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Decoupling Interfacial Reactions between Plasmas and Liquids: Charge Transfer vs Plasma Neutral Reactions

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Supporting Information

ABSTRACT: Plasmas (gas discharges) formed at the surface of liquids can promote a complex mixture of reactions in solution. Here, we decouple two classes of reactions, those initiated by electrons (electrolysis) and those initiated by gaseous neutral species, by examining an atmospheric-pressure microplasma formed in different ambients at the surface of aqueous saline (NaCl) solutions. Electrolytic reactions between plasma electrons and aqueous ions yield an excess of hydroxide ions (OH^-), making the solution more basic, while reactions between reactive neutral species formed in the plasma phase and the solution lead to nitrous acid (HNO_2), nitric acid (HNO_3), and hydrogen peroxide (H_2O_2), making the solution more acidic. The relative importance of either reaction path is quantified by pH measurements, and we find that it depends directly on the composition of the ambient background gas. With a background gas of oxygen or argon, electron transfer reactions yielding excess OH^- dominate, while HNO_2 and HNO_3 formed in the plasma and by the dissolution of nitrogen oxide (NO_x) species dominate in the case of air and nitrogen. For pure nitrogen (N_2) gas, we observe a unique coupling between both reactions, where oxygen (O_2) gas formed via water electrolysis reacts in the bulk of the plasma to form NO_x, HNO_2, and HNO_3.

Chemical interactions between low temperature plasmas and liquids have become an important research topic due to recent developments in plasma medicine[1] and nanomaterials synthesis.[2] Plasmas produce a wide variety of reactive gaseous species, especially in atmospheric air, that can dissolve into and react at the interface or bulk of the liquid.[3,4] For example, hydroxyl radicals (OH) and hydroperoxyl (HO_2) radicals formed in the plasma phase can dissolve in water to react and form H_2O_2.[5,6] Similarly, NO_x formed in the plasma will readily dissolve in aqueous solution to form HNO_2 and HNO_3.[7] It is well-known that free electrons in the plasma play an important role in the formation of reactive gaseous species, as each reaction path is initiated by an electron impact reaction. However, the free electrons can also directly induce reactions in the liquid. For example, we have recently shown that metallic cations can be reduced in solution by plasma electrons to form suspended metallic nanoparticles.[8] Subsequent work has also demonstrated the reduction of ferricyanide ions to ferrocyanide ions,[9] and reduction of protons to H_2 gas[10] by plasma electrons.

In general, previous research on plasma−liquid interfaces has considered charge transfer reactions and reactions with reactive plasma neutral species independently, potentially neglecting any competing or coupling effects. However, in many cases, it is likely the two classes of reactions occur simultaneously, and it is unclear if one is dominant and, if so, under what conditions. In order to decouple these processes, here we carefully examine a plasma−liquid system in which electron transfer and plasma neutral-initiated reactions both occur as shown in Figure 1. Our system consists of a DC, atmospheric-pressure microplasma jet at the surface of an aqueous NaCl solution and a Pt counter-electrode operated as the cathode and anode, respectively. Electrolytic reactions producing oxygen and chlorine gas yield excess OH^- via the classic chlor-alkali process, making the solution more basic. Reactions between plasma neutrals and the solution yield HNO_2, HNO_3, and H_2O_2, making the solution more acidic. The relative importance of each reaction is

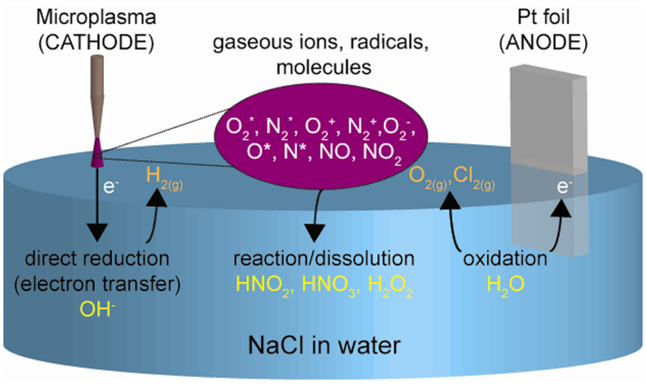

Figure 1. Potential reaction paths occurring in a plasma−liquid system with an aqueous solution of NaCl. Electron transfer from the plasma cathode produces hydrogen gas $H_2(g)$ while oxidation at the anode produces $Cl_2(g)$ and $O_2(g)$. A wide variety of excited, ionized, and molecular/atomic gaseous species produced in the plasma can dissolve or otherwise interact at the solution interface ultimately producing HNO_2, HNO_3, and H_2O_2.

