Catalyst-free ammonia synthesis using DC-driven atmospheric-pressure plasma in contact with liquid

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Abstract: DC-driven atmospheric-pressure plasma was used as a green and catalyst-free approach for ammonia synthesis. The plasma was stably generated using nitrogen gas flow by submerging the discharge in liquid. The results showed that the rate of ammonia production was highest (~0.98 µmol/min) when the conductivity of water was low and the current and the gas flow rate were high. It was also found that the discharge was affected by the liquid conductivity which in turn affected the synthesis of ammonia.

Keywords: DC-driven atmospheric-pressure plasma, ammonia synthesis, nitrogen plasma, plasma in contact with liquid

1. Introduction

Conventionally, large-scale production of ammonia (NH_3) is done through the Haber-Bosch process where pure hydrogen (H_2) and nitrogen (N_2) react on a metal catalyst under high temperatures and pressures [1]. Although this method provides high efficiency and purity, the exothermic rection requires a lot of energy to carry out and produces a large amount of the carbon dioxide emission [2].

Thus, studies on developing alternative methods for synthesizing ammonia have been gaining interest in recent years. Plasma processes are one promising method since it can be done in a catalyst-free form, in normal temperatures and pressures, and do not require pure hydrogen as water can be the source of hydrogen. Many studies such as using plasma and UV irradiation on atmospheric air and water [3] and a hybrid plasma electrolytic system with the plasma as the cathode [4] have been successful in producing ammonia. However, the selectivity and energy efficiency of these processed can be further improved.

Exploring other plasma configurations may provide a way for this. In particular, atmospheric-pressure discharges with DC voltages, which employ liquid electrodes, can be used in many applications and characterizations, namely for nanoparticle synthesis [5], droplet generation, optical emission analyses [6], and the correlation between gas-phase radical density and chemiluminescence [7]. These examples show the potential of DC-driven atmospheric-pressure plasma-liquid interactions as a viable method for ammonia production.

This study aims to synthesize ammonia through atmospheric-pressure plasma in contact with liquid using DC voltage. The effects of the plasma configuration, the liquid conductivity, the gas flow rate, and the discharge current on the rate of the ammonia synthesis were investigated.

2. Method

Figure 1 shows the schematic diagram of the experimental setup using two plasma configurations. The experimental setup shown in Fig. 1(a) was similar to the conventional electrochemical setup except the plasma generated by DC voltage was used as an electrode (either a cathode and anode) along with the platinum (Pt) electrode. Nitrogen gas was used to generate the plasma and ensured a nitrogen-rich environment. Since the plasma generation in air using nitrogen gas was unstable, another configuration shown in Fig. 1(b) was utilized, where plasma was produced in a dielectric tube that was inserted into water. A metal tape was used for the counter electrode instead of platinum in this case.

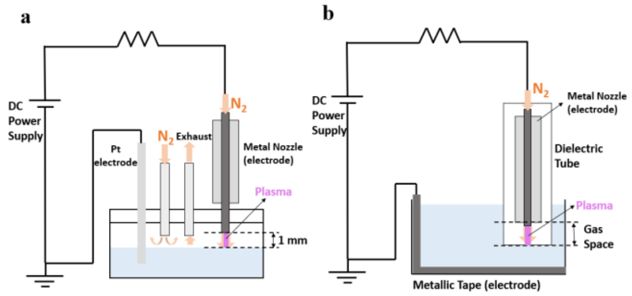

Fig. 1. Schematic diagrams of the experimental setup for (a) plasma at the surface and (b) plasma in liquid.

In testing the plasma configurations, the plasma generation was done at a discharge current of 10 mA and a gas flow rate of 200 sccm for 3 – 5 mins in 10 mL of tap water. The effects of the following plasma parameters, the discharge current, the gas flow rate, and the liquid conductivity, were investigated using tap water for the cathode of the discharge. The dependence on the liquid conductivity was examined by using tap water, distilled water, and 1% (wt) NaCl solution. PACKTEST (indophenol blue spectrophotometry, WAK-NH4-4) was used to determine the ammonium concentration in the liquid. The images of the plasma discharges were taken using a highspeed camera (NAC MEMRECAM HX-3).

3. Results and Discussion

Plasma was successfully generated using the experimental setups. Note that stable plasma was obtained using nitrogen gas even when the liquid worked as the cathode (plasma acting as the anode of the electrolytic system). The summary of the ammonium production rates is shown in Fig. 2. It was observed that the ammonia synthesis was most efficient when the plasma was generated in the tube inserted into water and the water worked as the cathode of the discharge. The maximum production rate was 0.18 μmol/min. Moreover, the presence of a metal surface significantly increased the production rate in the case of generating plasma in the liquid (Fig. 1(b)). This suggests that the metal surface stretches the plasma, increasing the contact area between the plasma and water.

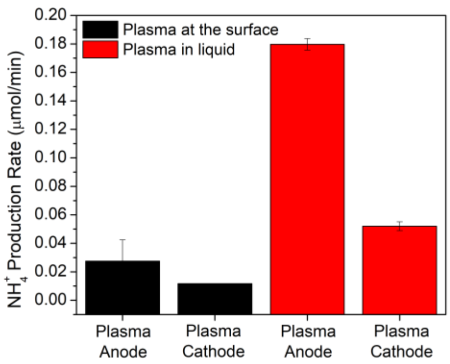

Fig. 2. Ammonium production rates using different plasma configurations.

