Negative ion species in atmospheric-pressure helium dc glow discharge produced in ambient air

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Abstract. Experimental investigation on negative ions in atmospheric-pressure plasmas is insufficient to date. In this work, we examined negative ion species in atmospheric-pressure helium dc glow discharge produced in ambient air by laser photodetachment spectroscopy, where the pulsed increase in the discharge current was measured as a function of the laser wavelength. A major negative ion species was O\(^-\) which was originated from molecular oxygen in the ambient air. OH\(^-\) and Cl\(^-\) were also major negative ion species when we used an NaCl solution as the cathode of the dc discharge. O\(_2\)\(^-\) was minor in comparison with O\(^-\), and H\(^-\) was negligible. The production process of OH\(^-\) was not dissociative electron attachment to H\(_2\)O. The experimental results are consistent with the dominant production of OH\(^-\) due to dissociative electron attachment to H\(_2\)O\(_2\).

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1. Introduction

Recently, atmospheric-pressure plasmas attract much attention, because they have opened new applications of plasmas in medicine [1–3] and agriculture [4–6]. The plasma sources developed with the intention of applying them to medicine and agriculture are usually operated in ambient air [7–10]. Noble gases such as helium and argon are widely used for producing atmospheric-pressure plasmas, but the plasmas usually contain oxygen and nitrogen which are admixed from the ambient air to the noble gas flow. In addition, the admixture of water vapor is not negligible in many atmospheric-pressure plasmas, especially in the cases that the plasmas interact with water-containing objects such as biological tissues. Water vapor is the ingredient of OH [11] which is understood to be the most important radical species in medical and agricultural applications as well as in plasma-liquid interaction [12].

Oxygen and water vapor are electronegative gases. It is well known that plasmas produced with electronegative gases contain negative ions. Low-pressure plasmas with negative ions were investigated intensively in conjunction with the development of dry
etching technology more than twenty years ago [13, 14]. It has been understood by a numerical simulation that the transport and the confinement of charged particles in electronegative plasmas are different from those in electropositive plasmas [15]. The chemical kinetics and the spatial structures of atmospheric-pressure plasmas with negative ions have been investigated by many authors using numerical modeling [16–21]. In contrast, experimental investigations of negative ions in atmospheric-pressure plasmas are seriously insufficient to date. The influence of negative ions to the propagation of ionization waves is discussed in some experimental works [21, 22], but the negative ion density has not been measured in atmospheric-pressure plasmas.

A reason for the small number of experimental investigations on negative ions in atmospheric-pressure plasmas is the difficulty in the diagnostics. A widely used method for detecting negative ions in electronegative low-pressure plasmas is laser photodetachment combined with Langmuir probes [23, 24]. However, the Langmuir probe does not work in atmospheric-pressure plasma due to the high collision frequency inside the sheath around the probe tip. An alternative method is laser absorption spectroscopy [25], where laser photons are lost during the propagation in the electronegative plasma by the photodetachment reaction with negative ions. This method needs the combination with cavity ringdown spectroscopy (CRDS) because of the small absorption coefficient due to photodetachment [26, 27]. However, the CRSD measurement may be problematic in atmospheric-pressure plasmas with sizes in the millimeter range, since the light refraction at the curved boundary between the plasma and the ambient gas influences the optical alignment of the cavity [28]. According to these reasons, the experimental investigations of the detection of negative ions in atmospheric-pressure plasmas exclusively employ mass spectrometry [29–31]. However, mass spectrometry may have difficulty in the extraction of negative ions, since placing the sampling orifice is the significant disturbance to atmospheric-pressure plasmas with small sizes [32]. The potential difference between the plasma and the sampling orifice is another problem in the extraction of negative ions.

