

# Plasma-liquid interactions: Separating electrolytic reactions from plasma/gas phase reactions

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**Abstract**—Chemical reactions occurring at a plasma-liquid interface generally fall into one of two categories: electrolytic reduction-oxidation reactions or the dissolution of gaseous products from the plasma phase. The former is most often observed in direct current (DC) systems, while the latter is typically associated with alternating current (AC) dielectric barrier discharges (DBD). In this work, an argon DC microplasma jet was used as a cathode to electrolyze saline solutions. Electrolytic reduction-oxidation reactions yield sodium hydroxide, while reactions occurring in the plasma phase produce nitric acid and hydrogen peroxide. It is found that the final products in the solution depend heavily on the composition of the ambient background gas in the reactor vessel. With a background gas of oxygen or argon, electrolytic production of sodium hydroxide (NaOH) dominates, while nitric acid (HNO<sub>3</sub>) formed by the dissolution of NO<sub>2</sub> dominates in the case of air and nitrogen. For pure nitrogen, the production of nitric acid is limited by the rate at which oxygen is produced from water electrolysis.

## I. INTRODUCTION

Plasma interactions with aqueous solutions have important historical significance in the field of chemistry. For example, in 1784, Henry Cavendish discovered that an electrical arc in atmospheric air would make a nearby solution of water acidic—an effect he attributed to “the conversion of phlogisticated air into nitrous acid”. From these experiments, Cavendish concluded that air was primarily composed of two substances that were almost completely converted to acid when mixed in a 7:3 ratio. Despite his best efforts Cavendish found that atmospheric air could never be entirely converted to acid, and there always remained a small amount of gas on the order of 1% of the initial volume<sup>1</sup>. Over a

century later, in 1894, Lord Rayleigh repeated Cavendish's experiments and concluded that the remaining gas was an entirely new substance called argon<sup>ii</sup>.

Emerging developments in atmospheric-pressure, low-temperature plasmas have spurred a renewed interest plasma-liquid interactions. For example, dielectric barrier discharge (DBD) plasmas have recently been used in atmospheric air for various medical applications such as wound treatment and sterilization<sup>iii</sup>. Researchers have found that these DBD plasmas produce both hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and nitric acid ( $\text{HNO}_3$ ) in aqueous solutions. It has been shown that hydrogen peroxide and various other reactive oxygen species have a sterilizing effect on bacteria cultures<sup>iv</sup>. All of the important reactions in these systems occur in the plasma phase, and chemical changes in the neighboring aqueous environment are the result of gaseous products being dissolved. It is generally assumed that the aqueous environment forms a dielectric barrier that does not allow charge to be transferred from the plasma into the bulk of the liquid, and electrolytic reactions are typically neglected. Additionally, it has been shown  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  can be produced by a gliding arc discharge near the surface of an aqueous solution<sup>v</sup>. In these systems, water vapor in the plasma phase reacts to form  $\text{H}_2\text{O}_2$ . Electrolytic reactions are neglected in these systems as well, because no current is passed through the solution.

Others have used a DC microplasma jets to synthesize metallic nanoparticles in aqueous solutions<sup>viii</sup>. In these systems, free electrons from the plasma jet directly reduce silver cations ( $\text{Ag}^+$ ) in the solution, and the reduced Ag atoms then agglomerate to form nanoparticles. Subsequent work has found that these atmospheric pressure plasma jets can be used for other electrolytic reactions, such as the reduction of ferricyanide to ferrocyanide<sup>viii</sup> and water electrolysis under acidic conditions<sup>ix</sup>. Thus far, these systems appear to produce the same chemical reactions as a traditional electrochemical cell with a metallic cathode. It still unclear how reactions occurring in the plasma phase can effect the final chemical composition of the solution.

Several decades before the use of microplasma jets, considerable research was devoted to glow discharge electrolysis (GDE), in which an aqueous solution is used as a cathode in a low pressure (~50 torr) DC glow discharge. In these systems, positively charged ions, rather free electrons, are transferred from the plasma to the liquid and induce both electrolytic and dissociative reactions. Above the liquid surface, there is usually a large cathode fall of ~400 V, which accelerates free electrons away from the solution<sup>x</sup>. In this region, inelastic collisions between electrons and water molecules produce hydroxyl radicals, which combine to form  $\text{H}_2\text{O}_2$ <sup>xi</sup>. A thorough review of the reaction pathways to form hydrogen peroxide can be found in Ref. [xii]. Considerable research in GDE systems has revealed that both electrolytic and plasma phase reactions, namely  $\text{H}_2\text{O}_2$  formation, are equally important. However, the interaction between positive ions and solution is substantially different than the interaction between electrons and solutions. It is not clear, therefore, whether both electrolytic and plasma phase reactions are also important in situations where the plasma acts as the cathode.

