Catalyst-free synthesis of ammonia using dc-driven atmospheric-pressure plasma in contact with water

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Abstract. Atmospheric-pressure plasma, generated using a dc power supply, in contact with water was investigated as a green, catalyst-free method for the ammonia synthesis. Stable nitrogen plasmas were generated inside bubbles which were obtained by inserting a dielectric tube with the gas flow into water. A higher production rate was obtained at a higher discharge current, a higher flow rate of nitrogen, and a lower conductivity of water. In addition, the production rate when the water worked as the cathode of the discharge was higher than that with the inverted polarity of the dc power supply. The maximum production rate of ~ 0.98 μmol/min was realized at the optimized discharge condition, which is higher than the literature value obtained using a dc discharge in contact with water [R. Hawtof, *et al.*, Sci. Adv. **5**, eaat5778 (2019)]. We also discussed the possible reaction fields for the ammonia synthesis in the experimental condition.

Ammonia is a major resource in various industries like agriculture and manufacturing, commonly producing fertilizers, cleaning products, refrigerants and cooling liquids [1,2]. Recently, it has been explored as energy carriers and sources [3,4]. Generally, ammonia is mass produced through the Haber-Bosch process in which an exothermic reaction between pure hydrogen (H_2) and nitrogen (N_2) occurs with a metal catalyst under high temperatures and pressures [5]. This process provides high purity and efficiency; however, it has high energy consumption and carbon dioxide emissions [6–8]. Hence, alternative techniques to synthesize ammonia have been gaining interest recently.

Improvements with catalysts such as iron, ruthenium, cobalt, nickel, metal nitrides, and electrides can provide high electron donating power and chemical stability allowing for the synthesis of ammonia at moderate temperatures and pressures [9–16].

Recently, several studies have been reported on the combination of catalysts and plasma. Atomic nitrogen produced by the plasma may increase the probability of adsorption on the catalyst, and recently it has been reported that nitrogen molecules vibrationally excited by the plasma increase the probability of adsorption on the catalyst surface. [17,18]. On the other hand, a completely different approach to research has also been reported that utilizes the interaction of atmospheric pressure plasma and water

without the use of a catalyst. This approach is characterized by the use of water rather than hydrogen as the raw material, and since it does not use expensive catalysts, it has a low environmental impact and could be an excellent method if it can be put to practical use. These include atmospheric-pressure systems using plasma and UV irradiation on water and air [19], plasma-water droplet reactors [20,21], and even hybrid electrochemical cells where plasma is used as a cathode [22]. Although these plasma processes have been successful in synthesizing ammonia, the energy efficiency and the selectivity still need refinement.

One way to improve them is investigating more plasma setups, particularly, utilizing dc power to generate plasma with liquid electrodes. This has already been used for various applications and characterizations such as optical emission analysis, droplet generation [23,24], chemiluminescence and gas-phase radical density relationship [25,26], and nanoparticle synthesis [27, 28]. Thus, dc-driven atmospheric-pressure plasma interacting with liquid has potential as a method for ammonia synthesis. This study aims to synthesize ammonia by using dc-driven atmospheric-pressure plasma in contact with water. The dependence of the synthesis rate on the plasma setup, the discharge current, the gas flow rate, and the liquid conductivity was examined.

Experiments were performed using two discharge setups: plasma on water surface and plasma inside a bubble in water, as shown in Figs. 1(a) and 1(b), respectively. The experimental setups were similar to that in conventional electrochemistry except that the plasma produced between a stainless-steal nozzle electrode (outer diameter: 0.8 mm, inner diameter: 0.5 mm) and the water surface was used as an electrode. The nozzle was used for flowing the working gas for the discharge toward the water surface. In Fig. 1(a), the plasma was generated in atmosperic pressure condition. The plasma worked as the anode and a platinum (Pt) wire was used as the counter electrode in the system illustrated in Fig. 1, but the plasma production was possible even with the inverted polarity. This setup was similar to that in our previous work [23, 24], where an atmospheric-pressure dc discharge was generated using a liquid as an electrode. Nitrogen (N_2) was utilized for the plasma generation and for maintaining a nitrogen-rich environment. Aside from the metal nozzle electrode, we introduced nitrogen gas through another tube before plasma generation. This was done to ensure a nitrogen-rich environment. In the second setup as shown in Fig. 1(b)., a bubble was formed inside and below a dielectric tube (outer diameter: 1.2 mm, inner diameter: 0.8 mm) submerged in the water, and the plasma was generated inside the bubble. An aluminum tape attached to the bottom of the water container was used as the counter electrode. The setup shown in Fig. 1(b) was better for realizing stable nitrogen discharges. Plasma is generated in the air bubble between the nozzle and the liquid. Although the plasma in this system can be viewed as an electrode for electrolysis, the metal nozzle and liquid are represented here as the electrode, consistent with Fig. 1 (a).

