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## Ion irradiation effects on ionic liquids interfaced with rf discharge plasmas

K. Baba,<sup>a)</sup> T. Kaneko, and R. Hatakeyama

*Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan*

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The availability of plasma ion irradiation toward a gas-liquid interface is investigated in a rf discharge system incorporating an ionic liquid. The introduction of the ionic liquid to the plasma causes the formation of a sheath electric field on the ionic liquid surface, resulting in the acceleration of the ions to the ionic liquid and the generation of secondary electrons from the ionic liquid by the ion irradiation. These effects are found to advance the discharge process and enhance the plasma production. © 2007 American Institute of Physics. [DOI: 10.1063/1.2739327]

Combinations of plasma and electrochemical techniques, which are possible to initiate reactions in gas and liquid phases containing ions, have attracted many interests long before.<sup>1</sup> Liquid incorporated plasma systems have potential applications in many fields, such as microchemical analysis of liquids for micro total analysis systems,<sup>2,3</sup> optical emission source for direct analysis of dissolved metal contents of aqueous solutions,<sup>4</sup> transport of hydroxyl radicals to the liquid side for the oxidation treatment,<sup>5</sup> and so on. Specifically, an atmospheric pressure plasma which can easily introduce liquids enables us to carry out researches on microplasmas including biological macromolecules which stably exist in liquids. For utilizing complex reactions in the liquid system on demand, it is required to deepen an understanding of plasma dynamics at the liquid surface.<sup>6-8</sup> However, since plasma processes with liquids have been promoted around the atmospheric pressure, the mean free path of the ions is quite short (less than 1  $\mu\text{m}$ ) and the control of ion behavior is impossible. Therefore, the establishment of a plasma process under the intervention of liquids in the region of low gas pressures, where the ion behavior can be controlled, is urgently desired. For the operation of low pressure plasmas coming into contact with liquids, we adopt ionic liquids,<sup>9,10</sup> which are known as organic molten salts at room temperature, as alternative liquids due to their extremely low vapor pressure.<sup>11</sup> In addition, ionic liquids can be regarded as a liquid electrode for discharge plasmas at low gas pressures owing to their unique characteristics such as high conductivity and thermal capacity.

In this letter, we generate reactive interfacial regions composed of glow discharge plasmas (gas phase) and ionic liquids (liquid phase) in the region of low gas pressures in order to clarify the dynamic behavior of ions in the gas-liquid interface, such as an ion irradiation from the plasma, an ion transport from the ionic liquid, and so on, which could promote the physical and chemical reactions on the nanocomposite synthesis. In particular, the ion irradiation from gas phase to liquid phase due to the formation of the sheath electric field on a liquid surface is investigated.

Figure 1 shows a schematic diagram of the experimental setup which has a Teflon cell of 20 mm in diameter and 2.5 mm in depth in a cylindrical glass chamber of 15 cm in diameter and 50 cm in length. A mesh electrode which is made of stainless steel with 8 meshes/cm, 15 mm diameter,

and 0.5 mm thickness is located inside the Teflon cell and an ionic liquid is introduced on the mesh electrode. A rf power of 13.56 MHz is supplied to the mesh electrode in the ionic liquid through a matching box (M. B.) and a blocking capacitor  $C_B$ . On the other hand, a grounded copper plate is set in a gas phase region at a distance of 30 mm from the mesh electrode. This discharge mode is defined as "A mode". In order to examine the effects of the rf power supplied to the electrode in the ionic liquid on discharge-related phenomena, the powered electrode is switched to the copper plate in gas phase and the mesh electrode in the ionic liquid is grounded instead, which is defined as "B mode". Helium gas is adopted as a discharge medium, and the gas pressure  $p$  is varied from 80 Pa to 6 kPa approximately. One kind of ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{BMI}^+\text{BF}_4^-$ ), is introduced into the Teflon cell and the amount of the ionic liquid is 0.4 ml. A Langmuir probe is inserted at the position of  $z=15$  mm and  $r=10$  mm to measure the parameters of the plasma in contact with the ionic liquid ( $z=0$ : surface of mesh electrode). A high voltage probe is directly connected to the powered electrode.

By using the above-mentioned device furnished with the ionic liquid, we achieved the generation of ionic liquid incorporated plasmas at low gas pressures with a high stability similar to normal glow discharge plasmas. Figure 2 gives dependences of breakdown voltage  $V_b$  on gas pressure  $p$  for a fixed discharge gap  $d(=30$  mm) without (open circle) and with the (closed circle) ion liquid, which are well known as Paschen curves in rf discharges.<sup>12</sup> In the case of A mode [Fig. 2(a)],  $V_b$  has the minimum value of about 220 V at  $pd$

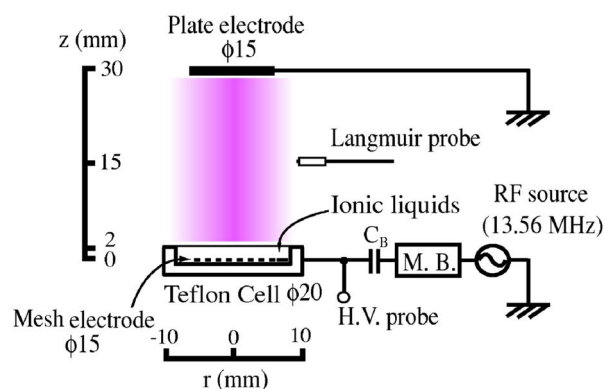


FIG. 1. (Color online) Schematic diagram of the experimental setup (A mode).