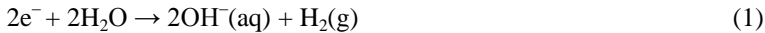
In this work, the relative importance of electrolytic and plasma reactions are explored using an argon (Ar) DC microplasma jet as a cathode in electrolytic reactions using aqueous solutions of sodium chloride (NaCl). In particular, the role of the plasma reactions is

studied by varying the ambient background gas, using nitrogen (N<sub>2</sub>), pure oxygen (O<sub>2</sub>), air, and Ar gases and measuring the final composition of the solution.

## II. EXPERIMENTAL PROCEDURE

### A. Background

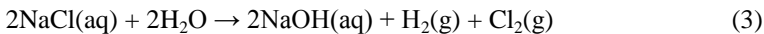
The chlor-alkali process is commonly used to produce both sodium hydroxide (NaOH) and chlorine gas (Cl<sub>2</sub>) by passing DC current through a saline solution via the half-cell reactions



occurring at the cathode and



occurring at the anode. The net reaction can be written as

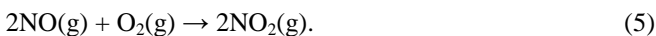


where Cl<sup>-</sup> ions oxidized at the anode are replaced by OH<sup>-</sup> ions formed at the cathode<sup>xiii</sup>. This reaction has the overall effect of making the solution more basic and therefore can be easily quantified by pH probe measurements. It should be noted that OH<sup>-</sup> is also oxidized at the anode to form water and oxygen gas. This reaction is in direct competition with reaction (2), making the system much less efficient in terms of NaOH produced per unit charge transferred. This effect will be discussed in greater detail in subsequent sections.

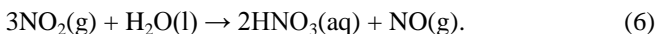
It is also well known that nitrogen and oxygen gas will combine in plasmas to form nitric oxide,



which readily combines with oxygen to form nitrogen dioxide,



Nitrogen dioxide dissolves in water to form nitric acid,



This acidic solution can also be easily quantified by pH probe measurements. This reaction has a long history, and was used in the early 1900s to synthesize nitrates for fertilizer production in the Birkeland-Eyde process<sup>xiv</sup>. It also occurs in lightning strikes, providing vegetation with naturally fixed nitrogen<sup>xv</sup>. Note that reactions (1) and (2) involve the passage of an electron to or from the solution. This makes them fundamentally different from reactions (4) – (6), in which products from the plasma/gas phase reactions

dissolve into solution.

### B. Experimental Procedure

Shown in Figure 1, a stainless steel capillary (cathode) with an inner diameter of 200  $\mu\text{m}$  was placed 1 mm above 50 mL of saline solution at a concentration of 0.34 M. A platinum foil anode was submerged in the solution and grounded, while the stainless steel capillary was connected to a high voltage DC power supply through a 1.5 M $\Omega$  ballast resistor. Argon was flowed through the capillary at  $\sim 50$  sccm. The reactor cell is sealed and purged for 5 minutes with either Ar, N<sub>2</sub>, O<sub>2</sub>, or air at a flow rate of  $\sim 500$  sccm. The flow rate of the purging gas was then reduced to  $\sim 200$  sccm to form a controlled ambient environment, and a plasma was struck between the stainless steel capillary and liquid surface at a current of 1.62 mA for all cases. The plasma voltage and appearance depended strongly on the ambient background gas in the headspace of the reactor cell. Plasma voltages of approximately 250 V, 1100 V, 1350 V, and 1100 V were measured for Ar, N<sub>2</sub>, O<sub>2</sub>, and air, respectively. The pH of the solution was measured with a pH probe (Oakton pHTestr 30) before and after the solution was treated with the plasma for a given amount of time. Fresh saline solution was used for each measurement. Similar pH measurements were also conducted for a convention cell using a platinum foil cathode. The conventional cell was driven at a constant current of  $\sim 1.6$  mA at a potential of  $\sim 2.2$  V.

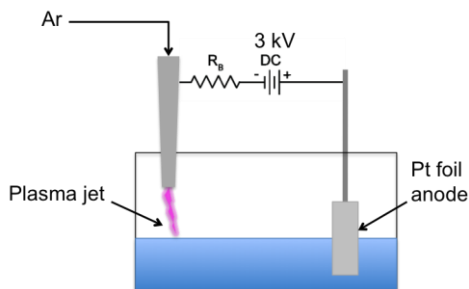


Fig. 1. Schematic of a plasma-electrochemical reaction vessel.