For both the setups, the plasmas were generated at a discharge current of 10 mA and an N_2 flow rate of 200 sccm using tap water with a volume of 10 mL. In examining the effects of the discharge current and the gas flow rate, the plasma generated in

the water (Fig. 1(b)) was employed and tap water was used as the cathode of the discharge. The influence of the liquid conductivity was examined by using three types of water: tap water, distilled water, and 1% (by weight) NaCl solution. The conductivities of tap water, distilled water, and 1% NaCl solution are 200μS/cm, 10μS/cm, and $1.7\times10^6\mu$S/cm, respectively. Impurities in tap or distilled water do not affect the reaction of ammonia synthesis. The ammonium concentration in the water was measured by indophenol blue spectrophotometry. A water trap was set at the outlet of the exhaust gas and the ammonia dissolved in the water trap was measured. A high speed camera (NAC MEMECAM HX-3) was utilized to capture the optical emission images of the discharges.

Both the experimental setups were able to generate plasmas using nitrogen as the working gas, even when the liquid worked as the cathode (the plasma is acting as the anode of the setup). The photographs of the discharges using the two configurations are shown in Fig. 2. These photographs shown in Figs. 2(a) and 2(b) are succeeding frames of movies captured at 30 and 2000 fps, respectively. When the discharge was generated on the water surface (Fig. 2(a)), the plasma exhibited the typical glow discharge structure composed of a positive column and a negative glow region. However, the unstable plasma operation was noticed particularly at a low discharge current since the nitrogen flow was not able to stabilize the glow discharge at the atmospheric pressure due to its high breakdown voltage [29, 30]. For the plasma in the water (Fig. 2(b)), a more stable discharge was observed. It showed glow-to-spark-like transitions that started from the tip of the nozzle electrode, then stretched along the bubble and moved towards the aluminum tape electrode. The better stability of the discharge using the setup shown in Fig. 2(b) can be attributed to the dielectric tube that acted similarly to micro-hollow cathode discharges (MHCD), where a dielectric spacer is used between two electrodes, usually a cathode containing a hollow structure and an anode with an arbitrary shape [31–33]. The plasma was confined within the spacer, and the micro-hollow cathode supplies electrons to the positive column instead of the instability-prone negative glow region, allowing the stable plasma operation [31–40]. Although the structure of this experiment is slightly different from that of MHCD, the dielectric tube confines the discharge in a similar manner to ensure stable operation.

Figure 3 shows the difference in the optical emission images of the discharges produced using different liquid conductivities in the setup shown in Fig. 1(b). For water with low conductivity such as tap water and distilled water, the plasma exhibited long and bright optical emissions. The purple colors of the plasmas are the typical characteristic of nitrogen plasmas. For NaCl solution which had high conductivity, the plasma remained near the tip of the nozzle electrode, and it showed corona-like characteristics. Moreover, the color of the plasma changed from purple to yellow-red hue. This yellow optical emission is thought to be the line emission of sodium atoms, which has been observed in a liquid cathode discharge [23, 24].

