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The influence of pH value on nitrate and nitrite formation in air-plasma-treated aqueous solutions

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Abstract

A DC air discharge plasma is operated over an aqueous solution of Na_2SO_4. Nitrate and nitrite are formed in the solution after the plasma treatment. In order to trace the origin of the nitrate and nitrite, we investigated the processes of the nitrate and nitrite formation as a function of the solution's pH value. We measured the nitrate with a nitrate ion selective electrode and the nitrite with Griess assay. The results show that air is activated to form nitrogen oxides by discharge plasma, and the dissolution of these nitrogen oxides leads to the formation of nitrate and nitrite. The total nitrogen content of the nitrate and nitrite in the solution is independent, while the nitrate and nitrite production rates are dependent on the solution's pH value. A high pH environment is beneficial for nitrite formation, while a low pH environment is better for nitrate production. Moreover, the production rates of both nitrate and nitrite are greater in the solution cathode than those in the solution anode.

Keywords: air discharge plasma, plasma-liquid interface, nitrate, nitrite, pH value

(Some figures may appear in colour only in the online journal)

1. Introduction

When discharge plasma is in contact with an aqueous solution, the physical and chemical processes taking placing in the plasma-liquid interface can cause matter and charge exchange between the plasma and the solution [1]. The matter and charge transfer can produce many reactive species in the solution, accompanied by novel plasma electrochemical processes [2, 3]. The reactive species and all the complicated processes at the plasma-liquid interface render many potential applications of the plasma-liquid system, such as wastewater treatment [4–10], plasma medicine [11–14], nanomaterial fabrication [15–31] and nitrogen fixation [32–34]. For instance, the formation of nanoparticles from the reduction of metal ions is based on the reducing species generated from the plasma-liquid interactions, including solvated electron, atomic hydrogen and hydrogen peroxide under certain conditions [35–37]. Specific applications need special reactive species. For example, some applications require oxidizing species to take effect, while others may require reducing species. Moreover, the reactivity and the concentration of the produced reactive species are very different from each other. Therefore, controlling the production rate and the relative ratio of the reactive species is important for applying the plasma-liquid system.

Discharge plasma operated in gas containing some

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amount of air is often used in the plasma-liquid system because it is rich in reactive species. In air-plasma-activated aqueous solutions, there exist short-lived and long-lived reactive species produced from the plasma-liquid interactions. The former, such as hydroxyl (OH) radicals, atomic hydrogen and solvated electrons, are responsible for many immediate effects. However, the latter are of importance when the plasma-activated solutions are used off-line, which is always the case. For example, the reactive species in the plasma-activated water (PAW) [38–40]. Thus, it is important for controlling and adjusting the production of long-lived species in air-plasma-treated solutions. The very common long-lived nitrogen reactive species in the air PAW are nitrate and nitrite. The nitrate and nitrite offer the PAW potential benefits in agriculture and food preservation while being a more sustainable alternative to conventional fertilizer production, and also provide a sterilizing effect on plasma medicine application [38, 39]. It is well known that the pH value is one of the key factors for the chemical reactions taking place in an aqueous solution. Therefore, we explored the dependence of the pH value on the production of the two common long-lived species, nitrate and nitrite, in the air-plasma-exposed solution. The results suggest that the pH value can tune the liquid reactions and then affect the yield and production rate of the nitrate and nitrite, while the total amount of reactive nitrogen is not affected by the pH value.