In this work, we adopted laser photodetachment to atmospheric-pressure helium dc glow discharge produced in ambient air. This type of discharge is specific for the detection of negative ions by laser photodetachment, since the production of electrons from negative ions changes the electric conductivity of the plasma, resulting in the pulsed change in the discharge current. Tschiirsch and coworkers have applied laser photodetachment to the investigation of the pre-ionization stage of dielectric barrier discharges, and they also detected the electrical response of the discharge circuit to laser photodetachment [33, 34]. In this work, we examined the negative ion species in the plasma from the relationship between the photodetachment current and the laser wavelength.
2. Experiment

Figure 1 shows the plasma source and the electrical circuit used in the experiment. The plasma was produced by applying a dc high voltage between a planar electrode and a stainless-steel nozzle electrode which had inner and outer diameters of 0.5 and 0.8 mm, respectively. The nozzle electrode was connected to the positive side of a dc power supply via a 50 kΩ resistor. The planar electrode was connected to the negative side of the dc power supply via a 50 Ω register, which was used for measuring the current through the circuit from the voltage drop. The negative side of the dc power supply was electrically grounded. The planar electrode was a stainless-steel plate or the surface of NaCl solution. The distance between the tip of the anode and the planar cathode was 4 mm. The voltage between the anode and the cathode was dependent on the cathode material, and it was 900-1000 V when the discharge current was 20 mA. Helium flowed from the stainless-steel nozzle electrode at a flow rate of 400 sccm. In some experiments, the helium flow was surrounded by the flow of sheath gas which was provided by placing another gas nozzle around the stainless-steel nozzle electrode. We injected the pulsed laser beam yielded from a tunable dye laser or an optical parametric oscillator into the plasma from the radial direction. The duration of the laser pulse was approximately 8 ns. The laser energy was dependent on the wavelength, since we used the second harmonic generation of the dye laser, the fundamental oscillation of the dye laser, and the idler oscillation of the optical parametric oscillator for the ultraviolet, visible, and infrared wavelengths, respectively. The laser beam was not focused, and almost the entire region of the plasma was illuminated by the laser beam. We were careful in avoiding the ablation of the electrodes, since the ablation caused a serious electrical noise at the timing of the pulsed laser injection.

3. Results and discussion

3.1. Temporal variation of discharge current

The temporal variation of the discharge current at the timing of the pulsed laser injection is shown in Fig. 2. The origin of the horizontal axis corresponds to the timing of the Q-switching of the Nd:YAG laser which was used for the optical pumping of the dye laser. The cathode was the stainless-steel plate. In this measurement, the dc discharge current (20 mA in this example) and its pulsed temporal variation were observed using the dc and ac coupling modes of the oscilloscope, respectively. A higher sensitivity was adopted at the ac coupling mode. Figure 2 shows the waveform recorded at the ac coupling mode, and the dc current before the laser pulse injection is labeled by referring the signal recorded at the dc coupling mode. The wavelength and the energy of the dye laser beam were 682.6 nm and 40 mJ, respectively. The laser wavelength was measured using a wave meter with the accuracy of ±5 pm. As shown in the figure, we observed the pulsed increase in the discharge current at the timing of the pulsed laser injection. The duration of the pulsed current was approximately 100 ns. The amplitude of the pulsed
current was dependent on the ambient gas species. The highest and lowest amplitudes were observed when the helium flow was surrounded by oxygen and nitrogen sheath gases, respectively. The amplitude of the pulsed current was medium when we applied no sheath gases.

The pulsed increase in the discharge current is considered to be due to the production of electrons from negative ions in the plasma (laser photodetachment, \( X^- + h\nu \rightarrow X + e \)). The production of electrons from negative ions do not change the total amount of negative charges in the plasma. However, since the mobility of electrons is much higher than negative ions, we can expect the increase in the current passing through the plasma. The influence of the ambient gas species on the amplitude of the pulsed current is consistent with the speculation of laser photodetachment, since oxygen and nitrogen are electronegative and electropositive gases, respectively. Another possibility for the mechanism of the pulsed current is photoionization of neutral species [35]. However, the contribution of photoionization may not be dominant, since the amplitude of the pulsed current is sensitive to the laser wavelength and it is small at a longer wavelength than the photodetachment threshold (Figs. 4 and 5).