Figure 4 shows the summary of the ammonium production rates obtained using the different plasma setups. Both setups were operated under the discharge current of 10

mA, the N_2 flow rate of 200 sccm, and the use of tap water as the liquid. The amount of ammonia in the exhaust gas from the water trap was below the detection limit. It was found that the most efficient setup to synthesize ammonia was the discharge in the bubble inside and below the dielectric tube submerged in the water, and where the water worked as the cathode of the discharge. This configuration realized a maximum production rate of 0.18 μmol/min. Ammonia is not synthesized by bubbling nitrogen alone, and ammonia synthesis is below the detection limit in helium plasma. Figs. 5-7 show the ammonium production rates when varying the discharge parameters using the experimental apparatus shown in Fig. 1(b). In these experiments, the amount of ammonia in the exhaust gas from the water trap was also near or below the detection limit. It was observed that the production rate increased with the discharge current and the N_2 flow rate. The highest production rate of 0.98 μmol/min was obtained at a discharge current of 50 mA, when the N_2 flow rate was fixed at 200 sccm, as shown in Fig. 5. The plasma was unstable at lower discharge currents, which explained the low production rates. When the discharge current was fixed at 30 mA, a production rate of 0.54 μmol/min was observed at a flow rate of 600 sccm, as shown in Fig. 6. Note that distilled water was used in Figs. 5 and 6. The water conductivity exhibited a notable effect on the ammonia synthesis, as shown in Fig. 7, where water with low conductivity, *i.e.*, distilled water, had the highest ammonium production rate of 0.71 μmol/min, when the discharge current and the N_2 flow rates were 30 mA and 200 sccm, respectively.

The ammonia production was more efficient in the setup shown in Fig. 1(b), suggesting the importance of the contact area between the plasma and the water for the synthesis. In addition, the presence of the metal tape electrode increased the production rate significantly. The metal surface was effective for stretching the plasma and increasing the contact area between the plasma and the water, as shown in Fig. 2(b). The discharge parameters also had significant influence on the ammonia synthesis. When the nitrogen gas flow rate was increased, the length of the plasma in the bubble was extended, which expanded the contact area with the water and in turn improved the production rate. Likewise, a higher discharge current widened the surface area for the reaction. The efficiency of the ammonia synthesis was also dependent on the liquid conductivity, where water with a low conductivity produced a larger amount of ammonia. The low conductivity allowed the expansion of the plasma toward the metal tape electrode, which enlarged the area for the reaction, and consequently increased the synthesis rate of ammonia. In contrast, water with a high conductivity prevented the expansion of the plasma, so the size of the plasma in contact with water was small.

In the field of catalytic chemistry, it is generally known that the mechanism of the ammonia synthesis is that nitrogen adsorbed on the catalyst surface reacts with hydrogen, resulting in the desorption of ammonia from the surface. On the other hand, recent studies using the plasma-liquid interaction for the ammonia synthesis have reported that hydrated electrons generated at the plasma-water interface react with protons to produce atomic hydrogen, which can work as the intermediates for the ammonia synthesis [20–22]. For example, Hawtof and coworkers reported an ammonia

production rate of around 0.39 μmol/min by utilizing an electrolytic system with a liquid anode and a plasma cathode [22]. In comparison, the results of the present study yielded a higher production rate of 0.98 μmol/min at the maximum. It means the irradiation of ions by using the configuration with a plasma anode and a water cathode produces a larger amount of ammonia than the configuration with the inverted polarity of the dc power supply. Another paper reported by Haruyama and coworkers shows the ammonia synthesis with high selectivity when the water irradiated with ultraviolet radiation serves as the source of atomic hydrogen and the plasma serves as the source of reactive nitrogen [20,21]. In fact, the present experimental results show the importance of the expansion of the bubble surface to the ammonia synthesis, suggesting the production of ammonia at around the plasma-water interface. Roughly extracting the area of the discharge photo in Fig. 3 using image analysis software also confirmed that the larger the area of the discharge, the more ammonia synthesis correlates with the higher ammonia synthesis. In other words, the larger the area of contact between the plasma and the liquid, the greater the amount of ammonia synthesis. Although positive ions irradiated on the water surface may work as an oxidant, it is also possible that reduction reactions to synthesize ammonia may occur near the water surface irradiated with positive ions, since recent studies of plasma-liquid interaction have shown that the generation of hydrated electrons even when the water surface is irradiated with positive ions [41,42]. Another claims that the ammonia synthesis occurs mostly in the gas phase at the atmospheric pressure [43]. Although the density of water vapor in the plasma was not controlled in the present experiment, we reported a higher water vapor density in the water-cathode discharge than the water-anode discharge in a previous work [23]. Hence, the higher production rate of ammonia in the water cathode discharge, which is shown in Fig. 4, could be attributed to the higher water vapor density, supporting the gas-phase production of ammonia in the present experimental condition. Accordingly, further investigation is necessary to judge the reaction field and to understand the synthesis mechanism of ammonia in the present experimental condition.

