was the same as that observed using pure water. In addition, we observed the production of silver particulates. This result clearly indicates the reduction of Ag^+ in the silver nitrate solution by immersing it in the plasma. The lower production rate of hydrogen in the silver nitrate solution suggests the competition between the reductions of H^+ and Ag^+. Accordingly, it is sure that the productions of hydrogen and oxygen are attributed to the oxidation and reduction on the

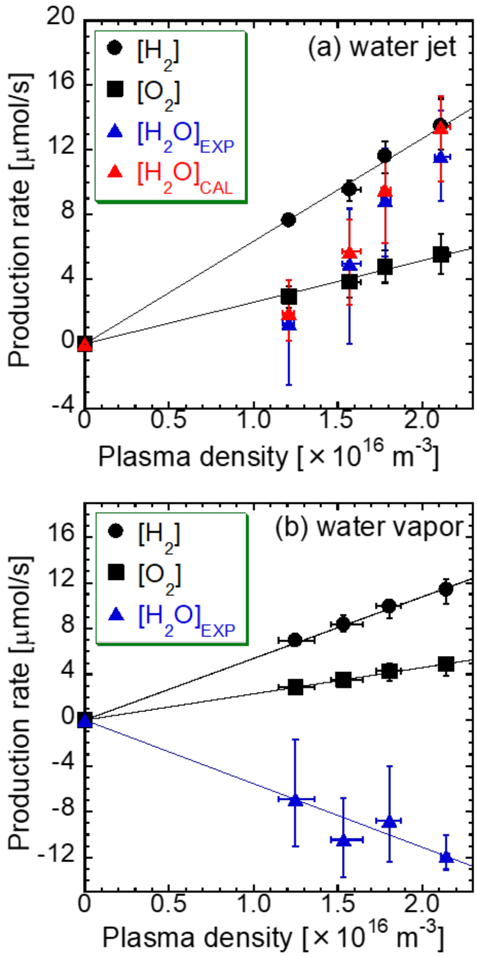

Fig. 1 Relationship between the production rates of H_2, O_2 and H_2O and the plasma density (a) in the water jet experiment and (b) in the water vapor experiment.

surface of the water jet. In contrast, the productions of hydrogen and oxygen in the experiment using the water vapor injection, which are shown in Fig. 1(b), can be explained by the conversion from water vapor, since the production rate of hydrogen is approximately equal to the loss rate of water vapor.

4. Discussion and conclusions

The production processes in the water jet experiment are considered to be

$$2H_2O \rightarrow O_2 + 4H^+ + 4e, \quad (1)$$

$$4H_2O + 4e_p \rightarrow 2H_2 + 4OH^-, \quad (2)$$

and

$$4He^+ + 4e \rightarrow 4He, \quad (3)$$

where e_p denotes electron transported from the plasma. He^+ transported from the plasma oxidizes H_2O to form O_2 and H^+, which is the combination of reduction reaction (3) an oxidation reaction (1). The electron transported from the plasma reduces H_2O to form H_2 and OH^- (reaction (2)). Note that H^+ produced in reaction (1) and OH^- produced in reaction (2) recombine to be H_2O.

This redox reaction has two peculiar features. One is that both the oxidation and reduction occur simultaneously on the same water surface with no current. This is significantly different from a usual redox reaction system where the anode is separated from the cathode and a power supply is used for transferring electrons between the anode and the cathode. The other peculiar feature is its nonequilibrium nature. The normal reaction after the arrivals of He^+ and e_p on the water surface is the neutralization since the energy state of the products is minimum. However, what we observed experimentally is that a part of the ionization energy of He (24.6 eV) is used for converting H_2O to H_2 and O_2 (the redox potential is 1.23 eV).

In summary, we observed the productions of molecular hydrogen and molecular oxygen when a water jet was immersed in an inductively coupled helium plasma. The water jet was electrically floating, and no current was supplied from the plasma. The consumption of water vapor was negligible. The experimental results suggest that oxidation and reduction of on the surface of the water jet are the production processes of oxygen and hydrogen, respectively.

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