To isolate the effect of plasma phase products dissolving into the solution, exhaust from a dry reaction vessel was bubbled to a secondary reaction vessel containing 50 mL of saline solution at a concentration of 0.34 M, as shown in Figure 2. The plasma in the dry cell was formed between the capillary and an aluminum anode with voltages and currents similar to those in the previous paragraph. The pH of the secondary cell was measured before and after bubbling for a given amount of time. Fresh saline solution was used for each measurement. For both configurations, the measurements were repeated three times to ensure repeatability.

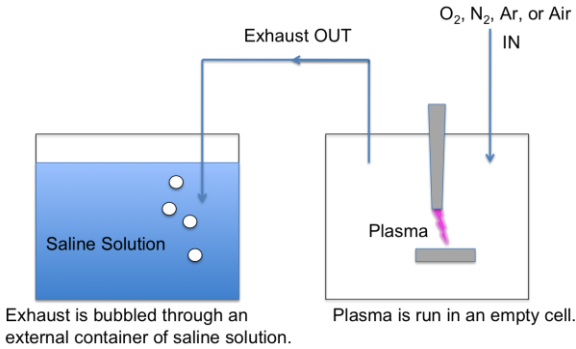


Fig. 2. The effects of gas phase reactions are easily distinguished from electrolytic reactions by bubbling exhaust from a dry plasma cell through a secondary reactor vessel containing saline solution.

### III. RESULTS

#### A. Primary Reactor Vessel

Using the experimental setup pictured in Fig. 1, pH measurements were taken as a function of plasma exposure time. As shown in Fig. 3, running the reactor with air or  $N_2$  in the headspace lead to an acidification of the solution. This was due to the formation of nitric acid via reactions (4 - 6). The presence of nitrate in the solution was confirmed using colorimetric test strips (Mardel Sentry 5 in 1 test strips). In the case of pure  $N_2$ , the oxygen necessary for reactions (4) and (5) likely came from water electrolysis occurring at the anode.

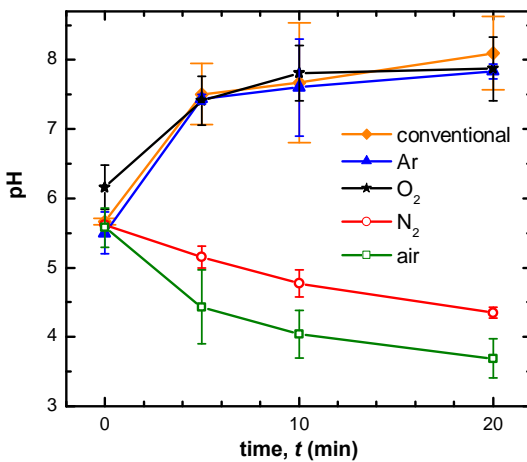


Fig. 3. pH of the saline solution in direct contact with the plasma jet is measured as a function of time for various different ambient background gases. Error bars reflect the precision uncertainty for the three measurements.

In the case of  $O_2$  and Ar as the ambient gas, an increase in pH was observed. These measurements are consistent with measurements from a conventional electrochemical cell using a platinum foil cathode at a similar current. This strongly suggests that the familiar electrolytic reactions of the chlor-alkali process produced NaOH. It was anticipated that hydrogen peroxide would be generated in all cases due to the presence of oxygen in the head space, either from the ambient gas (in the case of  $O_2$  and air) or due to the electrolytic reactions. Colorimetric potassium iodide titrations (LaMotte Hydrogen Peroxide Kit) indicated that a small amount of  $H_2O_2$  ( $< 5$  ppm) was produced in all gases except atmospheric air, which produced significantly more  $H_2O_2$  ( $\sim 40$  ppm). While  $H_2O_2$  is slightly acidic, it appears that in the case of  $O_2$  and Ar the production of NaOH is much greater, such that the overall effect is an increase in pH.

### B. Secondary Reactor Vessel

Exhaust from a dry reactor vessel was bubbled through a secondary reactor vessel containing 0.34 M saline solution. As shown in Fig. 4, oxygen, argon, and nitrogen yield negligible changes in the pH of the secondary vessel, while air yielded a strong acidification of the saline solution in the secondary vessel. Clearly, no current is passed through the solution in the secondary reaction vessel. Therefore, the acidification in the case of air must be due to the dissolution of plasma-produced gaseous species. In particular, nitrogen dioxide ( $NO_2$ ), formed in the dry plasma cell by reactions (4) and (5), is dissolved in the secondary vessel via reaction (6). Colorimetric tests confirmed the presence of nitrate ions in the secondary vessel for the case of air.

