Solvated Electrons at the Atmospheric Pressure Plasma-Water Anodic Interface

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This study was motivated by the experimental observations reported by Rumbach et al. [1] These authors report the presence of hydrated electrons just below the surface of water acting as anode to an atmospheric pressure argon dc discharge. They estimate the concentration and spatial extent of near-surface hydrated electrons using modulated visible light absorption measurements. Hydrated (or 'solvated') electrons are known to be important in radiation chemistry and other related areas. They are therefore important in plasma-liquid interactions as well. We modeled this experimental system using a 1-D particle-in-cell simulation of a dc argon discharge coupled with a model of the near-surface aqueous electrolyte, incorporating electrons, and various positive and negative ions. The charged species in the liquid electrolyte are coupled through the self-consistent electric field. In particular, we resolve the double layer region at the plasma-electrolyte interface in the model, including a number of the chemical reactions known to be important under these conditions.

The predicted structure of the plasma-water interface is shown in Fig. 1. The experimental current density is 40,000 A/m^2 and the anode sheath has a negative electric field that accelerates electrons into the liquid. The model assumes these electrons are immediately solvated at the interface and then drift and diffuse in the electrolyte. Note the difference in scales on the plasma side (left) and the electrolyte side (right). The peak electron density in the water is predicted to be ~ 0.5 mM whereas the experimental estimate is 1 mM under these conditions. The electric field on the plasma side is predicted to be about 6 x 10^5 V/m and is ~ 7 x 10^3 V/m on the liquid side, due to the relatively high water dielectric constant. It was assumed that there is no surface charge density at the phase interface.

There is much to learn about these complex plasma-liquid interfaces. For example, the plasma simulation predicts quite energetic electrons (~ 10 eV) impacting the water surface given this large electric field and current density. It seems likely that electron-impact initiated chemistry would be important under these conditions, but we currently have no direct evidence for this. I on and neutral chemistry is surely more complex than what is treated here as well. Many different plasma applications will have their special characteristics that we have not begun the address.

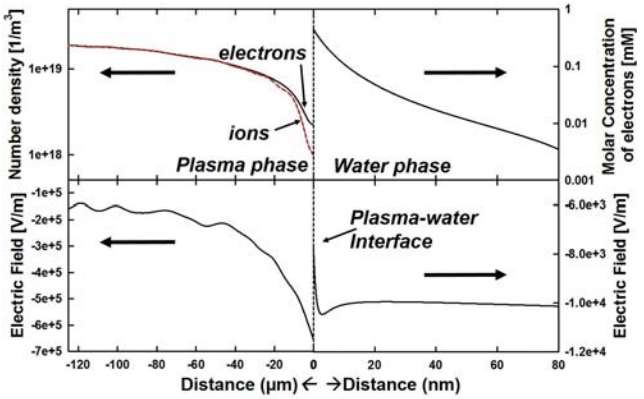


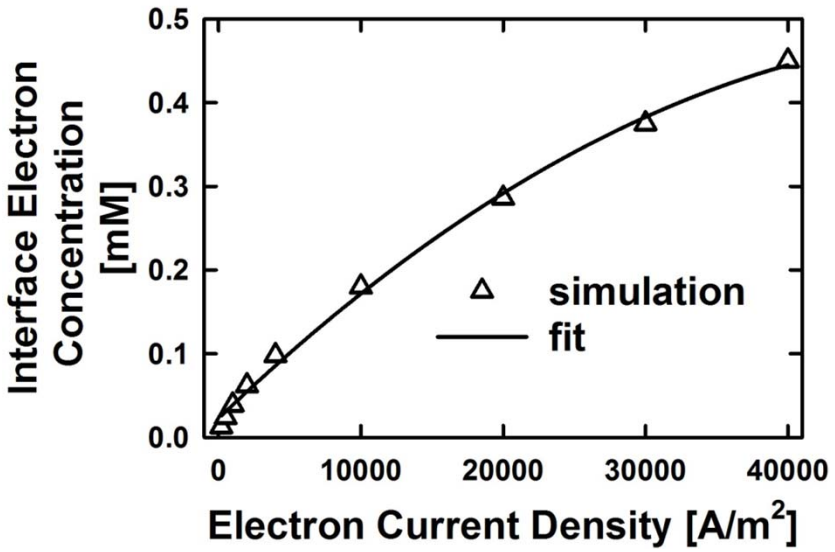
Figure 1 – Predicted interface between plasma (left) and electrolyte (right).