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quantified by a combination of pH measurements and systematic changes to the ambient gas environment.

In aqueous solutions, hydrogen (H_2) and oxygen (O_2) gas can be electrochemically produced at sufficiently high potentials by the electrolysis of water via the following half-cell reactions (under basic conditions):

$$\text{cathode: } 2e^- + 2H_2O \rightarrow 2OH^-(aq) + H_2(g) \tag{1}$$

$$\text{anode: } 4OH^- \rightarrow O_2(g) + 2H_2O + 4e^- \tag{2}$$

In the presence of NaCl, chlorine (Cl_2) gas can also evolve at the anode via

$$2Cl^-(aq) \rightarrow 2e^- + Cl_2(g) \tag{3}$$

Although reaction 2 is energetically favored over reaction 3 based on their corresponding standard reduction potentials, reaction 3 is kinetically favored, resulting in a net reaction known as the chlor-alkali process:

$$2NaCl(aq) + 2H_2O \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g) \tag{4}$$

which is commercially used to produce Cl_2 gas and NaOH.[11] In this study, we focus on this well-known chemistry to compare chemical pathways when a metal electrode (the cathode) is replaced by a plasma electrode.

Plasmas formed in the presence of air can produce HNO_2, HNO_3, and H_2O_2, as well as other products in solution such as peroxynitrous acid, through numerous reaction pathways.[3−6,12] Nitric oxide (NO) is initially formed in the plasma by the Zeldovich mechanism[13] and subsequently reacts with other species in the plasma to form nitrogen dioxide (NO_2). These compounds readily dissolve into aqueous solution to form nitrous and nitric acid through a variety of pathways, which have been well studied for the design of industrial scrubbers.[14] Simulation results from Sakiyama et al. have also shown that significant amounts of HNO_2 and HNO_3 can be produced in the bulk plasma,[15] which could subsequently dissolve into solution. These reactions are fundamentally different from reactions 1−3 as they do not involve the transfer of charge from the plasma to the solution.

The experimental setup used in this work has been reported elsewhere.[10] A stainless steel capillary with an inner diameter of 180 μm was placed 1 mm above 50 mL of 0.34 M NaCl solution. A platinum (Pt) foil was submerged in the solution as the counter electrode. A stable, atmospheric-pressure microplasma jet was formed at the liquid surface by flowing argon (Ar) through the capillary at ~30 sccm and applying high voltage to the capillary with a DC power supply. The electrodes were biased such that the plasma was negative with respect to the Pt electrode and electrons were injected into solution at the plasma/liquid interface. To control the ambient gas environment, the electrodes were sealed in a reactor cell and purged for 5 min with pure Ar, N_2, or O_2 gas, at a flow rate of ~500 sccm. The flow rate of the purging gas was then reduced to ~200 sccm. Experiments were also run in open room air. After purging and backfilling (or opening to air), the plasma jet was operated at a current of 1.62 mA for all cases. The plasma voltage and appearance depended strongly on the ambient gas. Plasma voltages of approximately 250, 1100, 1350, and 1100 V were measured for Ar, N_2, O_2, 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 NaCl solution was used for each experiment. Similar pH measurements were also conducted for a conventional electrochemical cell with a Pt foil cathode. The conventional cell was driven at a constant current of ~1.6 mA and potential of ~2.2 V so that the net number of electrons transferred was the same as in the case of the plasma electrode.

pH measurements were taken as a function of plasma exposure time. As shown in Figure 2, operating the microplasma jet in an ambient environment of Ar and O_2 gas yielded an increase in pH similar to a conventional cell with a Pt cathode. This suggests that the plasma electrode causes evolution of Cl_2 gas and generation of excess OH^- in solution via electrolytic reactions associated with the chlor-alkali process. However, when the plasma was operated in air or N_2 in the headspace, the solution became acidic, most probably from the formation of HNO_2 and HNO_3. The presence of NO_2^- and NO_3^- in the solution was confirmed using colorimetric test strips (Mardel Sentry 5 in 1 test strips) as well as ion chromatography (Thermo Scientific Dionex ICS-5000) for N_2 and air; no nitrate was detected above the limit of detection (10 mg/L) for Ar and O_2 as the headspace gas.