<sup>a)</sup>Electronic mail: baba@plasma.ecei.tohoku.ac.jp

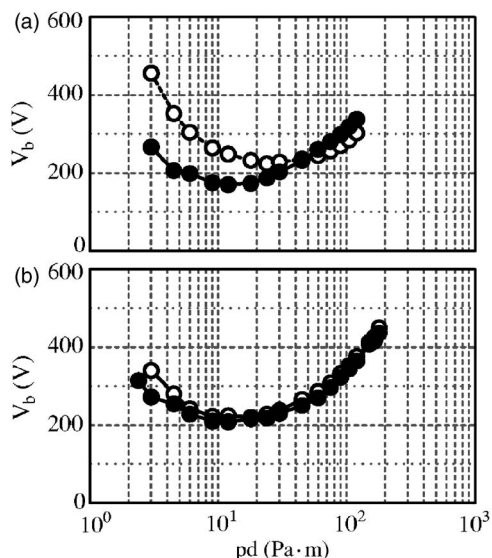


FIG. 2. Breakdown voltages  $V_b$  as a function of gas pressure  $p$  for fixed discharge gap  $d$  without (open circle) and with (closed circle) ion liquids, respectively. (a) A mode and (b) B mode.

= 15–30 Pa m in the absence of ionic liquids. When the ionic liquid is introduced, on the other hand,  $V_b$  obviously decreases compared with the case of no ionic liquids, which is especially observed in the low pressure region  $pd < 20$  Pa m. In contrast, the dependence of  $V_b$  on gas pressure is almost the same in both the presence and the absence of ionic liquids in the case of B mode, as shown in Fig. 2(b). The decrease in the breakdown voltage is attributed to the concentration of the electric field on the ionic liquid surface, which is reported to have a structural relief.<sup>13,14</sup> Furthermore, by effectively irradiating the gas-liquid interface with the plasma ions due to the structural specificity of the ionic liquid, the secondary electrons are more easily emitted from the ionic liquid, which can also decrease the breakdown voltage. Since the large electric field and the resultant ion irradiation are generated only in the A mode, the decrease in the breakdown voltage can be observed only in A mode. In accord with above results, the ionic liquid introduction is considered

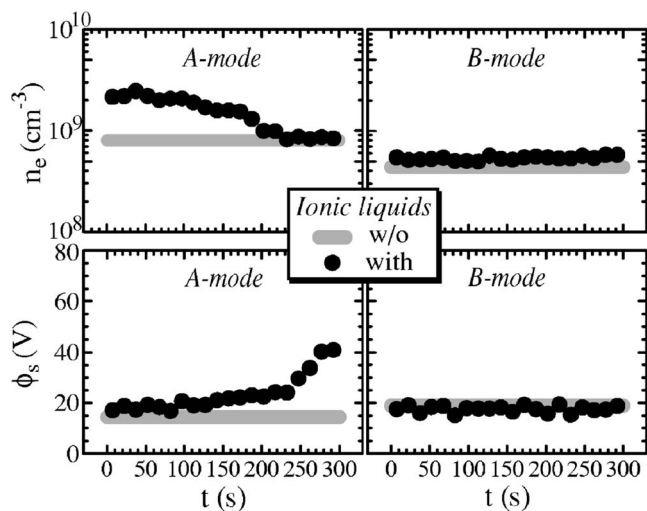


FIG. 3. Temporal evolutions of electron density  $n_e$  and space potential  $\phi_s$  of the plasma in contact with ionic liquid (closed circle) and without that (gray line) for  $P_{rf}=15$  W and 100 Pa at  $z=15$  mm and  $r=10$  mm. The resolution time is 15 s.

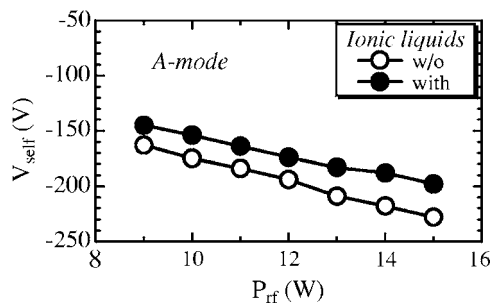


FIG. 4. Self-bias voltages  $V_{self}$  depending on rf power  $P_{rf}$  in the range of  $t=0-120$  s under A mode without (open circle) and with (closed circle) ionic liquids, respectively.

to be accompanied by the variation of plasma state in gas phase in the case of A mode.