References

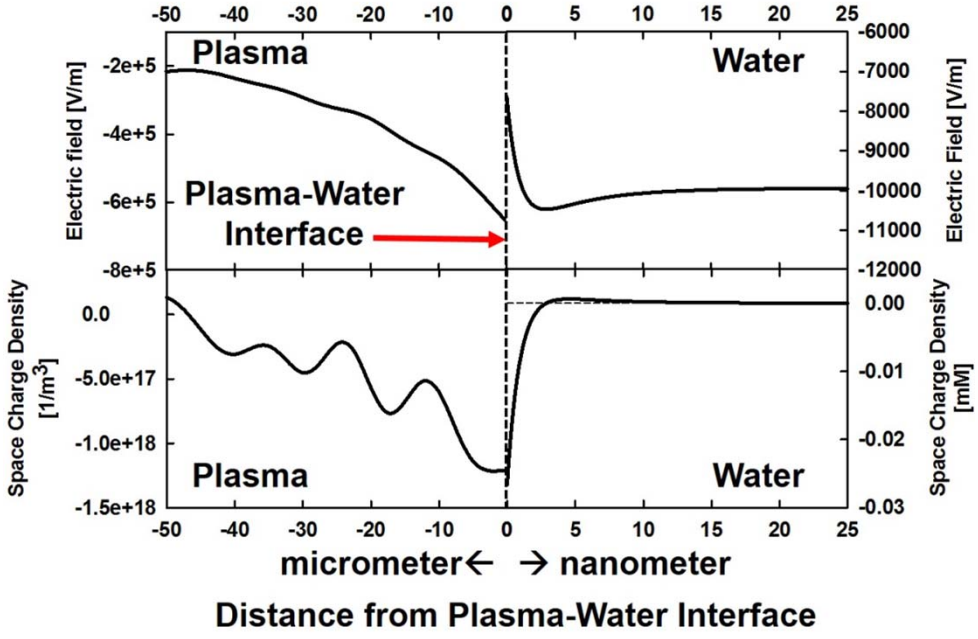
[1] P. Rumbach, D.M. Bartels, R.M. Sankaran, and D.B. Go, Nature Comm. **6**, Article 7248 (2015).

PLASMA-WATER: SOLVATED ELECTRONS

- Rumbach et al. (2015) measured solvated electrons at plasma-water interface
- We combined a PIC/MC plasma model and fluid electrolyte model to simulate the plasma-water interface with solvated electrons.
- We reproduced observed trends and the plasma-water interfacial structure,



- Predicted electron concentration at water interface vs. current density



- Predicted plasma-water interface structure

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HIGHLIGHT

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DC Atmospheric Pressure Air Glow Discharge with a Water Cathode: OH Kinetics and Water Concentration

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Interactions between gas phase plasmas and liquids are an important intellectual frontier in plasma science.[1] The complex interaction of gas phase plasmas with liquids offers a rich source of both short-lived and long-lived reactive species, many of which are critical for chemical and biological applications. Atmospheric pressure DC air glow discharges with water cathodes have been studied extensively.[1] The discharge typically operates with currents in the range of 10 mA and voltages of the order of 1 kV. In atmospheric pressure air significant gas heating can occur up to 3000 K. Electron densities and temperatures in the positive column of the discharge have been estimated to be of the order of 10^{19} m^{-3} and 1 eV respectively. Detailed information about spatially resolved reactive species densities in a DC air glow discharge in contact with a liquid electrode is currently not available. As significant water transfer from the liquid to the gas phase occurs due to water evaporation a high water concentration is expected to be present in the core of the discharge and OH is expected to be one of the important reactive species in this type of discharge.

We measured the OH density and gas temperature by broadband absorption.[2, 3] Assuming a Gaussian radial profile of the OH density and gas temperature, OH densities in excess of 10^{23} m have been found in the positive column (Fig. 1). The ground state OH density is much broader than the active plasma zone and local kinetics dominates transport. This is consistent with an OH production mechanism through atomic oxygen as has been suggested by 0-D models.[4] Assuming the OH density is dominated by O kinetics one can estimate a water concentration in the discharge core of approximately 5%. This amount of water is consistent with the measured effective lifetime of the OH(A) fluorescence signal (4.4±0.3 ns) in the core of the discharge.

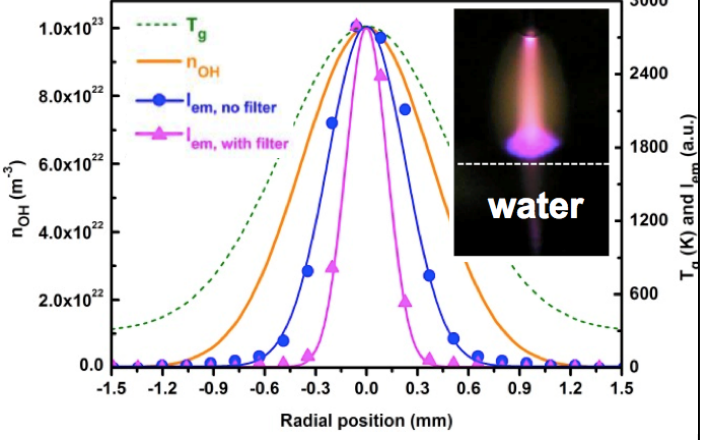

Figure 1 – Radial profile of the OH density, gas temperature and emission profiles.[3]

More detailed 2D measurements will be performed by laser induced fluorescence to assess the assumptions made about Gaussian radial profiles in the analyses of the absorption spectra.

