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Plasma Jet Interactions with Liquids in Partial Fulfillment of an NRL Karle's Fellowship

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Introduction:

Plasmas are a powerful medium that have enabled technologies across a wide spectrum of interdisciplinary fields due to their ability to synthesize (e.g. coatings and thin film deposition), modify (e.g. chemical functionalization), and etch (in Si technology) materials. In low-pressure non-equilibrium discharge plasmas, associated with the above processes, the electron population is much more energetic than both the ions and neutral gas background in which the plasma is created, which allows them to sustain the plasma and also drive the production of reactive neutral and excited species¹. Understanding and controlling plasma species production, their delivery to the surface and the response of the surface, have been and will continue to be crucial to the advancements of these fields^{1,2}.

Background:

Atmospheric-pressure, non-equilibrium (APNE) plasmas, like low-pressure plasmas, provide a controlled production of ions, radicals and photons, however APNE plasmas can be generated in full-density air and do not require confining vacuum systems. Expanding process utility to material and application space beyond that attainable with traditional low-pressure plasmas (liquids, biofilms, and cells are examples) which gives way for rich physics and chemistry at the plasma-surface interface. The different modes of operation for atmospheric pressure plasmas can also provide a larger scope or utility over the governing chemical reactions. For example, 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 phase³. In the first case, electrolytic reduction-oxidation reactions are most often observed in direct current (DC) systems where free electrons from the plasma jet directly participate, in the reduction of positive ions within the solution, thus reducing cations to synthesize, precipitate or form small solid reduced particles. Here, the plasma jet/source could be viewed as the cathode, analogous to the working electrode, in an electrochemical cell. In the second case, a discharge is produced via alternating current (AC) excitation with driving frequencies from a few Hz up to MHz. Glow discharges (GD) and dielectric barrier discharges (DBD) are some examples. Important reactions happen in the plasma (or gas) phase, and at the plasma-liquid interface due to the alternating charge and direction of the electron flow. Additionally, chemical changes in the neighboring aqueous environment can also be the result of gaseous products being dissolved in it. In this scenario, the aqueous solution participates as the dielectric barrier, and thus may play a role in determining both the global plasma properties (current magnitude and temporal evolution) and reactive species produced in the gas phase. Present challenges in the atmospheric plasma field relate to the understanding of the ionization process in the gas phase and plasma-induced processes occurring in the liquid phase.

The proposed work for this one year research effort was to study the interaction of atmospheric pressure non-equilibrium (APNE) plasmas with static and electrified liquids, focusing on the liquid property component as the diagnostic. The time-averaged chemistry in the liquid is

easily measurable in seconds time scale while the plasma chemistry happens on the microsecond time scales. To this end, it was desirable to extend typical bulk liquid measurement techniques from *ex situ* to *in situ* techniques, in order to capture plasma-induced liquid chemistry changes in real time. This was accomplished by designing a body of work that first interrogated the solution properties before and after plasma exposures, and then attempting to measure similar solution properties *in situ* to establish equipment set up, appropriate solution volumes, and time scales. New equipment was purchased (GAMRY potentiostat and ORION pH meter) to carry out the needed solution-phase measurements (pH, dissolved oxygen, conductivity, open circuit potential), and were purchased with the intent to be used as continuous *in situ* operational capabilities. The atmospheric pressure plasma source used was a custom built AC jet (built by personnel within Code 6756).

Experimental Results:

AC Jet: For this work a helium (He) AC jet was used for the atmospheric plasma production. The jet operates off of a power source that can deliver a sinusoidal, high voltage wave form with frequencies between 1 kHz to 1 MHz. The He flow rate is adjustable. The jet was first characterized across its parameter space to determine the output current, output voltage, and output frequencies at any given power, and He gas flow rate. Table 1 shows the He gas flow, in standard liters per minute (SLPM), driving signal (frequency and voltage delivered by the power source) and the corresponding jet current (magnitude and frequency), obtained by placing a current transformer (Pearson coil) at the tip of the plasma jet. The measured currents as reported by the Oscilloscope were converted to voltages, in a one to one scaling factor (1V = 1A). Note the transformer was located at same position of the liquid sample.