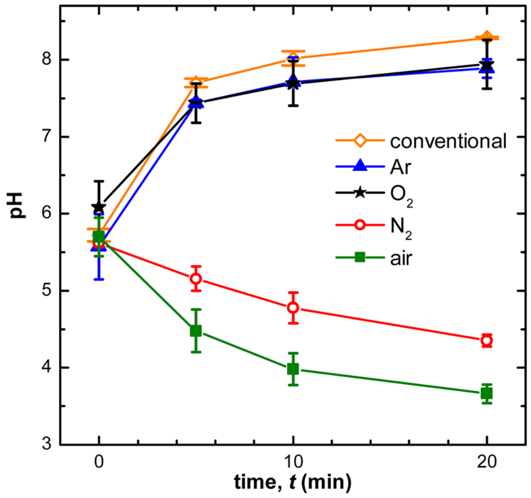

Figure 2. pH of the NaCl solution in direct contact with the microplasma jet measured as a function of time for various ambient gases. Error bars were calculated from three to seven measurements.

We note that although the pH increased in Ar and O_2 ambient environments, it was slightly less basic than the conventional cell. This is explained by the production of H_2O_2 in these (and all) cases, which is slightly acidic. Colorimetric potassium iodide titrations (LaMotte Hydrogen Peroxide Kit) confirmed that a small amount of H_2O_2 (<5 ppm) was produced in both Ar and O_2 ambient environments. Thus, it appears that, for a plasma electrode, there are chemical reactions forming hydrogen peroxide in addition to the electrolytic reactions that also occur for a metal electrode, with the electrolytic reactions (i.e., chlor-alkali process) dominating to cause a net increase in pH.

To decouple and isolate the electron transfer and plasma neutral reactions, the microplasma jet was operated remotely in a dry reactor cell with a controlled ambient environment, and the gaseous products were bubbled into a secondary reaction vessel containing NaCl solution (see Supporting Information), thereby eliminating any electrolytic processes from occurring in the aqueous solution. The remote microplasma was formed between the same capillary tube and an aluminum foil anode with flow rates, voltages, and currents similar to those for the plasma/liquid experiments. Similar pH measurements were performed on the remote NaCl solution after bubbling in the gaseous plasma products for fixed amounts of time.

Figure 3 shows that Ar and O_2 ambients produced negligible changes in the pH in the secondary vessel, indicating that excess OH^- was not being electrolytically produced. For the case of ambient air, the observed acidification is explained by the dissolution of NO_x gas formed in the plasma, yielding NO_2^- and NO_3^- when bubbled into the secondary vessel. Similar results were recently reported by Oehmigan et al. who observed the formation of HNO_2 and HNO_3, when filling the headspace of a vessel containing saline solution with NO gas.[16] Colorimetric and ion chromatography measurements confirmed the presence of NO_2^- and NO_3^- in the secondary vessel for the case of air. Interestingly, filling the reactor headspace with pure N_2 gas did not yield an acidification of the solution, suggesting that when the plasma is in direct contact with the liquid, the source of O_2 is water electrolysis occurring at the anode via (2).

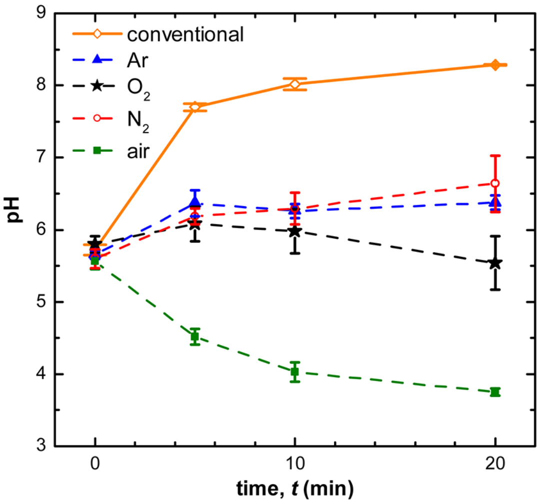

Figure 3. pH of the NaCl solution in the secondary vessel after bubbling exhaust from a remote microplasma reactor as a function of time for various ambient gases. The pH change for the conventional electrochemical cell from Figure 2 is also included for reference.