References

[1] P. Bruggeman and C. Leys, J. Phys. D: Appl. Phys. **42**, 053001 (2009).
[2] P. Bruggeman, G. Cunge and N. Sadeghi, Plasma Sources Sci. Technol. **21**, 345201 (2012).
[3] Q. Xiong, Z. Yang and P. J. Bruggeman, J. Phys. D: Appl. Phys. (in press)
[4] E. Bobkova, S. Smirnov, Y. Zalipaeva, V. Rybkin, Plasma Chem. Plasma Process. **34** 721-43 (2014).

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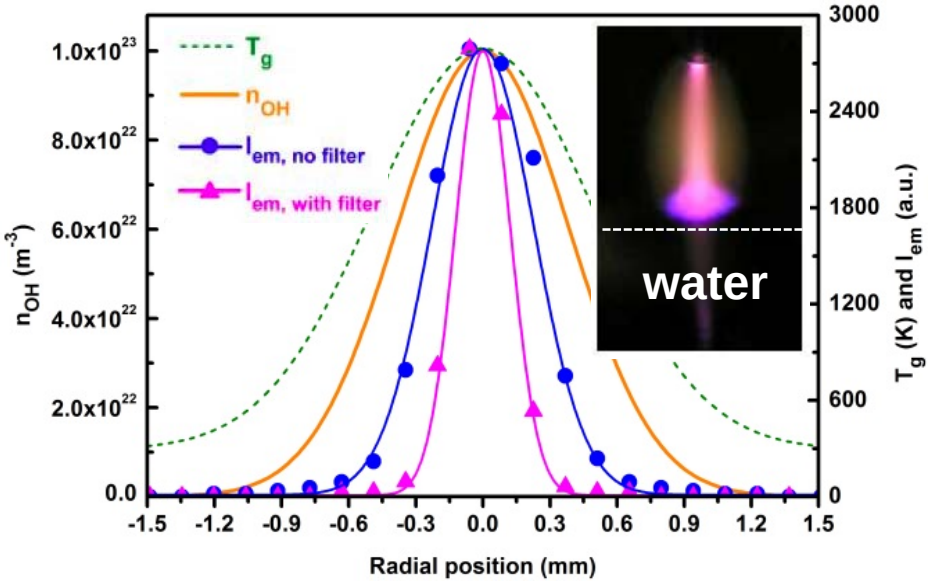
Highlight

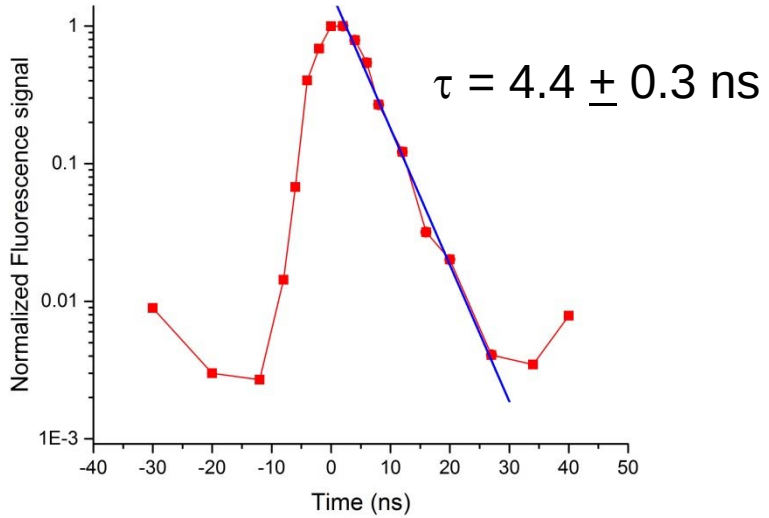
Center for Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems
Department of Energy Plasma Science Center

DC GLOW DISCHARGE WITH A WATER CATHODE: OH KINETICS AND H_2O CONCENTRATION

- **OH kinetics in an atmospheric pressure DC glow discharge in air with a water cathode has been investigated by broadband OH absorption spectroscopy.**
- **OH densities >10^{23} m^{-3} were measured, consistent with OH production mechanisms by O atoms as shown in 0D kinetic models.**
- **Estimates of the water concentration are ≈5% consistent with fluorescence lifetime measurements of OH(A) being impacted by the local water density.**



- **Gas temperature, OH density and emission profile of positive column**



- **Effective OH(A) lifetime**

HIGHLIGHT