2. Experiment

The experimental setup is given in figure 1 (inset of figure 1 is a discharge photograph). Air (50 standard cubic centimeters per minute (sccm)) is supplied via a tungsten steel electrode tube (slightly tapered at the nozzle, 1.02 mm in inner and 6.35 mm in outside diameters). An aqueous Na_2SO_4 solution (100 mL, 100 mL/min) is circulated via the polytetrafluoroethylene cylindrical reactor by a Runze Fluid YZ1515X peristaltic pump. A graphite rod is placed at the bottom of the reactor as a counter electrode. When the DC voltage (TESLA-MAN TRC2025N20-1000) applied to the tube and graphite electrodes is greater than the breakdown voltage between the tube and the liquid surface, air discharge plasma is generated. The tungsten steel electrode is attached to a vertical translation stage (VTS113, a range of 13 mm and an accuracy of 0.01 mm, BeiJing Optical Century Instrument Co., Ltd.) in order to adjust the discharge distance. The discharge distance between the solution surface and the powered plasma electrode is fixed at 3 mm. The discharge current is measured by dividing the voltage (measured using a Tektronix TPP0200 passive voltage probe) across the 10 Ω resistor and the discharge current is fixed at 20 mA. A 100 kΩ resistor is used in the circuit to prevent a glow to arc transition. The discharge voltage is measured by a high-voltage probe (Tektronix P6015A). A Tektronix oscilloscope TDS2024 is used to record the voltages. The solution is cooled by placing a water bath system (25 °C) in the circulation.

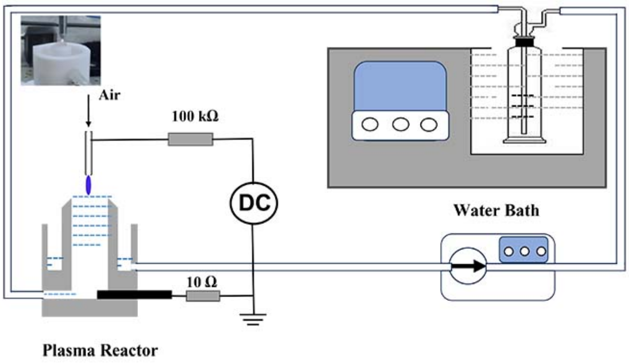

Figure 1. Diagram of the experimental setup.

The nitrite concentration is detected using the Griess assay. The nitrite reacts with the Griess assay to form a stable product, which is a red azo dye with a characteristic absorption peak at 540 nm, and then the nitrite concentration can be estimated from the intensity of the characteristic absorption peak [41]. The nitrate concentration is measured using a nitrate ion selective electrode (BANTE). The pH value of the solution is measured by a pH detector (Yesmylab SX620).

Four pH values of 2, 7, 12 and 13 are investigated. The solution with a pH value of 2 is tuned by adding diluted sulfuric acid, the solution with a pH value of 7 is tuned with a buffer mixture of Na_2HPO_4 and NaH_2PO_4 with a buffer strength of 10 mM (M = mol/L), and solutions with pH values of 12 and 13 are tuned by adding diluted NaOH solution.

3. Results and discussion

Figure 2 shows the characteristics of the discharge current and discharge voltage for solutions with different pH values in cases with the solution as the cathode and the solution as the anode. Obviously, the discharge voltage is relatively

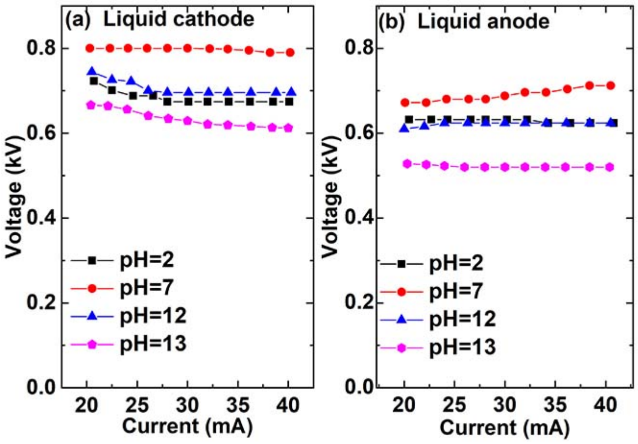

Figure 2. Characteristic curves of the discharge voltage versus the discharge current for air-plasma-treated Na_2SO_4 solutions with different pH values in cases with the solution as (a) the cathode and the solution as (b) the anode. Flow rate of the solution is 100 mL/min and the air supply is 50 sccm.

independent of the discharge current, which suggests that the plasmas are operating in the normal glow discharge mode.