3.2. Amplitude of pulsed current

We repeated the measurement of the pulsed current shown in Fig. 2 at various laser energies. Figure 3 shows the ratio between the amplitude of the pulsed current \( I_{pd} \) and the dc discharge current \( I_0 \) as a function of the laser energy. The same plasma produced in the ambient air at a discharge current of 20 mA was illuminated by laser pulses with various energies. The experimental results are represented by the plots, while the solid curve shows the theoretical prediction on the photodetachment ratio [23],

\[
\alpha = \frac{\Delta n_-}{n_-} = 1 - \exp\left(-\frac{\sigma \lambda E_L}{hcS}\right),
\]

where \( \Delta n_-/n_- \) shows the ratio of photodetached negative ion density to the total negative ion density, \( \sigma \) is the cross section of photodetachment, \( c \) is the speed of light, \( h \) is the Plank constant, and \( \lambda, E_L, \) and \( S \) are the wavelength, the energy, and the cross section of the laser beam, respectively. It is noted that \( \Delta n_- \) corresponds to the density of electrons produced from negative ions by laser photodetachment. As shown in the figure, we observed the agreement between \( I_{pd}/I_0 \) and the theoretical prediction of \( \Delta n_-/n_- \). Therefore, we can conclude that the photodetachment current \( I_{pd} \) represents the relative value of the negative ion density in the plasma.

3.3. Detection of \( O^- \)

Since photodetachment has the threshold for the photon energy, we can obtain the knowledge of the negative ion species if we carry out the photodetachment experiment at various laser wavelengths. Figure 4 shows the photodetachment current as a function of the laser wavelength between 835 and 860 nm. The infrared laser beam was obtained
by the idler oscillation of the optical parametric oscillator. The laser energy was approximately 12 mJ. The cathode was the NaCl solution with a concentration of 1%. The plasma was produced in the ambient air at a discharge current of 20 mA. As shown in the figure, we observed the decrease in the photodetachment current with the laser wavelength. The photodetachment ratio of O\(^-\) is shown by blue plots in Fig. 4, which was obtained by substituting the laser parameters and the photodetachment cross section of O\(^-\) [36] into eq. (1). As shown in the figure, the variation of the photodetachment current coincided with the photodetachment ratio predicted on the basis of the cross section data. Therefore, the experimental result shown in Fig. 4 gives us the evidence that O\(^-\) is a negative ion species in the plasma. Since the photodetachment cross section is negligible at 860 nm for O\(^-\), the photodetachment current observed at 860 nm is due to negative ion species which have the photodetachment threshold at a longer wavelength than 860 nm. The possibilities are O\(_2^-\) and H\(^-\) in the experimental condition, but O\(_2^-\) is more likely as will be described below. Figure 4 indicates that the density of O\(^-\) is higher than that of O\(_2^-\), which is consistent with the speculation reported by Nemschokmichal and coworkers [34].

The influence of the sheath O\(_2\) gas is shown in Fig. 5. As shown in the figure, we observed the significant increase in the photodetachment current of O\(^-\) when the helium flow was surrounded by the sheath O\(_2\) gas. This result suggests the production of O\(^-\) by dissociative electron attachment to O\(_2\) (O\(_2\) + e \rightarrow O\(^-\) + O). In addition, as shown in Fig. 5, we observed the increase in the photodetachment current at 860 nm. The source of H\(^-\) in this experimental condition is water vapor in the ambient gas. It is reasonably considered that the sheath O\(_2\) gas reduces the water vapor density in the ambient gas. Hence, if the negative ion species photodetached at 860 nm is H\(^-\), we may observe the decrease in the photodetachment current when the helium flow is surrounded by the sheath O\(_2\) gas. However, the experimental result is opposite as shown in Fig. 5, indicating that the negative ion species photodetached at 860 nm is O\(_2^-\) which is produced by three-body electron attachment O\(_2\) + e + M \rightarrow O\(_2^-\) + M.

