Plasma Science and Technology Division
Room 315 - Session PS-MoM

Plasmas for the Environment and Sustainability: Plasmas-Liquid Interactions, Water, Air, Soil Treatment

Moderators: David Go, University of Notre Dame, **Jeffrey Shearer**, TEL

9:00am **PS-MoM-3 Nitrogen Fixation by Atmospheric Plasma: Effect of Process Parameters on Product Yield and Selectivity***, N. Maira,* Université libre de Bruxelles, Belgium*; A. Remy,* Université libre de Bruxelles, Belgium/ Ghent University, Belgium*; K. Van't Veer,* Université libre de Bruxelles / Antwerpen University, Belgium*; C. Pattyn, N. Roy,* Université libre de Bruxelles, Belgium*; A. Bogaerts,* University of Antwerp, Belgium*; N. De Geyter,* Ghent University, Belgium*; **Francois Reniers**,* Université libre de Bruxelles, Belgium

Nitrogen fixation using atmospheric plasma is a possible alternative route to the Haber-Bosch process. Among these, microplasmas over water, DBD over water and DBD without water can be used to synthesize ammonium, nitrites and nitrates, depending on the reactants used, and the process parameters. The talk will present a summary of results obtained using the 3 types of plasmas mentioned above. Thanks to original setups, the production of nitrogen oxides and ammonia in the gas phase and in the liquid phase will be tracked. It is shown that simultaneous production of nitrates and ammonium can be obtained from pure nitrogen using a microplasma over water (plasma-induced disproportionation). Conditions for nitrite free solutions are established. The effect of the gas composition and the electrodes polarity on the obtained results is shown. The importance of water vapor as a source of OH and H for reactivity is highlighted. For DBDs without water, the influence of the streamers on the NOx synthesis (from N_2 and O_2) and on the NH_3 synthesis (from N_2 and H_2) is evidenced through heat sensitive experiments on one hand, and through modeling on the other hand. It is shown that, for NOx synthesis the streamers temperature have a significant effect on the oxidation mechanism, preventing the ozone route when too hot. For ammonia synthesis, if the streamers are beneficial for nitrogen splitting, it is shown that they also destroy ammonia, which is preferentially formed outside the streamers.

References:

N.C. Roy et al, Plasma Processes and Polymers, (2021) 18 (3), 2000087

C. Pattyn et al., Green Chemistry, submitted

C. Pattyn et al., Physical Chemistry Chemical Physics (2020) 22 (42), 24801-24812

K. Van’t Veer et al. The Journal of Physical Chemistry (2020) C 124 (42), 22871-22883

Acknowledgements : this work is funded by the Belgian Excellence of Science (EoS) "Nitroplasm" project.

9:20am **PS-MoM-4 Fundamental Insights Into Plasma-Liquid Interactions by Combined Experiments and Multiphase Modeling***, **Necip Uner**,* Middle East Technical University, Turkey*; S. Keniley,* LAM Research*; E. Perez, D. Curreli, M. Sankaran,* University of Illinois at Urbana-Champaign

Plasmas in contact with liquids are of interest because of the complex interactions and potential for novel physical and chemical processes. In general, the system is composed of the gas-phase, liquid-phase, and the gas-liquid interface. Experimental measurements have been made in the gas phase and liquid phase of a plasma-liquid process, and more recently modeling has also been performed. There remains a need to compare experiments and modeling to validate simulation outputs and develop predictive capabilities.

This talk will focus on two important aspects plasma-liquid processes: predicting the species densities and heat transfer phenomena near the interface. The focus of our study was a direct-current (DC) operated pin-to-plane electrode geometry with the liquid serving as an electrolyte and a counter electrode immersed in the solution. First, our recent studies on developing a one-dimensional, isothermal but unsteady-state model for coupled plasma-liquid interactions will be presented. Using a drift-diffusion-reaction formalism, plasma and aqueous chemistry was solved for in an argon-salt water system. In this system, one of the reactions that occurs is the formation of hydroxyl radicals, which subsequently produce hydrogen peroxide. We studied potential mechanisms for hydrogen peroxide production with the plasma operated as either the cathode or anode. Experiments were performed in support of modeling to characterize the plasma and measure the aqueous hydrogen peroxide, and both modeling and experimental results show that its production is substantially higher during anodic operation. Most importantly, the model can successfully predict the order of magnitude of H_2O_2 generation rate in the bulk liquid during anodic operation.