	<i>S: power source</i>	% Voltage					
	<i>J: out of jet</i>	100	80	60	40	20	0
2.5 SLPM	<i>S: f(k Hz)</i>	32.12	32.17	32.17	32.29	32.71	64.17
	<i>S: V_{pp} (kV)</i>	1.31	1.16	0.94	0.66	0.41	0.09
	<i>J: V (mV)</i>	0.46	0.31	0.31	0.09	0.09	0.1
	<i>J: f(k Hz)</i>	32.22	32.14	32.05	429.43	614.69	619.64
2.0 SLPM	<i>S: f(k Hz)</i>	29.59	29.51	29.57	29.58	29.45	33.1
	<i>S: V_{pp} (kV)</i>	1.63	1.44	1.16	0.81	0.5	0.09
	<i>J: V (mV)</i>	0.61	0.54	0.38	0.2	0.09	0.1
	<i>J: f(k Hz)</i>	29.54	29.55	29.7	29.61	588.42	641.29
1.0 SLPM	<i>S: f(k Hz)</i>	29.57	29.51	29.47	29.45	29.52	73.63
	<i>S: V_{pp} (kV)</i>	1.78	1.53	1.19	0.78	0.49	0.09
	<i>J: V (mV)</i>	0.52	0.37	0.25	0.17	0.08	0.11
	<i>J: f(k Hz)</i>	29.53	29.58	29.65	29.64	586.85	615.41

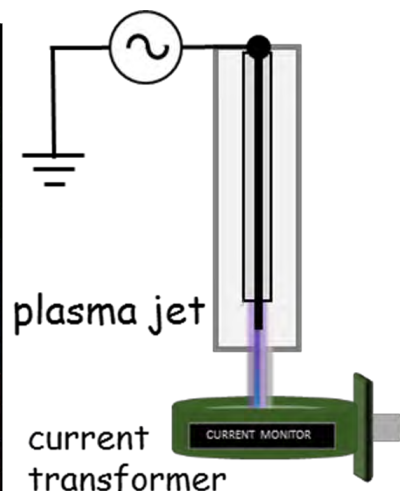


Table 1. Power source (S) and atmospheric plasma jet input and output frequencies, voltages; and diagram representation of a plasma jet with a current transformer.

Due to the stark differences in ion densities between the two mediums (gas $\sim 10^{14} \text{ cm}^{-3}$ versus liquid $\sim 10^{20} \text{ cm}^{-3}$), the first set of experiments was to determine liquid volume necessary

and minimum exposure time needed for a measurable change to occur in the liquid properties. The constraining minimum liquid volume was $\approx 3\text{mL}$ due to evaporation rates, the insertion of pH, dissolved oxygen (RDO) and conductivity probes. It was determined that volumes as small as 5mL were modified with exposures of 60 seconds or greater, and volumes larger than 20mL showed negligible changes within the same time frame. Thus from here forth, solution volumes were kept constant to 5mL, plasma experiments were performed at 2 SLPM He (standard liters per minute), 100 % applied voltage, and 30 kHz.



Figure 1. (A) AC jet in direct contact with Au electroless solution, (B) Ni electroless solution, and (C) Sn electroless solution after plasma exposure showing minor color change from clear to light brown-right hand side.

Plasma Interaction with a Liquid: As previously mentioned, important reactions happen in the plasma phase, and at the liquid interface due to the alternating charge and direction of the electron flow when using an AC Jet. Here, the aqueous solution participates as the dielectric barrier, and thus *may* play a role in both the resultant plasma properties and reactive species produced in the

gas phase. To this end, the effect of the plasma-species produced at identical plasma operating conditions on the various solvents and its effect on the liquid chemistry was investigated using a series of solutions with different conductivities (i.e. dielectric constants). The solutions chosen were aqueous based with increasing ion concentration. Specifically, distilled water (DI H₂O) as the reference solution, two concentrations of NaCl mixtures (0.6 Molar, and 1.0 Molar saturated NaCl), and three electroless solutions (gold, nickel & tin). Electroless deposition is an autocatalytic chemical process that relies on the presence of a reducing agent which reacts with the metal ions to deposit the metal. The reducing agent need not to be in the form of free electrons delivered from an electrode but instead electrons or charge exchange from chemical reactions could participate in the overall cation reduction. This means that charge exchange or electrons generated by the presence of hydrogen or hydrated ions which result in a slight change in pH, would suffice at the appropriate concentrations. The idea behind testing the electroless solutions was to advantageously utilize chemically active species (H₂O₂, OH, H) known to be produced by the atmospheric plasma jet^{3, 4} operating in humid air, to drive the redox reactions in the liquid. Thus relying solely on the gas and liquid phase chemistry to drive the appropriate reactions eliminating the need for a cathode physically inserted into the liquid, common to electrochemical cells.

