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14. ABSTRACT

The goal of this ARO STIR was to conduct preliminary investigations toward understanding electrochemical reactions promoted by microplasmas at the interface of aqueous solutions. We developed a novel total internal reflection absorption spectroscopy experiment directly at the plasma-solution interface leading to the first ever measurement and detection of plasma-generated solvated electrons. We found that the plasma-liquid interfacial environment produces different solvated electron behavior than other approaches to generating solvated electrons (e.g., pulse radiolysis) including a blue-shifted and narrower absorption spectrum as well as different reaction rate

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19a. NAME OF RESPONSIBLE PERSON
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19b. TELEPHONE NUMBER
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Report Title

Final Report: STIR: Probing Electrochemical Reactions at a Plasma-Liquid Interface (7.2 Electrochemistry)

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The goal of this ARO STIR was to conduct preliminary investigations toward understanding electrochemical reactions promoted by microplasmas at the interface of aqueous solutions. We developed a novel total internal reflection absorption spectroscopy experiment directly at the plasma-solution interface leading to the first ever measurement and detection of plasma-generated solvated electrons. We found that the plasma-liquid interfacial environment produces different solvated electron behavior than other approaches to generating solvated electrons (e.g., pulse radiolysis) including a blue-shifted and narrower absorption spectrum as well as different reaction rate coefficients. We attribute these differences to the electrochemical configuration of the plasma-solution system such as the strong electric field in the Debye layer of the plasma-liquid interface. We also developed a method to precipitate, separate, and weigh solid silver produced by plasma-initiated electrolytical reduction of silver cations (Ag+), leading to the first estimates of the efficiency (~80%) for the reduction of Ag+ by a plasma process. These results reveal that inherent competing chemical pathways must be accounted for when using plasma-solution systems, as effects such as second order recombination in the liquid phase or electron scavenging in the gas phase compete with direct cation reduction.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Invited
1. D. B. Go, International Conference on Reactive Plasma, Honolulu, HI, 2015.
2. P. Rumbach, R. Mohan Sankaran, D. M. Bartels, D. B. Go, “Direct Optical Measurements of Solvated Electrons at a Plasma-Liquid Interface,” Annual Meeting of the Electrostatics Society of America, Pomona, CA, 2015. (to be presented by P. Rumbach)
3. D. B. Go, “Atmospheric-Pressure Plasmas: A Radiation-Free Approach to Solvated Electrons,” International Workshop on Microplasmas, Newark, NJ, 2015.
4. D. B. Go, “Atmospheric-pressure Ionization Processes: New Approaches and Applications for Plasmas in Contact with Liquids,” International Conference on Electrostatics, Southampton, England, 2015.
5. D. B. Go, P. Rumbach, D. M. Bartels, R. M. Sankaran, “Detection of Solvated Electrons at a Plasma-Liquid Interface,” Gaseous Electronics Conference, Raleigh, NC, 2014.
6. D. B. Go, “Electron-Initiated Reactions at the Interface of Plasmas and Liquids,” International Symposium on Plasma Nanoscience, Málaga, Spain, 2014.

Contributed
1. P. Rumbach, R. M. Sankaran, D. M. Bartels, D. B. Go, “Understanding Charge Transfer Reactions at a Plasma-Liquid Interface,” AVS International Symposium and Exhibition, Baltimore, MD, 2014. (presented by P. Rumbach)

Number of Presentations: 7.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
11/03/2014	1.00	Paul Rumbach, David M. Bartels, R. Mohan Sankaran, David B. Go. The solvation of electrons by an atmospheric-pressure plasma, Science (10 2014)
TOTAL:		**1**

Number of Manuscripts:

Books

Received	Book
TOTAL:	

Received	Book Chapter
TOTAL:	

Patents Submitted

Patents Awarded

Awards

1. John Coburn and Harold Winters Student Award in Plasma Science and Technology, American Vacuum Society, 2014 – awarded to Paul Rumbach (Notre Dame graduate student)

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Paul Rumbach	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
David B. Go	0.00	
David M. Bartels	0.00	
R. Mohan Sankaran	0.00	
Rohan Akolkar	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**4**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Amy Aube	0.50	Chemical Engineering
Brittany Bishop	0.50	Chemical Engineering
FTE Equivalent:	**1.00**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Paul Rumbach
Total Number: **1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