In the second part of this talk, it will be shown that a major portion of the energy in the pin-to-plane electrode is dissipated as heat during cathodic operation. Optical emission spectroscopy indicates that even for a discharge power of less than 2 W, the gas temperature may surpass 1000 K in the cathode sheath, which subsequently heats up the electrode. For small electrode geometries, cathode heating is visible due to extensive blackbody radiation, which confirms the gas temperatures measured by spectroscopy. Despite being only 1 mm away from the cathode, infrared thermometry indicates that the water interface remains surprisingly cool, reaching a maximum of only 335 K. These findings suggest that in addition to the inherent local non-equilibrium between the electrons and larger species in the plasma, there exists a very strong thermal non-equilibrium across the plasma as well.

9:40am **PS-MoM-5 Merging the Fundamental and Applied: Understanding Plasma Kinetics and Energetics to Build Better Mousetraps***, Ellen Fisher*[1]*,* University of New Mexico **INVITED**

Historically, plasmas have been used extensively to increase the functionality of a myriad of materials for use in a wide range of applications.Despite this storied history, use of plasma-processed materials has been limited by a lack of understanding of fundamental mechanisms.Moreover, the applicability of various processes such as plasma-assisted catalysis is also limited by this lack of knowledge on the basic kinetics and energetics that contribute to plasma-catalyst synergy.This presentation will review a range of systems that have benefited from the use of optical spectroscopy to investigate gas-phase processes in inductively-coupled plasma systems revealing physical and chemical properties of the plasma systems.Perhaps more importantly, these data highlight details of molecule excitation pathways occurring in various plasma systems as well as how various species are involved in gas-surface interactions.Combined with materials characterization studies, these results emphasize the intimate connections between substrates, plasma parameters and fundamental plasma properties, all crucial components to creating better mousetraps.

10:40am **PS-MoM-8 Comparative Investigation of DC Plasma Versus Boron-doped Diamond Electrodes for Electrochemical Degradation of PFOA***, **Jasmine Dinari**,* University of Illinois at Urbana-Champaign*; N. Uner,* Middle East Technical University, Turkey*; P. Baldaguez Medina, M. Sankaran, X. Su,* University of Illinois at Urbana-Champaign

Per- and polyfluoroalkyl substances (PFAS) are a group of persistent man-made chemicals, currently found in water, that stagnate in the environment. There is a need to degrade PFAS such as perfluorooctanoic acid (PFOA) in our water supplies. In the last decade, two methods that have attracted attention for their capability of mineralizing PFAS into fluoride and CO2 are electrochemical processes and plasmas formed at the surface of a liquid.

Here, we performed a comparative investigation of a plasma and one of the most well-studied electrochemical electrodes, boron-doped diamond (BDD), for PFOA degradation. In addition to carrying out the experiments in the exact same direct-current (DC)-powered electrochemical setup, the plasma and BDD were operated as either the anode or the cathode, with the same platinum wire mesh as the counter electrode. While both the BDD and plasma achieved almost complete degradation of PFOA, the optimal configuration for each of them was found to be cathodic for the plasma and anodic for the BDD, with the plasma degrading the PFOA almost 3 times faster. Compared to the BDD, the plasma required more than an order of magnitude higher voltage, but lower current to achieve a similar degradation efficiency. As a result, both the plasma and BDD degradation resulted in similar energy efficiencies.

Fundamentally, the BDD electrode exhibited zero-order kinetics, revealing that PFAS degradation using the conventional electrochemical method was kinetically controlled. On the contrary, analysis using a film model indicated that the plasma degradation kinetics was mass-transfer-controlled because of the extremely rapid reaction kinetics. In addition, we found that in the case of the plasma electrode, the counter electrode played a critical role. Combined with their optimal configurations, these results suggest that an

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[1] **2020 PSTD Plasma Prize Winner**

asymmetric device with the plasma as the cathode and the BDD as the anode may lead to enhanced degradation.