Delgado *et al* [42] also observed a higher discharge voltage in a DC plasma-liquid system with an aqueous $NaClO_4$ solution as the cathode. In plasma theory, the secondary electron emission from the cathode due to the bombardment of energetic ions is very important for sustaining a glow discharge. Delgado *et al* found that the secondary electron emission coefficient for an aqueous solution is smaller than 10^{-5}, which is much less than that for most metals [42] (10^{-2}–10^{-1} for argon plasma [43]). We propose that the higher discharge voltage for the liquid as the cathode might be attributed to the low secondary electron emission coefficient of the aqueous solution, since a high cathode voltage is required to provide higher energy ions to bombard the liquid surface.

Figures 3 and 4 present the concentrations of nitrate and nitrite in the plasma-exposed solutions as a function of the plasma treatment time. In both cases with the solutions as the cathode and the anode, the production rate of nitrate (the slopes of the curves) decreases as the pH value increases, while the nitrite shows an opposite trend. The production rate for nitrate or nitrite is greater in the solution cathode than that in the solution anode.

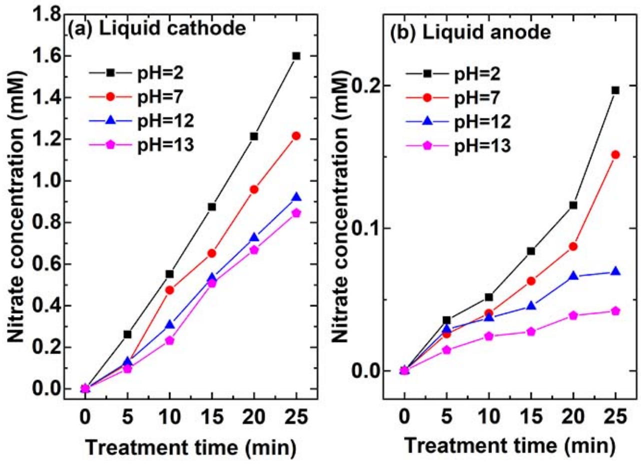

Figure 3. Nitrate concentrations in air-plasma-exposed solutions with different pH values as a function of the plasma treatment time for the solution as (a) the cathode and the solution as (b) the anode. Flow rate of the solution is 100 mL/min, the air flow rate is 50 sccm and the discharge current is fixed at 20 mA.

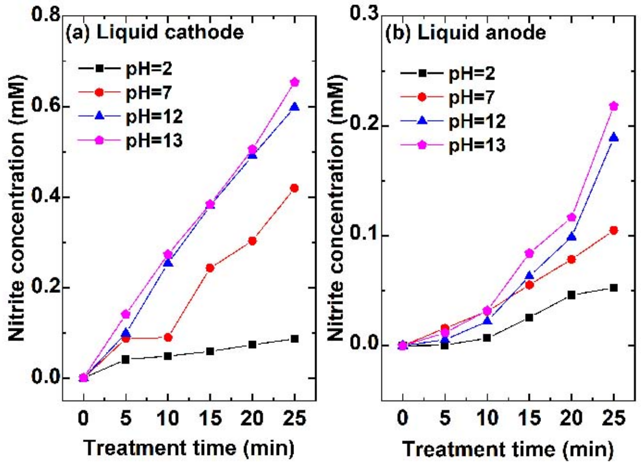

Figure 4. Nitrite concentrations in air-plasma-exposed solutions with different pH values as a function of the plasma treatment time for the solution as (a) the cathode and the solution as (b) the anode. Flow rate of the solution is 100 mL/min, air flow rate is 50 sccm and the discharge current is fixed at 20 mA.

When we sum the concentrations of nitrate and nitrite (figure 5), we find that the total concentration of nitrogen-related species for all solutions is almost independent of the pH values in both the solutions as the cathode and the anode (here the discharge current is fixed at 20 mA). Similar results for the solution as the cathode have been reported in our previous study [44].

The formation rate of nitrate, nitrite and total nitrogen species for air-plasma- treated solution is roughly linear for the cases with liquid as the cathode and we summarize this in table 1. The results suggest that the formation rate decreases for nitrate, while it increases for nitrite with increasing pH value. Moreover, the formation rate for total nitrogen species is almost independent of the pH value.

