Plasma Science and Technology Division
Room A106 - Session PS+SE-FrM

Atmospheric Pressure Plasmas and Their Applications

Moderators: Michael Johnson, Naval Research Laboratory, USA, **Floran Peeters**, LeydenJar Technologies

8:20am **PS+SE-FrM-1 Electrolyte Engineering for Nitrogen Fixation by Plasma Electrolysis***, **Brandon Kamiyama,*** University of Illinois at Urbana Champaign*; M. Eslamisaray,* University of Illinois Urbana-Champaign*; R. Pierrard, R. Sankaran,* University of Illinois at Urbana Champaign

The fixation of nitrogen is critical to our most basic need, the growth of plants for food. Industrially, nitrogen is fixed to ammonia (NH_3) by the Haber-Bosch process which has a large physical and environmental footprint. The development of alternative methods that are sustainable and deployable at a small scale has become one of the active areas of research. Among the different approaches being explored, plasma-based electrolytic reactors have shown the most promise, capable of activating nitrogen in air or with water as a source of hydrogen at atmospheric pressure and near room temperature without any catalyst and using only electricity which could in the future come from renewable sources. However, a key challenge is selectivity of products with typical processes producing NH_3, nitrates (NO_3^-), and nitrites (NO_2^-).

In this work, we studied direct-current plasma in contact with an electrolyte solution. Various products were characterized in the liquid phase including NH_3, NO_3^-, NO_2^-, as well as hydrogen peroxide (H_2O_2). To control the product selectivity, various conditions were mapped including gas feed, cathodic vs. anodic polarity, and pH. Our most promising result was that the pH and more generally, the electrolyte composition, was found to greatly influence the product distribution. At low pH, the product distribution shifted more to the reduced form, NH_3, and at high pH, the distribution shifted more to the oxidized form, NO_3^-, We also found a strong effect on the presence of O_2 (in air) and humidity. These results can be used to selectively synthesize nitrogen products, elucidate product formation mechanisms, or to inform scale up of similar plasma-liquid systems for sustainable nitrogen fixation.

8:40am **PS+SE-FrM-2 Two Atmospheric Pressure Plasma Jets Driven by Phase-Shifted Voltages: A Method to Control Plasma Properties at the Plasma–Surface Interface***, **Michael Johnson,*** Huntington Ingalls Industries*; G. Brown,* University of Texas, Austin*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory

Atmospheric pressure plasma jets project plasma away from their electrodes, enabling the treatment of remotely located surfaces, and making them appealing for a diverse range of surface treatment applications. However, their small effective areas pose a challenge to broader adoption and utilization. To circumvent this limitation, multiple plasma jets can be used in tandem to increase their effective area. The objective of this study is to examine the interactions between two plasma jets and leverage this relationship to manipulate plasma properties at the plasma-surface interface. The jets are positioned at a 130° angle from each other, converging at the surface of a glass substrate. Each jet is driven by an individual piezoelectric transformer, powered by identical but phase-shifted voltage waveforms, which provides precise control over their relative timing and influence plasma properties. As phase difference between the two jets is varied the jet behavior changes from a regime where the two jets repel each other to a regime of enhanced jet interaction, resulting in an expanded effective area for the plasma. Interestingly, increasing this phase difference led to reduced power consumption while simultaneously enhancing electron density at the intersection point. Consequently, this technique of utilizing phase-shifted jets presents a method for increasing the effective area of the plasma and controlling plasma properties at an interface, potentially benefiting a wide array of applications.

This work supported by the Naval Research Laboratory Base program

9:00am **PS+SE-FrM-3 Plasma Chemistry in Atmospheric Pressure Gases and Liquids: Fundamentals and Novel Applications***, **Alexander Fridman,*** Drexel University, Nyheim Plasma Institute **INVITED**

The presentation is focused on fundamental and applied aspects of the non-equilibrium plasma chemical processes performed in high pressure gases and liquids. As an example of the gas-phase processes, the plasma synthesis of NO from atmospheric pressure air is considered, with especial attention on minimizing energy cost of the process. As an example of the plasma-chemical processes in liquid water, the PFAS abatement in considered with especial attention to complete mineralization of these important impurities. As an example of plasma chemistry in cryogenic liquids, the plasma synthesis of polymeric nitrogen is considered. The process is accomplished in liquid nitrogen using the nanosecond-pulsed discharges organized with creation of bubbles during the synthesis.