In conclusion, dc-driven atmospheric-pressure plasma in contact with water was an effective method for synthesizing ammonia without using catalysts. Stable nitrogen plasmas were generated inside bubbles in the water even when the water surface worked as the cathode of the dc discharge. The possibility of improving the production rate of plasma-aided ammonia synthesis was broadened with the discharge system. Moreover, the discharge current, the gas flow rate, and the liquid cathode conductivity played substantial roles in increasing the production rate via their influence on the surface area between the plasma and the water. The production rate ranged between 0.18 and 0.98 μmol/min. Further investigation is still needed to identify the reaction mechanism and to improve the production efficiency and the selectivity, but it has been shown that atmospheric-pressure dc plasma in contact with water is a promising technique for the catalyst-free synthesis of ammonia.

Acknowledgments

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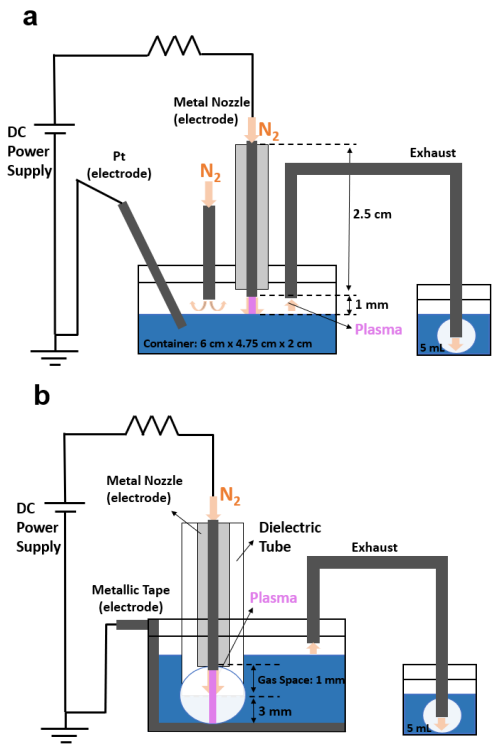

Figure 1. Schematic diagrams of plasma sources used for ammonia synthesis: (a) plasma on water surface and (b) plasma inside a bubble in water.

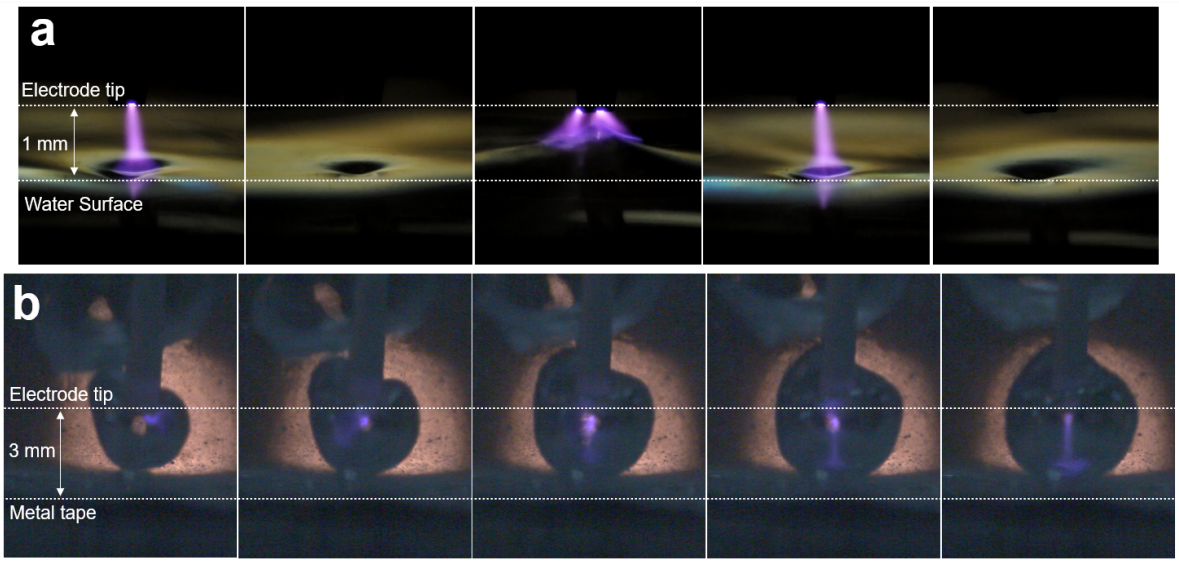

Figure 2. Photographs of (a) plasma on water surface and (b) plasma inside a bubble in water. They are succeeding frames of movies captured at 30 and 2000 fps, respectively.