1 a. Case Western Reserve University

1 b. 10900 Euclid Avenue
Cleveland OH 441067015

Sub Contractor Numbers (c): 202329
Patent Clause Number (d-1):
Patent Date (d-2):
Work Description (e): Conduct experiments on plasma electrochemistry per Objective 2 of the proposed work p
Sub Contract Award Date (f-1): 6/9/14 12:00AM
Sub Contract Est Completion Date(f-2): 3/8/15 12:00AM

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1 a. Case Western Reserve University

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Cleveland OH 441064919

Sub Contractor Numbers (c): 202329
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Sub Contract Est Completion Date(f-2): 3/8/15 12:00AM

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

STIR: Probing Electrochemical Reactions at a Plasma-Liquid Interface

Final Report
March 13, 2015

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Foreword

For this ARO STIR, the research teams at Notre Dame (PI Go and Co-PI Bartels) and Case Western Reserve University (Co-PI Sankaran and Co-PI Akolkar) performed research toward the goal of understanding the electrochemical reactions promoted by microplasmas at the interface of aqueous solutions. Specifically, the team conducted a series of experiments to understand how high-energy (~1-10 eV) electrons generated in an atmospheric-pressure microplasma traverse from the plasma into an aqueous solution and initiate solution-phase chemistry. Understanding these interactions will reveal the interesting chemistry that can be driven by high-energy electron injection into solutions and allow plasma-solution systems to be tailored and designed for specific applications relevant to the Army and Department of Defense, including rapid nanomaterial synthesis, water purification, environmental remediation (*e.g.*, destruction of halogens), and biological applications.

During this ARO STIR, the Notre Dame research team developed a novel total internal reflection absorption spectroscopy system leading to the *first ever* measurement and detection of plasma-generated solvated electrons directly at the plasma-solution interface. It was found that the plasma-liquid interfacial environment produces different solvated electron behavior than other approaches to generating solvated electrons (*e.g.*, pulse radiolysis) including a blue-shifted and narrower absorption spectrum as well as different reaction rate coefficients. We attribute these differences to the electrochemical configuration of the plasma-solution system. Unlike other solvated electrons sources, the electrons are solvated in the presence of a strong electric field in the Debye layer of the plasma-liquid interface, and the electron reactions and transport must satisfy constant current due to the completion of the circuit via oxidation at the anode. These effects could induce, for example, a Stark shift in the absorption spectrum. However, unlike conventional electrochemical systems with a solid cathode, the electrons enter the solution with energies above the vacuum level, which may promote new, high-energy electrochemical interactions.

The Case Western Reserve University (CWRU) team developed a method to precipitate, separate, and weigh solid silver produced by plasma-initiated electrolytical reduction of silver cations (Ag^+), leading to the first estimates of the efficiency (~80%) for the reduction of Ag^+ by a plasma process. These results reveal that inherent competing chemical pathways must be accounted for when using plasma-solution systems. These results are consistent with the findings of the Notre Dame team, which showed that effects such as second order recombination in the liquid phase or electron scavenging in the gas phase compete with direct cation reduction.

This 9 mo. STIR research resulted in one paper submitted for publication, two in preparation, and multiple conference presentations as outlined in Standard Form 298. Future work will be aimed at addressing persisting and new fundamental questions about the nature of the charge-transfer chemistry at the plasma-solution interface that have been opened up as a result of these preliminary findings. We anticipate that these studies will lead to a new area of electrochemical science as plasma-liquid systems challenge conventional understanding of electron chemistry at gas-liquid interfaces.

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List of Figures and Tables

1. Statement of Problem and Research Objectives

The primary goal of this research was to understand the electrochemical reactions promoted by microplasmas at the interface of aqueous solutions. In particular, the aim was to reveal how electrons generated in an atmospheric-pressure microplasma traverse from the plasma into an aqueous solution and initiate interesting chemistry. As such, the there were two primary scientific questions that this research aimed to answer:

(1) What is the fate of electrons produced in the microplasma and injected into solution? In particular, do the electrons solvate in the solution prior to initiating reduction reactions?

(2) What are the reaction pathways and kinetics for electrochemical systems using plasmas as electron sources? In particular, what is the reaction yield when using a plasma electrochemical system?

In order to answer these two questions, this research was organized into two corresponding research objectives:

> *Objective 1*: Measure and quantify the solvation of plasma electrons using laser absorption spectroscopy.
>
> *Objective 2*: Characterize the reactions involving solvated electrons at the plasma-liquid interface by measuring reaction yields of the silver redox couple ($Ag^{+/0}$) as well as other metal redox couples.

Answering these scientific questions will clarify how energetic electrons much different than those encountered in conventional electrochemical systems can be used to drive unique electrochemistry, leading to a more complete understanding of plasma electrochemical systems and how to optimize them for targeted applications.