The results of varying the plasma parameters are shown in Figs. 3-5. As seen in the figures, the amount of ammonia produced increased with the discharge current and the gas flow rate, with the highest ammonium production rates being 0.54 μmol/min and 0.98 μmol/min at 600 sccm and 50 mA, respectively. When gas flow rate was increased, the length of the plasma could possibly be extended. The extension of the plasma enhanced the contact area with water, resulting in the improved production rate. The flow rate could also be related to the gas residence time through the plasma. Similarly, when the discharge current was increased, the size of the plasma also increased which widened the surface area for reactions. Furthermore, the plasma discharge was unstable at low currents which explained the low rate of the ammonia production.

The conductivity of water showed significant effect on the amount of ammonia synthesized, and distilled water with a low conductivity had the highest ammonia production rate of 0.71 μmol/min. The low conductivity allowed the plasma to flow easily towards the metal tape electrode, which resulted in a long and bright (high electron density) plasma. Since the area for reaction became larger, the amount of synthesized ammonia increased. This can be seen in Fig. 6., where the plasmas produced in tap and distilled water have a glow-to-spark plasma characteristics that stretch along with the bubble. Whereas in NaCl solution (high conductivity), the plasma discharge stayed near the electrode and had corona-like characteristic. The colour of the plasma discharge also changed from purple to yellow-red hue that was not observed in the nitrogen discharge in tap and distilled water.

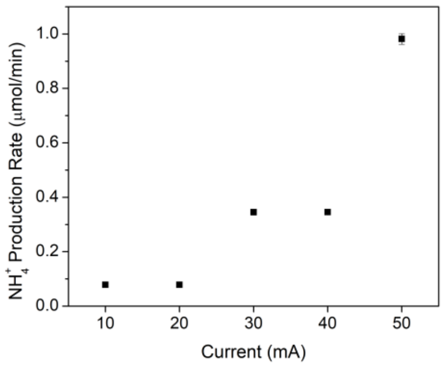

Fig. 3. Ammonium production rate as a function of discharge current.

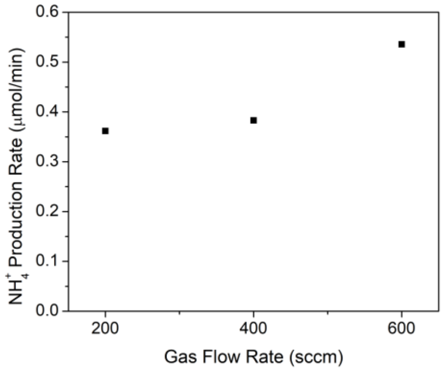

Fig. 4. Ammonium production rate as a function of gas flow rate.

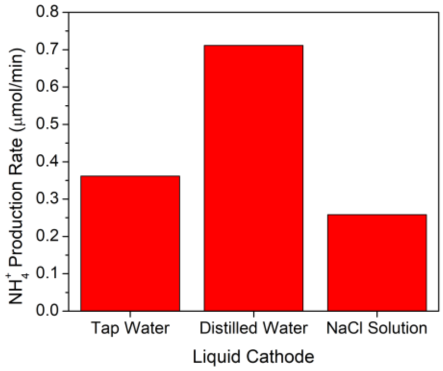

Fig. 5. Ammonium production rates using various types of water (acting as cathode).

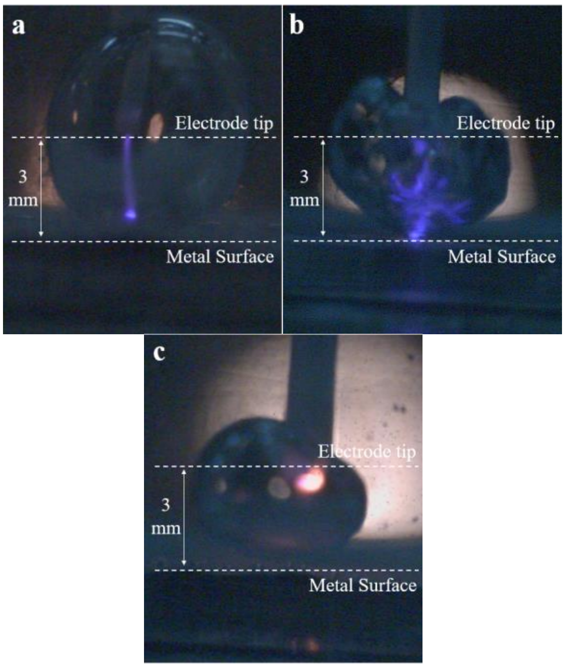

Fig. 6. Plasma discharge in (a) tap water, (b) distilled water, (c) 1% NaCl solution.

While this study has shown the importance of various plasma configurations and parameters, more research is still needed to verify its selectivity and energy efficiency. Furthermore, there is still a need to establish the reaction mechanism of ammonia synthesis through this method.

4. Conclusions

Atmospheric-pressure plasma, generated using DC voltage, in contact with liquid proved to be effective in synthesizing ammonia. Interestingly, a stable nitrogen plasma with water acting as the cathode can be obtained by placing a needle anode inside a dielectric tube inserted into water. This widens the possibility for improving the ammonia synthesis rate using plasma processes. Plasma parameters such as the discharge current, the gas flow rate, and particularly the liquid cathode conductivity play an important role in increasing the production rate of ammonia since these affect the size of the plasma and ultimately the area for reaction. Moreover, we report ammonium production rates of 0.18 – 0.98 μmol/min that are comparable to other studies. Although further investigation is still needed especially in identifying the reaction mechanism, it is clear that DC-driven atmospheric pressure plasma electrolysis is a promising alternative in producing ammonia.

5. Acknowledgement

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6. References

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