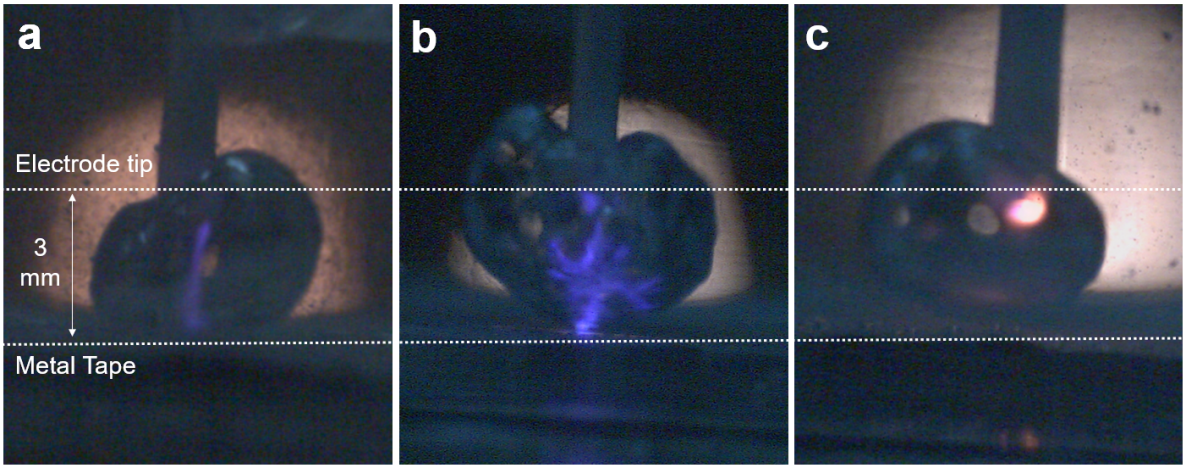

Figure 3. Photographs of plasmas inside bubbles in three types of water: (a) tap water, (b) distilled water, and (c) 1% (weight) NaCl solution. Movies of discharges are available as supplemental data.