2. Approach

In order to achieve these Objectives, the following approaches were used:

Objective 1: The aim of Objective 1 was to directly measure the solvation of electrons by a microplasma jet in contact with an aqueous solution.

- A *new* absorption spectroscopy system was developed to probe the plasma-liquid interface, and solvated electrons will be detected by their optical absorption. Because the anticipated signal is extremely small (1 part in 10^6), a total internal reflection configuration was employed and an amplitude modulation strategy was used whereby the plasma current was modulated at a designated carrier frequency and a lock-in amplifier will be used to detect the absorption at the carrier frequency. A schematic and picture of the experimental set-up is shown in Supporting Figure 1.
- An absorption spectrum was measured using a series of diode lasers at different wavelengths to investigate how plasma-injected solvated electrons might be different from those produced in bulk solutions using techniques such as pulse radiolysis.
- The reaction kinetics of solvated electrons were determined by measuring the reaction rate coefficients for multiple electron scavengers, *i.e.*, reactants reduced by solvated electrons, including anionic (NO_2^-, NO_3^-), cationic (H^+), and neutral (H_2O_2) scavengers.
- The impact of the plasma environment (gas composition) on the solvated electron yield was determined by measuring the absorption signal under different gas environments,

specifically argon/oxygen (Ar/O_2) and Ar/air mixtures where the electronegative oxygen starves the interface of solvated electrons.

Objective 2: The aim of Objective 2 was to characterize reactions involving solvated electrons to further confirm their presence, complementing Objective 1, and to understand their role in the reaction chemistry.

- Reaction yields of the well-understood reduction of silver (Ag^+) were measured. In electrochemistry, metals are electrodeposited on a substrate and the weight is measured to relate the charge passed to the rate of reaction. In the case of the plasma electrode, the reduction of Ag^+ leads to the nucleation of nanoparticles, which can disperse and in some cases dissolve. In order to measure the weight in a manner similar to electrodeposition experiments, we precipitated the Ag nanoparticles and separated them by filtration and drying.
- The weight of the Ag nanoparticles were measured systematically for different process times and plasma currents to relate the charge passed to the rate of reaction. The experimental data was compared to the Faradaic value to obtain an efficiency for the process (assuming that the plasma current passes 100% of the charge to the solution and all electrons reduce Ag^+).

3. Relevance to Army

Plasma-liquid systems have significant potential in a number of applications relevant to the Army and DoD. In particular, plasma electrochemical cells can be used for the rapid synthesis of colloidal nanoparticles, which can be used in catalytic and chemical analysis systems. Furthermore, as a cheap, radiation-free source of solvated electrons, plasma-liquid systems can be used for water purification, environmental remediation (*e.g.*, destruction of halogens), and biological applications. Future development of these DoD-relevant applications requires a comprehensive understanding of the electrochemistry that occurs in plasma-liquid systems, and in particular, the electrochemistry that can be driven by high energy electrons. This work will answer fundamental questions about the physics and chemistry of high-energy electrons injected into solution from plasma sources.

4. Scientific Progress and Accomplishments

Significant accomplishments during this STIR include:

- The first direct measurement of solvated electrons at a plasma-liquid interface, where absorption spectroscopy was used to confirm their existence.
- The first measurement of the absorption spectrum for solvated electrons produced by a plasma. Crucially, the measured absorption spectrum is distinct from the spectrum measured for bulk solvated electrons produced by pulse radiolysis. In particular, the peak of the spectrum is shifted approximately 50 nm to the blue and the typical Lorentzian blue tail is suppressed. This suggests that the environment for plasma-produced solvated electrons is distinct from other systems. One likely cause of these differences is the large interfacial electric field, which could cause a Stark shift in the spectrum, but further work is required to confirm this. The measured spectrum is shown in Supporting Figure 2.
- The first estimate of the average penetration depth for electrons traversing the interface from a plasma into an aqueous solution of 2.5 nm. This value strongly suggests that the electrons localize several monolayers below the solution surface and that they are

therefore *fully* solvated. It is unresolved whether electrons at liquid-gas interfaces are fully or partially solvated, so answering this question for plasma-liquid systems is essential.