We can further understand the coupling of electrolytic and plasma neutral reactions by evaluating reaction rates. Converting the pH measurements to absolute concentrations of H^+ for acidic cases and OH^- for basic cases, we find that the total amount of either product increases linearly with time, suggesting that both reactions proceed at nearly constant rates, as shown in Figure 4a and 4b. Ion chromatography measurements showed that the concentrations of NO_2^- and NO_3^- were of similar magnitude, and the net concentration of NO_2^- and NO_3^- agreed well with our pH measurements. We therefore assume that the increase in H^+ is due to a mixture of both HNO_2 and HNO_3. Linear regression indicates that OH^- is electrolytically produced at a rate of approximately 3.5×10^{-11} and 3.7×10^{-11} mol s^{-1} for Ar and O_2, respectively, which is similar to the reaction rate of 8.1×10^{-11} mol s^{-1} measured for the conventional cell. In contrast, H^+ ions corresponding to NO_2^- and NO_3^- are produced at much faster rates of approximately 8.9×10^{-9} and 1.6×10^{-9} mol s^{-1} in ambient air and N_2, respectively, and 7.2×10^{-9} mol s^{-1} for air in the bubbler, overwhelming the electron transfer process and causing the net decrease in pH. Notably, the rate of acidification was nearly the same for ambient air regardless of whether the plasma was in direct contact with the aqueous medium or indirect via bubbling from a remote reaction cell.

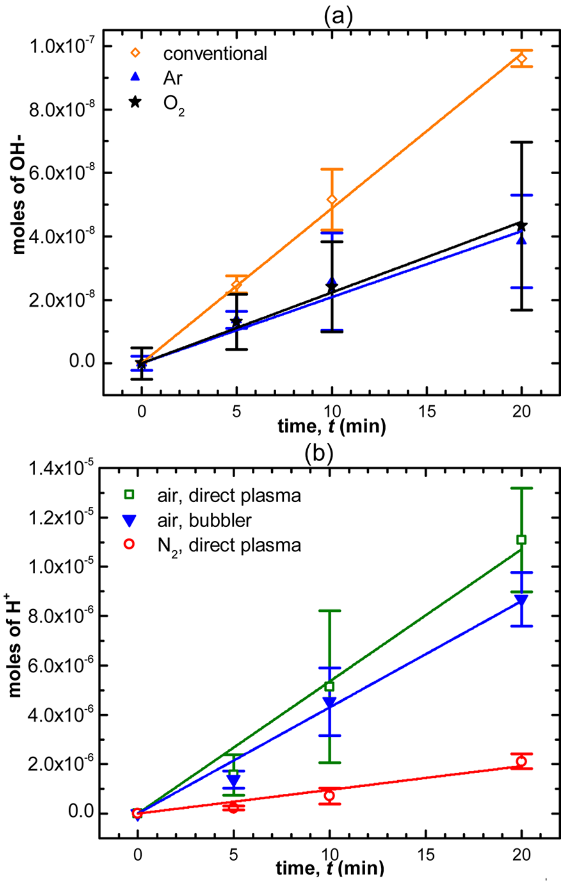

Figure 4. (a) OH^- production as a function of time and (b) H^+ production as a function of time as extrapolated from pH measurements. It is assumed that acidification is primarily due to the formation of both HNO_2 and HNO_3.