3.4. Detection of OH\(^-\)

Figure 6 shows the photodetachment current as a function of the laser wavelength between 670 and 710 nm. The energy of the laser pulse yielded from the dye laser was 47 mJ. The plasma was produced in the ambient air at a discharge current of 20 mA using the stainless-steel plate as the cathode. The photodetachment ratio expected from the photodetachment cross section of OH\(^-\) [37,38] is also shown in Fig. 6. The variation of the photodetachment current agreed well with the photodetachment ratio, as shown in the figure. Therefore, the experimental result shown in Fig. 6 is the evidence that OH\(^-\) is a negative ion species in the plasma. The photodetachment current observed at 700 nm is due to O\(^-\) and O\(_2^-\). The ratio of the photodetachment current due to OH\(^-\) to that due to O\(^-\) and O\(_2^-\) is small, as shown in Fig. 6, indicating that OH\(^-\) is minor in the negative ion composition in the plasma produced using the stainless-steel plate as
the cathode.

When the cathode was the NaCl solution with a concentration of 1%, we observed the photodetachment current shown in Fig. 7. The photodetachment current using the stainless-steel cathode (the same data as those shown in Fig. 6) is also plotted in Fig 7 for comparison. As shown in the figure, we observed the significant increase in the photodetachment current due to OH by using the NaCl solution as the cathode. In addition, we observed the increase in the photodetachment current at a wavelength of 700 nm. As will be described below, this increase is caused by the increase in the O\(^-\) density in the plasma.

3.5. Production process of OH

The enhancement of the photodetachment current or the increase in the OH\(^-\) density by using the liquid cathode is related with the increase in the water vapor density in the ambient air. However, considering the cross section data [39, 40], dissociative electron attachment to H\(_2\)O is not the production process of OH\(^-\). The cross section of dissociative electron attachment to H\(_2\)O to produce H\(^-\) is on the order of 10\(^{-18}\) cm\(^2\) and its threshold energy is approximately 5.5 eV. In addition, the cross section to produce O\(^-\) is on the order of 10\(^{-19}\) cm\(^2\) and its threshold energy is approximately 4.5 eV. The cross section to produce OH\(^-\) is on the order of 10\(^{-20}\) cm\(^2\) and its threshold energy is approximately 4.3 eV [39]. According to the experimental result shown in Fig. 7, the enhancement of the photodetachment current by using the liquid cathode was more remarkable for OH\(^-\) than O\(^-\), which cannot be explained by the smaller cross section of dissociative electron attachment to produce OH\(^-\) than O\(^-\). In addition, the increase in the photodetachment current at 860 nm was not remarkable by using the liquid cathode, suggesting that the increase in the H\(^-\) density is not significant when we used the NaCl solution as the cathode. This also contradicts the fact that dissociative electron attachment to H\(_2\)O has the largest cross section for the production of H\(^-\).

We believe that the major production process of OH\(^-\) in the plasma produced in the ambient humid air is dissociative electron attachment to H\(_2\)O\(_2\). The production process of H\(_2\)O\(_2\) may be three-body reaction OH + OH + M → H\(_2\)O\(_2\) + M. We have shown that OH radicals are available in the liquid cathode discharge [41]. The cross section of dissociative electron attachment to H\(_2\)O\(_2\) is on the order of 10\(^{-17}\) cm\(^2\) [42]. The cross section for the production of OH\(^-\) has a larger cross section than that for O\(^-\), and the ratio is approximately four. Therefore, the remarkable increase in the OH\(^-\) density, the moderate increase in the O\(^-\) density, and the negligible increase in the H\(^-\) density, which were observed by using the liquid cathode, are explained reasonably by assuming dissociative electron attachment to H\(_2\)O\(_2\). In addition, the cross section of dissociative electron attachment to H\(_2\)O\(_2\) is large at a low electron energy (the peak is located around 0.5 eV) [42]. Since the electron temperature of the atmospheric-pressure dc glow discharge, which was measured by laser Thomson scattering, is 2 eV [43, 44], dissociative electron attachment to H\(_2\)O\(_2\) can have a much larger rate coefficient than
that to H₂O with the threshold energy higher than 4.3 eV.