- The first determination of reaction rate coefficients for plasma-produced solvated electrons reacting with nitrite (NO_2^-), nitrate (NO_3^-), and hydrogen peroxide (H_2O_2). The measured rate coefficients are on the same order of magnitude as those measured for bulk solvated electrons, but not equivalent to those values. This further suggests that the environment and nature of plasma-produced solvated electrons is distinct from other methods of producing solvated electrons. The absorption signals and measured reaction rates are included in Supporting Figure 3 and Supporting Table 1.
- The first experimental demonstration that electronegative gases in the plasma environment will quench electron transfer across the plasma-liquid interface and inhibit the formation of solvated electrons. Absorption spectroscopy measurements using Ar plasmas with a small percentage of O_2 (up to 2%) or air were used to demonstrate that the absorption signal decreases with increased O_2 concentration. A representative measurement is shown in Supporting Figure 4.
- The first development of a method to electrolytically reduce Ag^+ to Ag nanoparticles by an atmospheric-pressure plasma electrode, precipitate, separate, and weigh the product, and relate the weight to the plasma process conditions (current, time, charge). Supporting Figure 5 shows a schematic of the experimental apparatus.
- The first estimate of an efficiency for the reduction of metal ions like Ag^+ by a plasma process (~80%), as indicated by the data shown in Supporting Figure 6. This efficiency points to the inherent competition between cation reduction and other chemical paths, including second order recombination and the scavenging of electrons by gas species such as O_2.

5. Future Work

Based on these initial accomplishments, there are many persistent as well as new questions that arise about the fundamental nature of electron-driven chemistry at the plasma-solution interface. The following lists specific areas for future work on this topic:

1. The nature of the absorption spectrum for plasma-generated solvated electrons is one of the most interesting questions that arose from these initial measurements. Specifically, it is unclear what causes the spectrum to shift (to the blue) and change shape (narrow). The current conjecture is that the interfacial electric field in the Debye layer plays an important role in this process, and preliminary estimates of a Stark shift induced by the electric field are somewhat consistent with the measurements shown in Supporting Figure 2. Future work will aim to resolve this discrepancy by measuring the full absorption spectrum using a tunable laser rather than discrete points with multiple diode lasers. By changing the conductivity and/or permittivity of the solution, *e.g.* by using more salt or different solvents, the size and nature of the Debye layer will change. By comparing the measurements of the absorption spectrum across different solution conditions, the nature of the blue shift and shape change can be identified.
2. One of the more important initial analyses of the experimental data produced an estimate the average penetration depth of the solvated electrons below the liquid surface before they react by second order recombination. This penetration depth is limited by the diffusion and drift of the solvated electrons and also sets an upper bound on the

localization depth of the plasma electrons – that is, the depth where the plasma electrons dissipate their initial kinetic energy and become solvated. The measured average penetration depth of 2.5 nm suggests the plasma electrons localize within the first few monolayers of water. However, the drift/diffusion model suggests that the average penetration depth is a strong function of the current (and current density) of the plasma. By conducting absorption measurements across multiple current densities, a more refined upper limit on the localization depth will be achieved and help answer whether the electrons partially of fully solvate before reacting. Further, the practical limit of the average penetration depth will also be revealed, and this is crucial to know in designing these systems for plasma-solution applications. Monte Carlo simulations can complement these measurements and confirm the localization depth.

3. The reaction kinetics, and specifically the rate coefficient measurements, should be refined to determine a more exact value and to understand why they are different from those obtained using radiolytic approaches. Improving the experimental apparatus to achieve better laser optics and also measure the plasma radius will reduce the uncertainty in these measured values. Performing these measurements over a range of solvent compositions and for a range of reactants will reveal under what conditions a plasma-solution interface produces different reaction kinetics from other solvated electron systems.
4. The inherent inefficiency in plasma-driven cation reduction can be attributed to the competing reaction paths for plasma electrons. However, careful control of the solution- and gas-phase environments should enable more precise control over these paths, leading to controllable efficiency. Experiments with solution-based scavengers (including scavenging electrons, hydroxyl radicals, and other intermediate species) and gas-phase scavengers, will be used to discover the conditions where cation reduction is optimized and point the way to how to design plasma-solution systems for maximum performance. These experiments can be supported by reaction modeling, which can be used to guide and design the experiments.

6. Supporting Figures

See following pages.