11:00am **PS-MoM-9 Integrated circuit Manufacturing with Plasma Activated Chemical Treatment (IMPACT): A Potential Approach for Reducing the Dose-to-Clear in a Commercial Photoresist***, **Christian Williams**, S. Dubowsky, E. Barlaz, S. Marcinko, M. Sankaran,* University of Illinois at Urbana-Champaign*; E. Suga, A. Matsuyama,* TOK America, Japan*; D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

One of the main characteristics that determine how suitable a photoresist formulation is for industrial applications is referred to as the "dose-to-clear", defined as the amount of energy from the light source necessary to remove (in this case positive) resist from the exposed area. This is an important factor when it comes to chemically amplified resists (CARs), as there is a trade-off between line edge roughness and the dose provided. The Illinois Plasma Institute (IPI) along with the Center for Plasma Material Interactions (CPMI) have developed a method[1] where the polymer component of two commercially available photoresists (designed for wavelengths of 193 nm and 13.5 nm) are treated with an atmospheric AC jet plasma with the intent of reducing the bond energies in the polymer. Some Density Functional Theory (DFT) modeling done at the Laboratory for Computational Plasma Physics (LCPP) indicates the injection of a charged species, in this case, solvated electrons can lower the bond energy of polymers such as those commonly used in commercial photoresist formulations. Preliminary experimental results indicate that the treatment leads to the ability of the resist to be removed at lower exposure times (lower dose) for the 13.5 nm resist by up to 20%. There has also been some experimental evidence that there is a reduction in the residue present after the same exposure times between the untreated and plasma-treated samples when using the 193 nm resist. The exposure tool of choice was a 172 nm VUV lamp that is commercially available and was created by Cygnus Photonics. These results were obtained using an optical profilometer to measure the size of the mask patterns and the reductions that take place at varying exposure times. Rheometry (viscosity) measurements have also been done to ensure that the observed effect is not due to reducing the viscosity and therefore the film thickness. Results from a time-dependency study, to determine if the effects are temporary or permanent, will also be discussed in the context of commercial viability and product shelf life, as this will factor into the usefulness of the project in an industrial context. Ongoing efforts towards a pulsed DC plasma jet setup will be discussed as well.

[1] Patent application submitted Nov. 2020

11:20am **PS-MoM-10 Low Power Degradation of Perfluorooctane Sulfonate (PFOS) in Water Using a Nanosecond Pulsed Atmospheric Pressure Plasma***, **Michael Johnson**,* Syntek Technologies*; W. Maza, V. Breslin,* Naval Research Laboratory, Chemistry Division*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory

The prevalence and persistence of perfluoroalkyl substances (PFAS) has led to significant concerns over the damage they can have on human health and the environment, particularly when they contaminate bodies of water. Plasma-based water treatments offer a potential solution to this issue, as they offer a rich chemical environment that can degrade contaminants and are flexible enough to operate in different geometries. In particular, atmospheric pressure plasmas driven with short, high voltage pulses produce the requisite chemistry while maintaining high energy efficiency. In this work, a plasma driven with high-voltage (>10 kV) pulses of varying duration (50-400 ns) and frequency (0.5-10 kHz) is investigated for degrading perfluorooctane sulfonate (PFOS) in water. It was found that after exposure to the plasma caused the concentration of PFOS in solution to decrease with repeated passes through the reactor. Increasing the power consumption of the plasma, either by increasing the pulse width or the frequency, improved the rate of PFOS loss but decreased the energy efficiency. For instance, reducing the frequency of the pulse from 10 kHz to 500 Hz decreased the power consumption by over an order of magnitude while requiring about twice as much time to reduce 50% of the PFOS signal. Time-averaged emission spectroscopy showed that increasing the frequency decreased the average electron density of the plasma and while increasing the temperature of the reactor. In contrast, increasing the pulse width from 50 ns to 400 ns did not have a significant impact on the average electron density or the reactor temperature. Infrared (IR) measurements of the reactor indicated that changes in operating conditions caused only modest changes in reactor temperature. Spectroscopy revealed the presence of photons with energies >5 eV were also observed and could contribute to PFOS loss. This work shows that the main factor determining PFOS loss is the contact time between the plasma reactor and the solution, which implies the most energy efficient operating parameters for PFOS degradation comes from minimizing the duration and frequency of the high-voltage pulses to reduce power consumption.

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