9:40am **PS+SE-FrM-5 Integrated Circuit Manufacturing with Plasma Activated Chemical Treatment (IMPACT): Effect of Plasmas on Photoresist and Cleaning Solutions in Semiconductor Processing***, **Christian Williams,** S. Dubowsky, D. Curreli, M. Sankaran, D. Ruzic,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas open various chemical and material applications because of their ability to be in contact with temperature-sensitive surfaces such as plastics and liquids. In this work, we investigated the potential of plasmas to modify two key components of semiconductor processing [1]: the photoresist and cleaning solution used to remove the photoresist after lithographic exposure. Two different plasma sources were used in experiments, a dielectric-barrier discharge and a pulsed direct current discharge jet. Characterization of the gas phase was performed by optical emission spectroscopy (OES) and the chemical modification of the treated solutions was examined using ion chromatography (IC). Ultraviolet-visible (UV/Vis) spectroscopy was also used to measure OH radical concentrations in the treated samples. In parallel, a reaction network was constructed using CRANE, a MOOSE-based tool for plasma chemistry modeling. Simulations provided the concentrations of species which could then be compared to experiments to understand potential reaction mechanisms.

10:00am **PS+SE-FrM-6 Increasing Adhesion of Polyurethane Painting on Aluminum by Atmospheric Pressure Plasma Jet Treatment***, **Jorane Berckmans,** C. Tubier,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium*; R. Revilla Castillo,* Research Group Electrochemical and Surface Engineering (SURF), Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*; C. Poleunis,* Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, Louvain-la-Neuve, Belgium*; H. Terryn,* Research Group Electrochemical and Surface Engineering (SURF), Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*; A. Delcorte,* Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, Louvain-la-Neuve, Belgium*; F. Reniers,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

Nowadays, industries are looking for replacement of chromium VI in aluminum pretreatment. In this quest, plasma treatments could represent an interesting approach. Indeed, atmospheric plasmas enable a wide range of possible modifications of materials (etching, grafting, surface functionalization) but also allow an easy industrial upscale.[1,2]

In this work, aluminum 99,99% surfaces were modified by an atmospheric pressure plasma jet (APPJ) and the effect on polyurethane paint adhesion was studied. The difference in wettability, chemistry and roughness induced by plasma treatments were investigated by water contact angle, X-ray photoelectron spectroscopy and atomic force microscopy respectively. In parallel, optical emission spectroscopy (OES) was used to characterize the plasma phase. The correlation between plasma species, identified by OES, and the resulting surface modification was investigated. Then, the adhesion of the polyurethane coatings on the plasma-modified surfaces was studied by a tape test according to ASTM D3359. The coating – aluminum substrate interface has been also characterized by Tof-SIMS, to identify specific fragments characteristics for bonding.

Different plasma sources were used, with different plasma conditions (PlasmaTreat Openair FG5001, 2 bars of dry air, at varying distances from 5 mm to 10 mm and treatment times of 0,5 to 60,0 s by tuning the number of scans and the scan rate of the APPJ over the surface, SurfX Atomflo 600, with 30,0 L/Min of Ar at varying flow of oxygen from 0,00 to 0,60 L/ Min, distance from 5 mm to 30 mm and treatment times of 0,04 s to 25 s by tuning the number of scans and the scan rate of the APPJ over the surface). Varying humidity containing in plasma, by water injection, was also studied with the SurfX Atomflo 600.

It is shown that, for most of the plasma treatments used, an increase of the adhesion of polyurethane coatings is observed (Fig. 1) and associated with the surface modification of the aluminum and with the plasma chemistry.

References

[1] H. Butt, K. Graf, M. Kappl, Phys. Chem. Interfaces 2013, 28,1379.

[2] K. G. Kostov, T. M. C. Nishime, A. H. R. Castro, A. Toth,L. R. O. Hein, Appl. Surf. Sci. 2014, 314, 367.

Acknowledgements

This work is partly supported by the ULB-VUB "joint research group" fund.