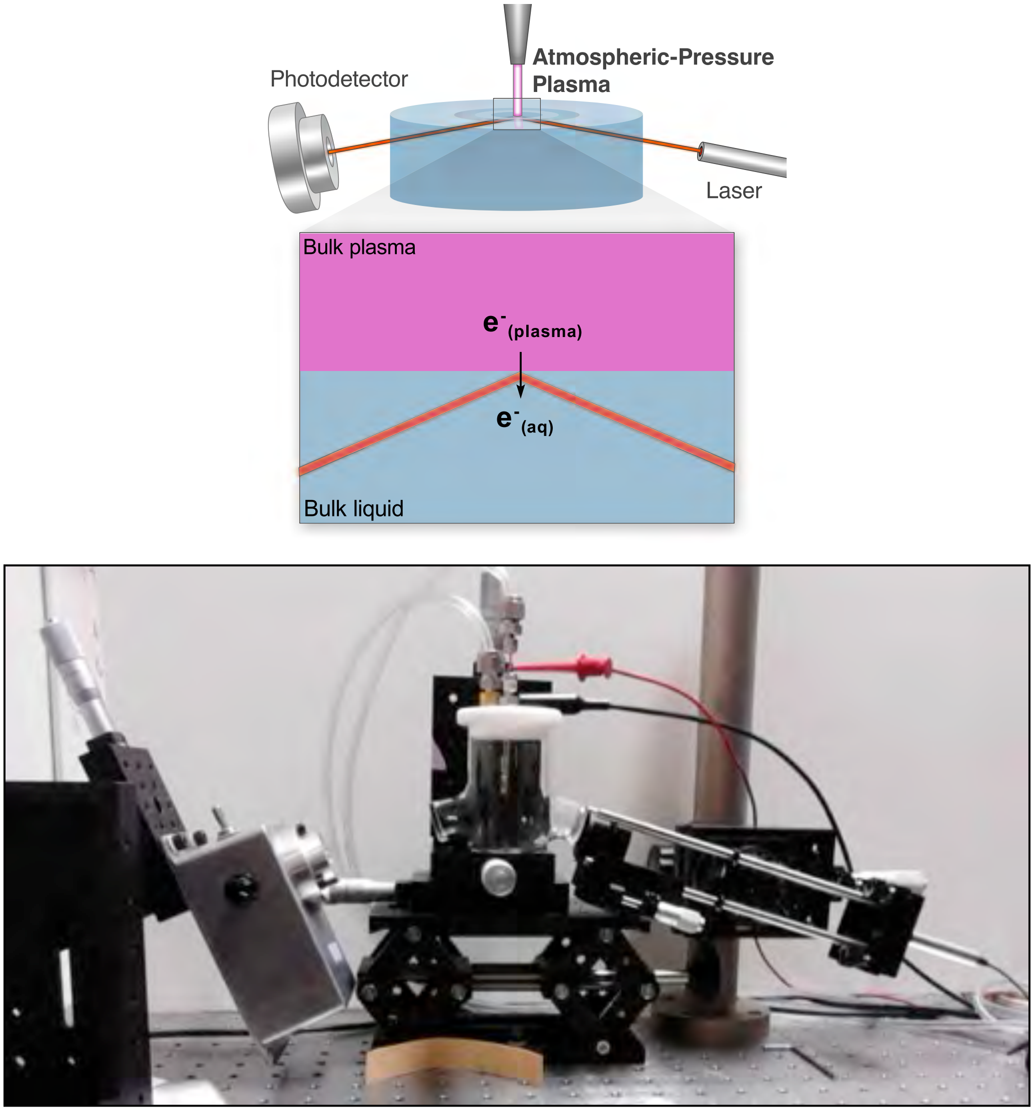

Figure 1. Generation and detection of solvated electrons by an atmospheric-pressure plasma (top) Schematic of optical absorption spectroscopy measurement to probe the interface of the plasma and liquid, where solvated electrons are detected by their optical absorption. A total internal reflection approach is used to increase the signal-to-noise and reduce the effects of spurious signals due to reflections off the interface. (bottom) Photograph of experimental set-up including the laser, plasma electrochemical cell, and photodetector.