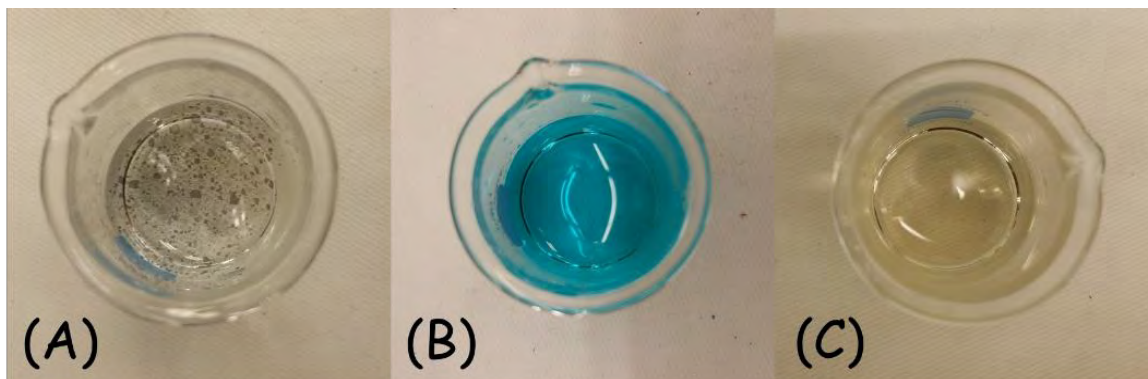


Figure 2. Top down optical images of electroless solutions after atmospheric plasma exposure. (A) Au electroless solution showing solid precipitates, (B) Ni electroless solution, and (C) Sn electroless solution showing a light brown color change.

Five mL volumes of each solution were exposed to identical plasma jet operating conditions, the solution conductivity, pH and dissolved oxygen content were monitored before and after each plasma exposure. Figure 1 shows images of the plasma jet operating and interacting with 5 mL of Au and Ni electroless solutions, Fig. (A) and (B), respectively. Figure 1C shows the Sn electroless solution before (left hand side) and after (right hand side) atmospheric plasma exposure. Visually noticeable is the slight color change in the bulk solution, which indicates a change in the solution composition possibly due to small reduction of the Sn cations. Most notably, the Au electroless solution formed small precipitates that aggregated as a thin layer on the plasma-liquid interface, shown in Figure 2A. These precipitates were then isolated from the solution and imaged under optical microscopy and X-ray photoelectron spectroscopy. As seen in Figure 3, the

precipitates are thin sheets with a granular morphology, the various colors indicate difference sheet thicknesses. Also visually evident is small salt crystals (clear rocky particles that appear to be outlined in black) which differ in size, color, texture and morphology compared to the other sheets.

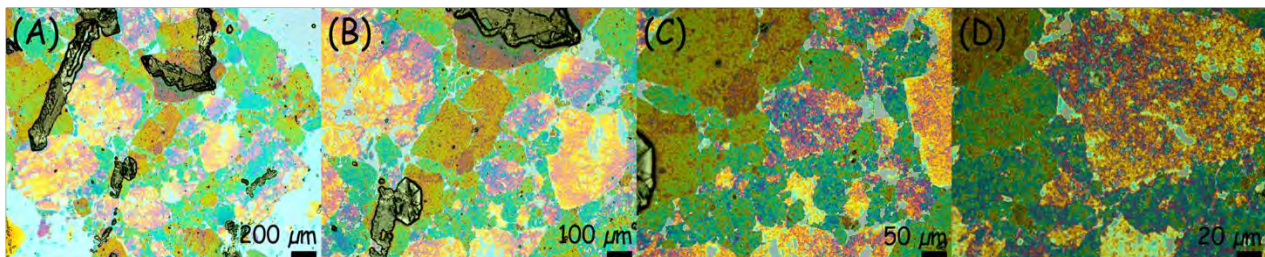


Figure 3. Optical micrographs of precipitates formed in the Au electroless solution at the liquid-plasma interface. Images (A) through (D) are near locations at increasing magnifications. Individual scale bars are noted.

Since the small precipitates formed during plasma jet treatment, they are assumed to be thin sheets of Au.

Results and Discussion:

Further material analysis by XPS indicates that the isolated thin sheets are indeed reduced gold (zero valent). Figure 4a shows the XPS survey spectra which indicate the presence of metallic gold (shown in red) peaking between 80 and 90 eV. As expected, additional elemental analysis also shows presence of some residual salt constituents (iodine and chlorine), as well as substrate peaks for Si and O (the substrate was SiO₂/Si wafer). The high resolution core level spectra, shown in figure 4b, displays the gold doublet for 4f_{5/2} and 4f_{7/2} at 83.2 eV and 86.9 eV, respectively. The red curve is the raw data, shaded areas indicate the peak deconvolution, and the blue curve shows the overall envelope fit with very good agreement. The distance from peak-to-peak is 3.65 eV,