Figure 3 depicts temporal evolutions of electron density  $n_e$  and space potential  $\phi_s$  of the plasma in contact with the ionic liquid for  $P_{rf}=15$  W and  $p=100$  Pa at  $z=15$  mm and  $r=10$  mm. In the case of A mode, the electron density is about  $n_e \approx 8 \times 10^8$  cm<sup>-3</sup> in the absence of ionic liquids. However, the introduction of the ionic liquid enhances the electron density up to  $2 \times 10^9$  cm<sup>-3</sup> in the range of  $0 < t < 200$  s. Interestingly, for  $200 < t < 300$  s, the space potential gradually increases, being accompanied by a decrease in the electron density. This phenomenon is interpreted as that the secondary electrons from the ionic liquid, which enable the electron density in gas phase to be enhanced, gradually decrease for  $t > 200$  s and the lack of the electrons leads to the space-potential rise. In the case of B-mode, on the other hand, no differences of  $n_e$  and  $\phi_s$  between the cases in the presence and the absence of ionic liquids are found even if the plasma is maintained until  $t=300$  s.

In order to estimate the profile of potential structure along  $z$  axis, the self-bias voltage  $V_{self}$  in the A mode is measured in the range of  $t=0-120$  s and plotted as a function of  $P_{rf}$ , as shown in Fig. 4, where  $V_{self}$  is reduced with a decrease in  $P_{rf}$ .  $V_{self}$  is about  $-200$  V for  $P_{rf}=15$  W in the presence of ionic liquids in the A mode. Thus, the potential difference  $\phi_s - V_{self} \approx 220$  V between the plasma and liquid forms a sheath electric field on the ionic liquid, giving rise to the ion irradiation owing to the electrostatic acceleration by the sheath. The sheath depth  $d_s$  is estimated to be 7 mm using the Debye length  $\lambda_D$ . When the plasma is generated in the absence of ionic liquids, the absolute value of  $V_{self}$  increases compared with the case in the presence of ionic liq-

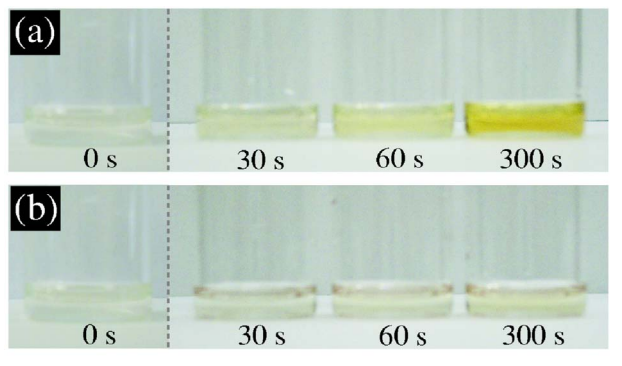


FIG. 5. (Color online) Images of ionic liquid colors as a function of discharge time. (a) A mode and (b) B mode for  $P_{rf}=15$  W.

uids. These results afford the possibility of the secondary electron emission from the ionic liquid, which has a reduction effect on the self-bias voltage. On the other hand,  $V_{\text{self}}$  in the B mode is always 0 V because the mesh electrode in the ionic liquid is grounded. Therefore, the ion energy of irradiation to the ionic liquid is about 20 eV which is much less than that in the A mode.

Figures 5(a) and 5(b) show colors of the ionic liquid after the discharge in the cases of A and B modes, respectively. In the former case, the yellowish color is observed to gradually change with time and found to become thick yellow at  $t=300$  s. On the other hand, the color of the ionic liquid keeps yellowish in the latter case. The remarkable color change in A mode is caused by irradiating the plasma ions with high energy such as 220 eV. On the other hand, the ionic liquid color in B mode does not change because the irradiation energy of the plasma ions is low such as 20 eV. Based on these results, the color change of the ionic liquid is considered to be attributed to the decomposition of the ionic liquid caused by the high-energy ions. At least, the change of color does not result from ultraviolet rays radiating from the plasma. Thus, the color change observed in Fig. 5 is believed to be related to the plasma parameters, especially the ion energy modified by the enhanced sheath-potential drop. Based on the above-mentioned results, the ions in the gas phase plasma convincingly appear to be accelerated by the sheath electric field and be irradiated to the ionic liquid.

In conclusion, we have achieved the generation of ionic liquid incorporated plasmas under the condition of low gas pressures. As a result of interactions between the gas phase plasma and ionic liquid, the discharge easily proceeds and the electron density obviously increases compared with the case in the absence of ionic liquids. The results indicate that the sheath electric field can be formed on the ionic liquid surface only in the case where the powered electrode is in the

liquid, causing the ion irradiation toward the ionic liquid. This ion irradiation induces specified chemical and physical processes in the gas-liquid phase interfacial region. Ionic liquids have a potential ability of matrixes as a buffer material for the thermal energy originated from plasmas, which enables the plasma to involve soft matters such as DNA, protein, and colloid particles. Thus, such a kind of the plasma-ion behavior control in hybrid systems composed of ionic liquids and gas phase plasmas could contribute to the effective creation and modification of nanocomposite materials consisting of biomolecules, metal particles, nanocarbons, and so on, which are dispersed in the ionic liquids.

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