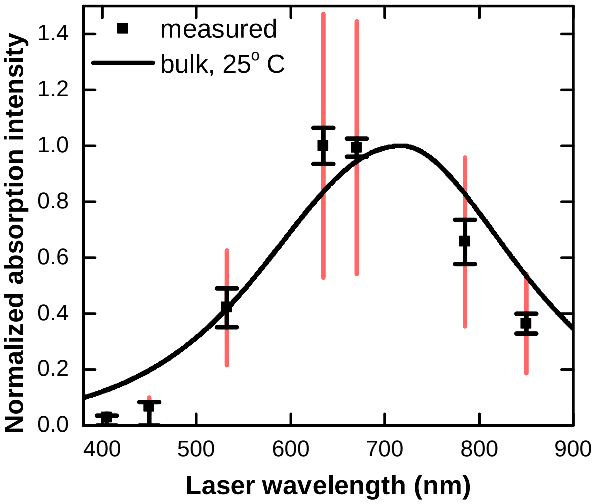

Figure 2. Measured absorption spectrum compared to bulk solvated electrons. Measured optical absorption signal corresponding to solvated electrons measured at the plasma-solution interface by using laser diodes at different wavelengths. Black error bars with capped ends represent the root mean square (RMS) variance in the raw data, and the overlaid red error bars also account for the systematic uncertainty in the laser-plasma overlap. Both sets of error bars represent 90% confidence. A Gaussian-Lorentzian bulk spectrum (solid line) measured in pulse radiolysis experiments for a temperature of 25°C [Bartels et al. *J. Phys. Chem. A* 109, 1299 (2005)] is included as a guide. The data indicate a blue shift to the left by approximately 50 nm as well as suppression of the Lorentzian tale at wavelengths less than 500 nm. These two features strongly suggest that the plasma-liquid environment is fundamentally different from other environments used to produce solvated electrons.

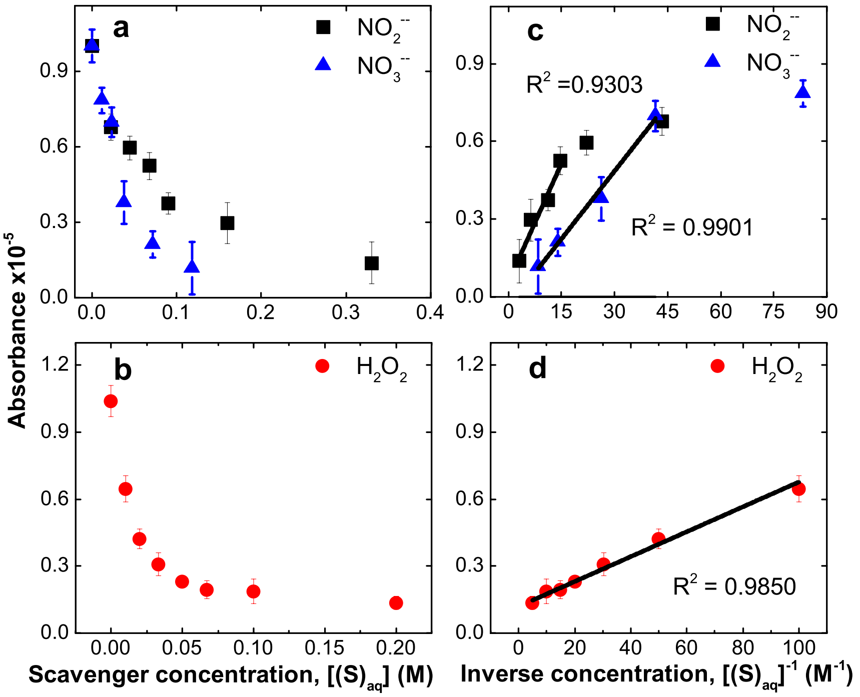

Figure 3. Absorbance behavior for different scavengers. (a) Absorbance measurements as a function of concentration $[(S)_{aq}]$ for anionic scavengers NO_2^- and NO_3^-. (b) Absorbance measurements for neutral scavenger H_2O_2. (c) Corresponding absorbance as a function of the inverse concentration $[(S)_{aq}]^{-1}$ for NO_2^- and NO_3^-, where the solid lines are linear curve fits. (d) Corresponding absorbance as a function of the inverse concentration $[(S)_{aq}]^{-1}$ for H_2O_2, where the solid line is a linear curve fit. The linear curve fits in (c) and (d) are used to extract rate constants for the scavenging reactions, as shown in Table 1.

Table 1. Measured rate constants extrapolated from absorption measurements of solvated electrons at the plasma-solution interface. Literature values for bulk reactions obtained from pulse radiolysis experiments as well as values corrected for the ionic strength of our solutions are also shown [Buxton et al. *J. Phys. Chem. Ref. Data* 17, 513-886 (1988)]. The values are on the same order of magnitude, but not identical, indicating that the plasma-liquid interface is a fundamentally different environment for solvated electrons.