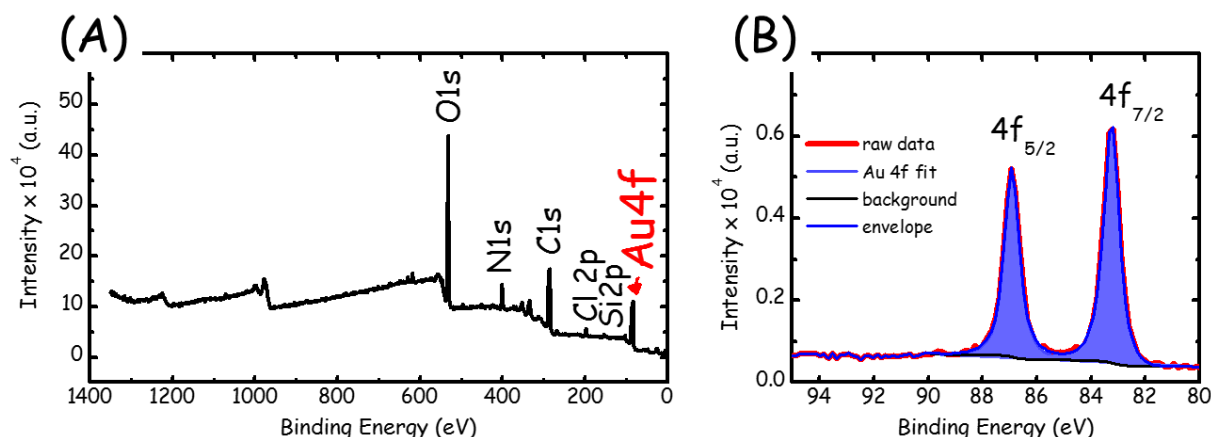


Figure 4. XPS (A) survey spectra of Au sheets indicating the presence of Au, and (B) high resolution Au 4f core level spectra showing the Au doublet peaks.

which is typical for elemental reduced gold. This surface analysis shows that the isolated sheets are composed of reduced gold, via a reduction process carried out by plasma mediated chemistry.

In all of these cases, it is worth noting that initial results indicate the formation of small precipitates in both the Au and Sn solutions at the given plasma exposure times, and it is expected that greater plasma exposures (either by longer run times or larger duty factors), or parameter changes that increase the density of species (higher driving voltages, perhaps) will further enhance the reactions in the liquid bulk. The specifics of the bulk solution changes are tabulated in Table 2. In most cases, the solution conductivity generally dropped, the pH (which is inversely proportional to the concentration of protons in the solution) decreases making the solution more acidic, and the presence of dissolved oxygen in the aqueous bulk decreases. These measurements indicate that H^+ are either being produced in the plasma phase and delivered (by diffusion) to the bulk surface in net excess; that oxygen ions/radicals are being consumed from the bulk by an electrolysis path way; or that the liquid phase chemistry is generating protons by secondary reactions producing H_2 evolution³. Of course contribution of all three things could also simultaneously take place. In order to identify the different possibilities in reaction pathways, there is a need to be able to decouple the effects of the positive versus negative charge delivered to the liquid in order to isolate different chemistry mechanisms and understand the components effecting the liquid chemical reaction pathways^{5, 6}. More control over the plasma jet source is needed in that fashion, and is currently being investigated. Additionally, different configurations of the liquid vessels/containers need to be investigated to isolate and decouple atmospheric-liquid interactions.

Solution phase measurements *in situ* were attempted but unsuccessful due to the nature of the diagnostic instruments and the plasma source production. Specifically, the diagnostic instruments are designed to detect minute fluctuations in current, proton and electron concentrations, but at the time when the measurements were conducted, the plasma jet source (which operates in AC mode) produced parasitic frequencies, that cross talked with the potentiostat and meters, same ones described in Table 1. Since then, efforts have been taken to design and shield the jet and power source as to minimize the frequency effects on neighboring instruments. These tests will be part of follow-on efforts.

	σ (mS/cm)		pH		DO (%)	
	before	after	before	after	before	after
DI H_2O	0.1461	0.707	6.71	6.738	86.2	28.4
0.6 M NaCl	51.2	49.5	5.819	4.097	41.8	26.1
1.0 M NaCl	246.1	246.2	6.162	6.082	18.4	9.2
Au Electroless	136.7	94.1	6.006	5.997	35.7	21.2
Ni Electroless	130.2	81.1	9.098	8.881	42.2	10.9
Sn Electroless	1.00E+07	4.54E+05	-0.782	-0.961	60.4	41.8

Table 2. Solution properties such as conductivity, pH and dissolved oxygen content (DO) measured before and after plasma jet exposure for 60min.

This body of work has illustrated the potential in manifesting liquid phase reactions by interaction with an atmospheric pressure plasma. The results demonstrate visual bulk color changes, formation of solids in the liquid, and measurable changes in the solution properties, such as conductivity, hydrogen ion concentration, and dissolved oxygen content. Additionally, it has laid a foundation for future design of experiments to adequately isolate and thus address the complex variables governing the plasma-induced mechanisms occurring in the liquid phase.

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