3.6. Detection of Cl⁻

Finally, we examined the existence of Cl⁻ in the plasma when we used the NaCl solution with a concentration of 1% as the cathode. Figure 8 shows the photodetachment current as a function of the laser wavelength between 340 and 348 nm. The ultraviolet laser beam was obtained by the second harmonic generation of the dye laser. The laser energy was 13 mJ. The photodetachment ratio expected from the photodetachment cross section of Cl⁻ [45, 46] is also shown in Fig. 8. Just three plots in Fig. 8 for the photodetachment ratio is due to the limited number of the cross section data in the wavelength range. The agreement between the photodetachment current and the photodetachment ratio indicates the existence of Cl⁻ in the plasma. The photodetachment ratio at 340 nm is estimated to be 0.5, as shown in Fig. 8, since this wavelength is close to the photodetachment threshold of Cl⁻. This means that we expect a two times higher photodetachment current if we can detach electrons from all Cl⁻ negative ions. Therefore, it is speculated that Cl⁻ is a major negative ion species in the plasma. It has been reported that the optical emission of Na is observed in the atmospheric-pressure dc glow discharge when the NaCl solution is used as the cathode [47, 48]. However, the optical emission of Cl is never observed in the same plasma, suggesting that the Cl density is considerably low. The reason for the low Cl density has not been clarified yet, but the present experimental result shows that a part of Cl is converted to Cl⁻ in the plasma. The production process of Cl⁻ has not been understood yet. Since we may need molecular species with Cl to produce Cl⁻ by dissociative electron attachment, the first step to understand the production process of Cl⁻ is the detection of Cl₂ and NaCl in the plasma.

3.7. Possibility of other negative ion species

We did not examine other negative ion species such as O₃⁻, O₄⁻, O⁻(H₂O), and O₂⁻(H₂O)ₙ, which are considered in numerical simulation [17, 20]. The O₄⁻ density increases with the O₂ density, and it can be a major negative ion species when the O₂ concentration is ~ 10 % [17]. Hence, it is expected that O₄⁻ is negligible in the helium-based discharge used in the experiment. The O₅⁻ density is significantly affected by the O₃ density [17, 20]. It has been reported that the O₃ density in a dc discharge is much lower than that in a dielectric barrier discharge [49]. In addition, the gas temperature in the helium dc glow discharge is as high as 2500 K [41], which is a harmful condition for the effective production of O₃. Therefore, we presume that the densities of O₅⁻ and O₃ are low in the helium dc glow discharge. We also presume that O⁻(H₂O) and O₂⁻(H₂O)ₙ cannot survive in the active discharge plasma with the high gas temperature.
4. Conclusions

In this work, we examined negative ion species in atmospheric-pressure helium dc glow discharge produced in ambient air by laser photodetachment spectroscopy. It has been shown that the dominant negative ion species is $\text{O}^-$ which is originated from molecular oxygen in the ambient air. $\text{O}_2^-$ is a minority in comparison with $\text{O}^-$, and $\text{H}^-$ is negligible. $\text{Cl}^-$ is a major negative ion species when we used a NaCl solution as the cathode of the dc discharge. $\text{OH}^-$ is another major negative ion species in the liquid cathode discharge. The production process of $\text{OH}^-$ is not dissociative electron attachment to $\text{H}_2\text{O}$. The experimental results are consistent with the dominant production of $\text{OH}^-$ due to dissociative electron attachment to $\text{H}_2\text{O}_2$.

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Figure 1. Experimental arrangement.
Figure 2. Temporal variation of discharge current at the timing of the pulsed laser injection. Three results observed with three types of ambient gas are shown.
Figure 3. Amplitude of the pulsed increase in the discharge current as a function of the laser energy. The theoretical prediction of the photodetachment ratio is also shown.
Figure 4. Photodetachment current as a function of the laser wavelength. The photodetachment ratio predicted by the photodetachment cross section of O\textsuperscript{-} is also shown.
Figure 5. Comparison of the photodetachment current with and without the sheath \(O_2\) gas around the He flow.
Figure 6. Photodetachment current as a function of the laser wavelength. The cathode was the stainless-steel plate. The photodetachment ratio predicted by the photodetachment cross section of OH⁻ is also shown.
Figure 7. Comparison of the photodetachment current when we used the stainless-steel plate and the surface of the NaCl solution as the cathode of the dc discharge.
Figure 8. Photodetachment current as a function of the laser wavelength. The cathode was the surface of the NaCl solution. The photodetachment ratio predicted by the photodetachment cross section of Cl$^-$ is also shown.