The reactive species in the plasma-exposed solutions usually originate from the gaseous plasma species or from the *in situ* generation in the solution. For air discharge plasma, the N_2 and O_2 molecules are decomposed or activated by the plasma and then form many compounds containing nitrogen and oxygen. A partial neutral reactive species can enter the liquid phase by diffusion. For charged

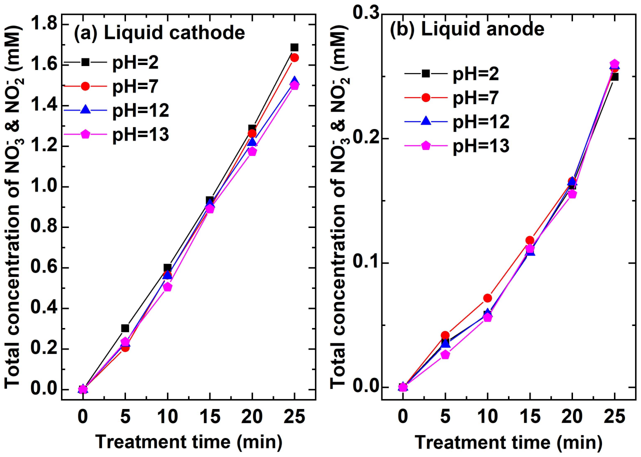

Figure 5. Total nitrogen content in the air-plasma-exposed solutions with different pH values by summing the nitrate and nitrite concentrations for the solution as (a) the cathode and the solution as (b) the anode. Flow rate of the solution is 100 mL/min, air flow rate is 50 sccm and the discharge current is fixed at 20 mA.

Table 1. The formation rates of nitrate, nitrite and total nitrogen species for air-plasma-treated Na_2SO_4 solutions with different pH values in the case of liquid as the cathode.

Initial pH value	Formation rate of nitrate (10^{-2} mM/min)	Formation rate of nitrite (10^{-2} mM/min)	Formation rate of total nitrogen species (10^{-2} mM/min)
2	6.387	0.309	6.696
7	5.014	1.657	6.671
12	3.779	2.454	6.233
13	3.553	2.556	6.109

species, most of the species transferring to the liquid surface are positively charged when the liquid is the cathode, and are negatively charged when the liquid is the anode, due to a different liquid surface voltage fall [45]. It is strongly proposed that the nitrate and nitrite species in plasma-exposed solutions are from the dissolution of nitrogen oxides generated in the gas phase of the air plasma. The Henry's law constants for nitrogen oxides of N_2O, NO, NO_2, N_2O_3, N_2O_4 and N_2O_5 in water at $T = 298.15$ K are 2.4×10^{-4}, 1.9×10^{-5}, 1.2×10^{-4}, 5.9×10^{-3}, 1.4×10^{-2} and 2.1×10^{-2} mol/(m^3 Pa) [46], respectively. The solubility of gas is proportional to its Henry's law constant. Therefore, the solubilities of the former three nitrogen oxides are relatively low. Furthermore, N_2O and NO are stable in water and the others can react with water to produce nitrate and/or nitrite ions as shown in reactions (1)–(4) [47–50].

$$\begin{gathered}2NO_2 + H_2O \rightarrow HNO_2 + HNO_3\\ k_1 \approx 1.2\times10^4\ M^{-1}s^{-1},\ T = 25\ °C,\end{gathered}\tag{1}$$

$$\begin{gathered}N_2O_3 + H_2O \rightarrow 2HNO_2\\ k_2 \approx 9.5\ M^{-1}s^{-1},\ T = 25\ °C,\end{gathered}\tag{2}$$

$$\begin{gathered}N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3\\ k_3 \approx 1.6\times10^5\ M^{-1}s^{-1},\ T = 25\ °C,\end{gathered}\tag{3}$$

$$\begin{gathered}N_2O_5 + H_2O \rightarrow 2HNO_3\\ k_4 \approx 2.0\times10^6\ M^{-1}s^{-1},\ T = 25\ °C.\end{gathered}\tag{4}$$