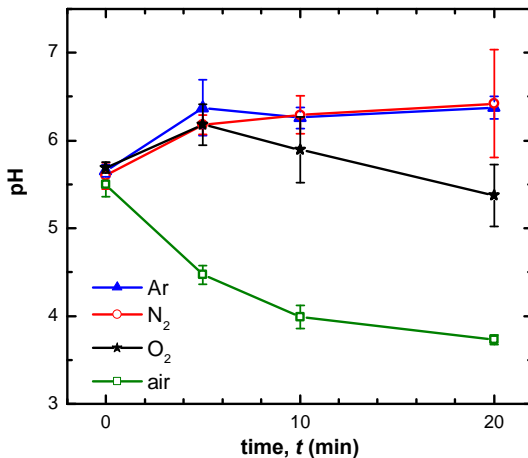


Fig. 4. pH of the saline solution in the secondary vessel after bubbling exhaust from a dry plasma reactor for a given amount of time.

## IV. DISCUSSION

Converting the pH measurements to absolute concentrations, one finds that the total amount of either product increases linearly with time, as shown in Figs. 5a and 5b, suggesting that both reactions proceeded at nearly constant rates. Curve fits indicate that NaOH is electrolytically produced at a rate of approximately  $5 \times 10^{-11} \text{ mol s}^{-1}$ , while  $\text{HNO}_3$  is produced at a much higher rate of approximately  $8.6 \times 10^{-9} \text{ mol s}^{-1}$  and  $1.8 \times 10^{-9} \text{ mol s}^{-1}$  in ambient air and  $\text{N}_2$ , respectively.

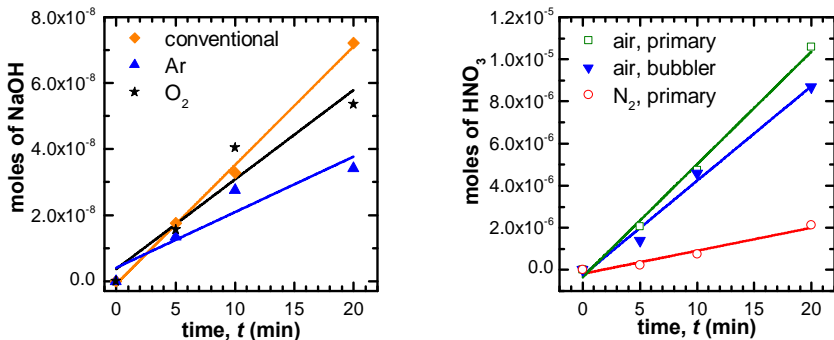
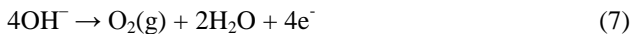


Fig. 5. The number of moles produced in either reaction increases linearly with time for both cases. The production of (a) NaOH occurs at a rate of approximately  $5 \times 10^{-11} \text{ mol s}^{-1}$  via conventional electrolysis, while (b)  $\text{HNO}_3$  is produced at a rate  $8.6 \times 10^{-9} \text{ mol s}^{-1}$  in air and  $1.8 \times 10^{-9} \text{ mol s}^{-1}$  in nitrogen.

According to Faraday's law, products should be formed at the anode at a constant rate proportional to the total current. With a current of 1.62 mA, one would expect the total electrolytic reaction rate to be on the order of  $10^{-8} \text{ mol s}^{-1}$ . Because NaOH is produced at an observed rate of only  $5 \times 10^{-11} \text{ mol s}^{-1}$ , one must conclude that, in addition to reaction (2), there is also oxygen evolution



occurring at the anode, which is energetically more favorable. Now, consider the case of ambient  $\text{N}_2$ , where  $\text{HNO}_3$  is produced in the primary reaction vessel (Fig. 1a), but not in the bubbler connected to the dry cell (Fig. 1b). This is because there is no available oxygen in the dry cell necessary to produce  $\text{HNO}_3$ . However, in the primary reaction vessel, water is electrolyzed to form  $\text{O}_2$  gas at the anode at a rate of  $3.9 \times 10^{-9} \text{ mol s}^{-1}$  according to Faraday's law. This demonstrates that the production of  $\text{HNO}_3$ , with a rate of  $1.8 \times 10^{-9} \text{ mol s}^{-1}$ , is limited by the rate at which oxygen is formed via water electrolysis. Further, it implies that, if water electrolysis is the sole source of oxygen in the reactor vessel, then approximately two thirds of the oxygen gas produced at the anode is converted to nitric acid.

## V. CONCLUSIONS

Saline solutions have been electrolyzed using an argon DC microplasma jet to form NaOH. In addition to the electrolytic production of NaOH, reactions occurring in the plasma phase produce NO<sub>2</sub>, which dissolves to form HNO<sub>3</sub>. When the plasma jet is run in ambient air, HNO<sub>3</sub> is produced at a rate two orders of magnitude higher than NaOH. For plasma electrolysis in ambient N<sub>2</sub>, nitric acid is also produced, but the rate of production is limited by the rate of oxygen evolution occurring at the anode. Additionally, small amounts H<sub>2</sub>O<sub>2</sub> (~1-10 ppm) were detected in all cases.

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