Reaction	Measured *k* (10^9 M^{-1} s^{-1})	Published *k* (10^9 M^{-1} s^{-1})	Published *k* cor. for I (10^9 M^{-1} s^{-1})
$(e^-)_{aq} + (NO_2^-)_{aq} \rightarrow (NO_2^{2-})_{aq}$	5.2 ± 1.7	4.1	9.7
$(e^-)_{aq} + (NO_3^-)_{aq} \rightarrow (NO_3^{2-})_{aq}$	7.0 ± 2.6	9.7	17.9
$(e^-)_{aq} + (H_2O_2)_{aq} \rightarrow (OH)_{aq} + (OH^-)_{aq}$	14.1 ± 3.1	11.0	11.0

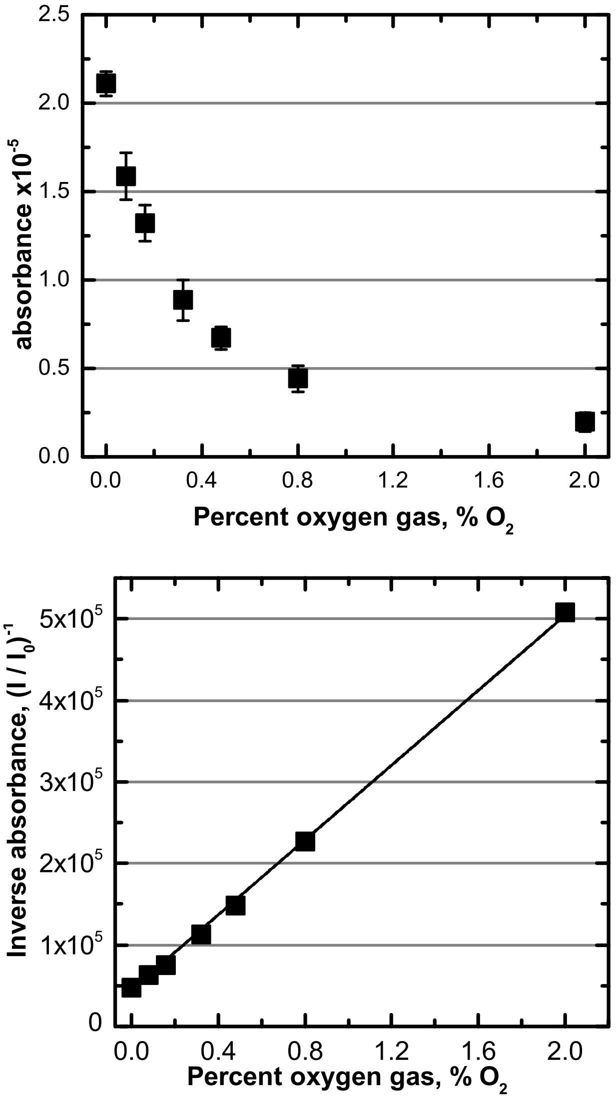

Figure 4. Absorbance behavior for different plasma gas environments. (top) Absorbance measurements as oxygen gas $(O_2)_g$ is introduced into the Ar plasma environment. (bottom) Corresponding inverse absorbance as a function of $(O_2)_g$ percentage in the Ar plasma environment, where the solid line is a linear curve fit. The linear curve fit confirms an inverse scaling relationship with $(O_2)_g$ concentration, were the electronegative oxygen depletes the plasma electrons and reduces the solvated electron concentration.