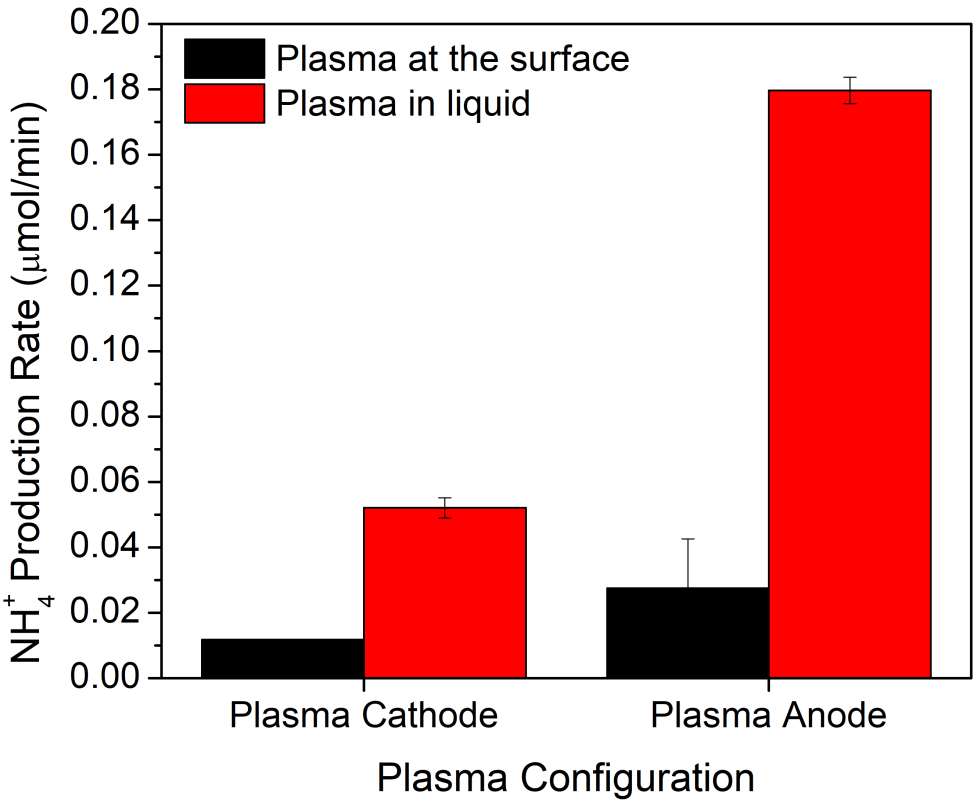

Figure 4. Ammonium (NH_4^+) production rates using the two plasma setups with different polarities of dc power supply.

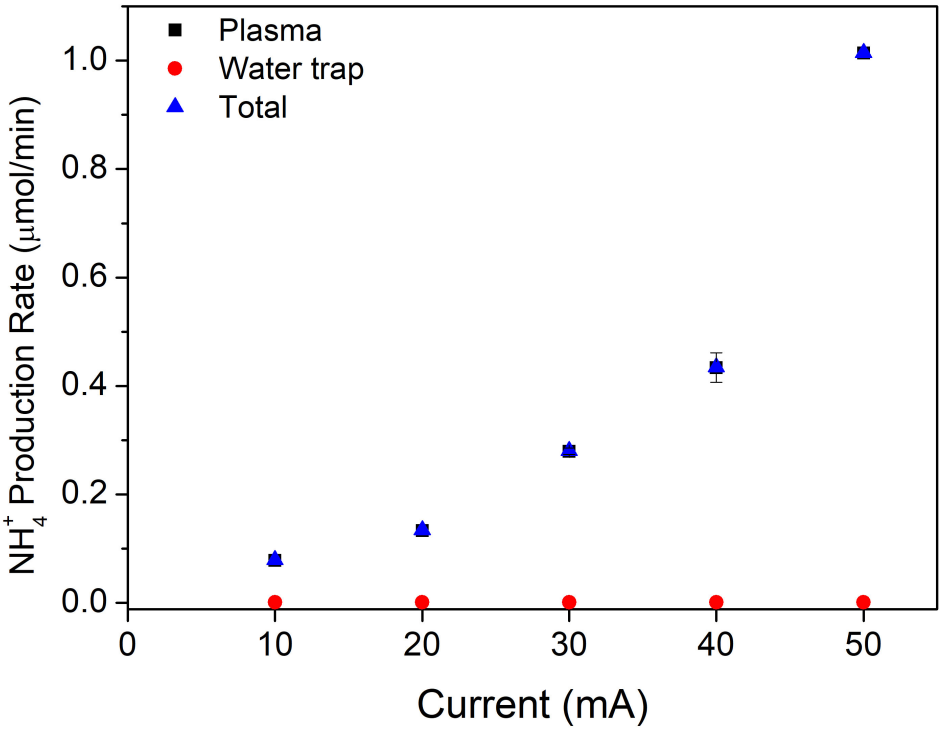

Figure 5. Ammonium (NH_4^+) production rate as a function of discharge current. Plasma was produced in tap water and N_2 flow rate was 200 sccm.