Hydrogen peroxide always exists in the plasma-treated aqueous solution [51, 52], and therefore, the nitrite can also turn into nitrate by reacting with H_2O_2 in acidic solution, as shown in reaction (5) [44, 53] or by its decomposition as shown in reaction (6) [44, 53]. Therefore, the decrease in nitrite and increase in nitrate concentration with decreasing pH value, as shown in figure 3, can be attributed to reaction (6).

$$H_2O_2 + NO_2^- + H^+ \rightarrow ONOOH + H_2O \rightarrow H^+ + NO_3^- + H_2O \tag{5}$$

$$3HNO_2 \rightarrow H^+ + NO_3^- + 2NO + H_2O \tag{6}$$

Based on the data in figure 4, one can estimate the production rates for nitrate and nitrite in the plasma-treated solutions. Figure 6 shows the ratio of the production rates for nitrite to nitrate in plasma-treated solutions with the solutions as the cathode and the anode. For the solution with a pH value of 2, the production rate for nitrate is much greater than that for nitrite, which can be ascribed to the conversion of nitrite to nitrate at a lower pH value (reactions (5) and (6)). In the solution with a pH value of 13, the nitrite production rate is close to the nitrate production rate when the solution is the cathode, which indicates that reactions (1) and (3) are the major contributors of the nitrate and nitrite formation. However, when the solution is the anode, the nitrite production rate in the solution with a pH value of 13 is five times greater than the nitrate production rate. This result implies that reaction (2) plays an important role when the solution acts as the anode. From the above analysis, one might assume that for a fixed discharge current, the type and density of the nitrogen oxides in the air plasma are independent of the solution pH value, while being dependent on the polarity of the applied voltage on the solution. We conjecture that the applied voltage polarity dependence of the total nitrogen species, as shown in figure 5, presumably originates from the different yield of primary gaseous nitrogen oxides with liquid as the cathode or the anode. However, the different yield of primary gaseous nitrogen oxides for different voltage polarity remains unknown to us. It is possible to tune the production of nitrate and nitrite in air-plasma-treated solution by the pH value and polarity of applied voltage.

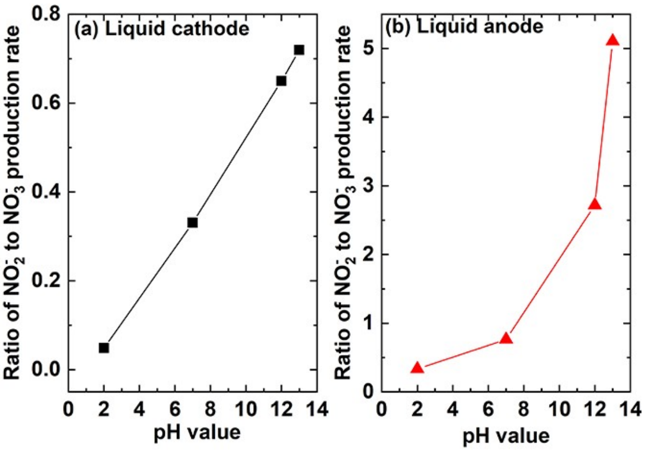

Figure 6. Ratio of the nitrite to nitrate production rates as a function of the pH value for the solutions as (a) the cathode and (b) the anode. Flow rate of the solution is 100 mL/min, air flow rate is 50 sccm and the discharge current is fixed at 20 mA.

4. Conclusion

When air plasma is used to treat an aqueous solution, nitrate and nitrite can be formed in the solution. The total nitrogen content for nitrate and nitrite is independent of the solution's pH value for a fixed discharge current. The concentration ratio of nitrate to nitrite can be tuned by the solution's pH value; a high pH favors nitrite formation, while a low pH value favors nitrate formation. The production rates for both nitrate and nitrite with the solution as the cathode are much greater than those with the solution as the anode. The solution's pH value and the polarity of the applied voltage are two key parameters for controlling the production of nitrate and nitrite in air-plasma-treated solutions.

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Data availability statement

All data that support the findings of this study are included within the article.

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