Faraday's law predicts that electrolytic products are formed at a rate proportional to the total current. At a current of 1.62 mA, the total electrolytic reaction rate can be estimated to be $\sim 10^{-8}$ mol s^{-1}. Because OH^- is produced only as a consequence of Cl_2 gas evolution at a rate of $\sim 3.5 \times 10^{-11}$ mol s^{-1} from the pH measurements, we assume that the majority of electrons produce O_2 gas. More precisely, using Faraday's law, we estimate that O_2 gas was produced at a rate of 4.1×10^{-9} mol s^{-1} via water electrolysis. In ambient N_2, we can compare this to the observed nitric and nitrous acid production rate of 1.6×10^{-9} mol s^{-1}, and we find excellent agreement. This suggests that NO_2^- and NO_3^- production in N_2 ambient atmospheres are likely limited by the rate at which O_2 gas is formed via water electrolysis. Although the NaCl system could have additional reaction paths, such as oxygen generated by reactions producing hydrogen peroxide[6] and chlorine−oxygen compounds formed from Cl and OH^-,[11] our analysis indicates that, in addition to competition between electrolytic and plasma neutral reactions in plasma-liquid systems, these reactions can also couple, whereby gaseous products from electron transfer reactions directly influence plasma reactions.

Our results show that both electron transfer and plasma neutral reactions occur when plasmas interact with aqueous media. These two classes of reactions are often in competition with one another, depending on a number of factors including reaction kinetics, gas environment, and direct vs remote plasma exposure. However, under certain conditions, these two effects can couple to one other, with electron transfer reactions generating products that directly influence plasma chemistry and ultimately modify the liquid environment. As applications of plasma–liquid systems continue to emerge, understanding and potentially controlling specific interactions will become more critical.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematics of the microplasma electrochemical cell and the remote microplasma reactor configuration; experimental details about solution preparation, microplasma operation, pH calibration, measurement, and uncertainty calculations; nitrate, nitrite, and hydrogen peroxide indicator tests and ion chromatography measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Fridman, G.; Friedman, G.; Gutsol, A.; Shekhter, A. B.; Vasilets, V. N.; Fridman, A. *Plasma Processes Polym.* **2008**, *5*, 503–533.

(2) Mariotti, D.; Sankaran, R. M. *J. Phys. D: Appl. Phys.* **2010**, *43*, 323001.

(3) Laroussi, M.; Leipold, F. *Int. J. Mass Specrom.* **2004**, *233*, 81.

(4) Graves, D. B. *J. Phys. D: Appl. Phys.* **2012**, *45*, 263001.

(5) Burlicaa, R.; Kirkpatrick, M. J.; Locke, B. R. *J. Electrostatics* **2006**, *64*, 35.

(6) Locke, B. R.; Shih, K.-Y. *Plasma Sources Sci. Technol.* **2011**, 20.

(7) Cavendish, H. *Phil. Trans. R. Soc. London* **1784**, *74*, 119.

(8) Richmonds, C.; Sankaran, R. M. *Appl. Phys. Lett.* **2008**, *93*, 131501.

(9) Richmonds, C.; Witzke, M.; Bartling, B.; Lee, S. W.; Wainright, J.; Liu, C.-C.; Sankaran, R. M. *J. Am. Chem. Soc.* **2011**, *133*, 17582.

(10) Witzke, M.; Rumbach, P.; Go, D. B.; Sankaran, R. M. *J. Phys. D: Appl. Phys.* **2012**, *45*, 442001.

(11) Hocking, M. B. *Handbook of Chemical Technology and Pollution Control*; Academic Press: 2006; p 229.

(12) Gils, C. A. J.; Hoffman, S.; Boekema, B. K. H. L.; Brandenburg, R.; Bruggeman, P. J. *J. Phys. D: Appl. Phys.* **2013**, *46*, 175203.

(13) Warnatz, J.; Maas, U.; Dibble, R. W. *Combustion*; Springer: Berlin, 2001; pp 243–249.

(14) Thomas, D.; Vanderschuren, J. *Ind. Eng. Chem. Res.* **1997**, *36*, 3315–3322.

(15) Sakiyama, Y.; Graves, D. B.; Chang, H.-W.; Shimizu, T.; Morfill, G. E. *J. Phys. D: Appl. Phys.* **2012**, *45*, 425201.

(16) Oehmigen, K.; Hähnel, M.; Brandenburg, R.; Wilke, Ch.; Weltmann, K.-D.; von Woedtke, Th. *Plasma Processes Polym.* **2010**, *7*, 250–257.