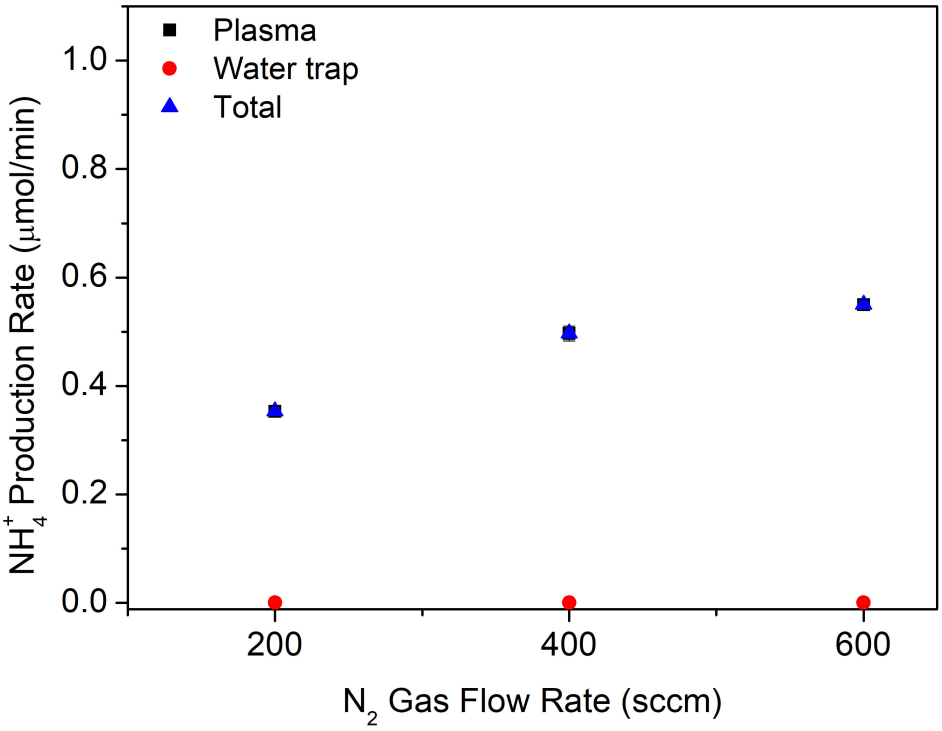

Figure 6. Ammonium (NH_4^+) production rate as a function of N_2 flow rate. Plasma was produced in tap water and discharge current was 30 mA.

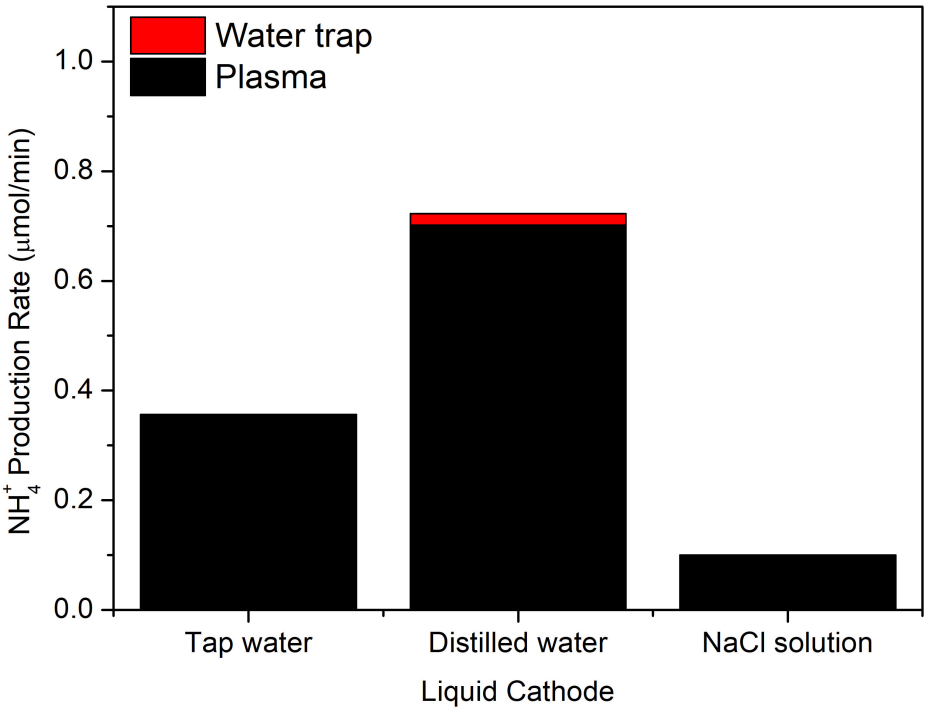

Figure 7. Ammonium (NH_4^+) production rates using tap water, distilled water, and 1% (weight) NaCl solution. Discharge current and N_2 flow rate were 30 mA and 200 sccm, respectively.