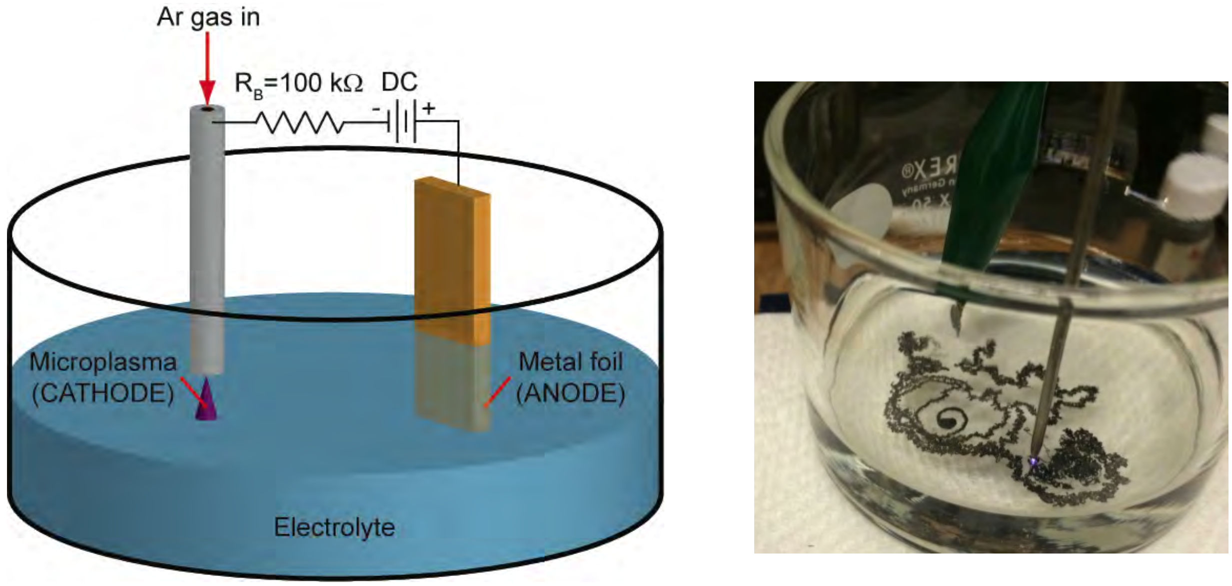

Figure 5. Electrolytic reduction of aqueous solutions of $AgNO_3$ by an atmospheric-pressure microplasma electrode. (left) Schematic of experimental setup consisting of a cathodic atmospheric-pressure microplasma formed at the surface of an aqueous electrolyte, which is $AgNO_3$ in water, and the anodic metal foil, which is Pt. (right) Photo of the process after solid Ag nanoparticles have formed and begin to precipitate.

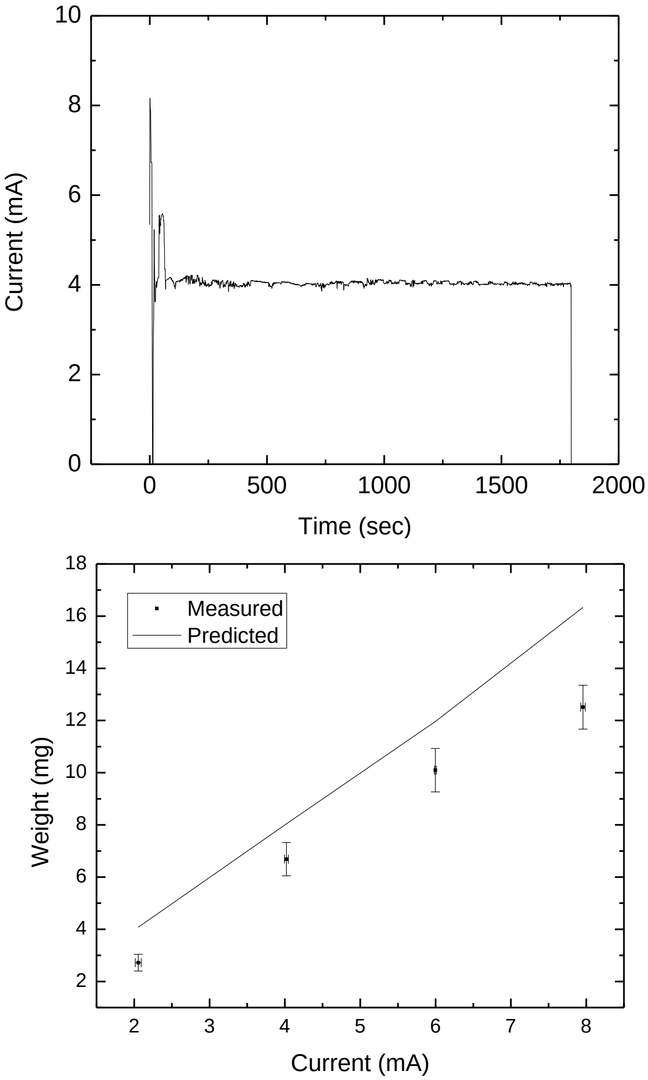

Figure 6. Current monitoring during plasma reduction of Ag^+ and correlation of weight of Ag product to plasma current. (top) Current fluctuations are observed during the plasma process, particularly initially when the plasma is ignited. The set point for the experiment was 4.0 mA. The fluctuations are accounted for in the data analysis by integrating over time to obtain the total charge injected into solution. (bottom) The weight of the Ag product obtained by precipitating the Ag nanoparticles, filtering, and drying, is measured at different plasma currents. The vertical error bars indicate the error in the measured weight for a minimum of three experiments at each current, and the horizontal error bars indicate the error in the current related to current fluctuations. The solid line is the weight predicted for the faradaic current, assuming all the plasma current reduces Ag^+. Based on the faradaic current, the efficiency of the process is estimated to be 80%.