10:40am **PS+SE-FrM-8 Fundamentals of Atmospheric Pressure Discharges for Plasma Catalytic Applications***, **Judith Golda**, D. Steuer, R. Labenski, H. van Impel, M. Böke, V. Schulz-von der Gathen,* Ruhr-University Bochum, Germany **INVITED**

A central challenge of our time is the energy transition from fossil energy sources to renewable ones. Plasma catalysis is one of the promising techniques that has been proposed to contribute to this transition. Research shows that synergies between classical catalysis and plasma processes can be obtained due to the distinct non-equilibrium character of atmospheric pressure plasmas and their interaction with surfaces. However, the underlying mechanisms are hard to entangle as typical reactor designs for plasma catalysis are packed bed reactors. While advantageous for industrial processes, the diagnostics of these reactors is challenging.

In this talk, we give an insight into the diagnostic challenges of plasmas for catalysis as well as possible approaches to overcome them. We will discuss alternative reactor designs for fundamental studies such as micro-structured surface dielectric barrier discharges. We will give an overview of global and local diagnostic techniques: Current-voltage characteristics for dissipated plasma power and estimation of electron densities, emission-based techniques for reactive species densities such as atomic oxygen (state-enhanced actinometry) or temperature (rotational bands), and electric field estimation (Stark splitting and shifting).

This research is funded by the German Research Foundation within CRC 1316 in project A6.

11:20am **PS+SE-FrM-10 Atmospheric Pressure Inductively Coupled Torus Torch System for 3D Printing the Silicon-Nanofiber (Si/CNF) Anodes for Li-ion Batteries***, **Yuri Glukhoy**,* Nanocoating Plasma Systems Inc*; M. Ryaboy,* UC Berkeley

Our approach to environmentally-friendly manufacturing low-cost Si anodes with the core-shell heterostructure includes 3D plasma beam printing. Excitingly, because of the merits of low price, high doping content, and no toxic emission during the process, Si sawdust, which is a waste of the solar cell industry, can be a fascinating raw material for Si shells with well-tailored functions and electrical properties. However, the transition of the Si sawdust requires a long resident time in the high-temperature plasma and a high RF power to sustain it. We offer a new method of generation of Si vapor and the simultaneous lamination of CNFthrough the recirculation of both Si and CNF in the high-temperature torus plasma torch. It allows the incremental sublimation of Si particles, while Si vapor is deposited in the fly on the fibers' preheated surfaces. This torus torch recirculated in the high-temperature doughnut-like reactor is generated by two tangentially injected in the opposite direction axial atmospheric plasma beams in the swirling mode. Besides the high-temperature plasma species, these beams are designed to bring the liquid Si droplets from the melted Si powder injected into the high-temperature plasma discharge generating such a beam.Two inductors with transversal RF fields are positioned on the opposite sides of the doughnut and surround this profile. They boost this torus plasma torch, increasing the plasma density and current until its magnetic field pinches into the high-temperature plasma cord. But RF power applied to the inductor should be limited to avoid melting the CNF at 3550 °C. This recirculation process in the high-temperature plasma reactor should provide a conformal Si lamination of CNF in the fly to achieve the Si shell's thickness of around 1 um. Two outlets are welded to this doughnut to extract the Si/CNF composites and generate the plasma sprays. Ended with the nozzles and directed to the opposite sides of the copper tape serving as a current collector, they provide 3D printing of the Si/CNF anodes in the roll-to-roll mode.

11:40am **PS+SE-FrM-11 Design and Functionality of a Low-Frequency Pulsed Plasma System***, M. Gulan,* Technological University Dublin, Ireland*; **Vladimir Milosavljevic**,* Technological University Dublin, Ireland & Faculty of Physics, University of Belgrade, Serbia, Ireland

This study presents the design and functionality of a kHz pulsing plasma generator at atmospheric pressure, which can be used for a range of applications, such as sterilization in food processing or plasma-based treatments for biological samples. This next generation plasma system is developed to operate in ambient air or on an argon/helium/oxygen/nitrogen gas mixture at atmospheric pressure, making it suitable for a range of applications such as surface modification, plasma-based sterilization, and material processing. The system's unique design allows for improved efficiency, higher plasma density, and greater control over plasma parameters compared to previous systems. The plasma tool is particularly suitable for sensitive and fragile materials. This work describes the development and operation of a non-thermal, dielectric-free atmospheric plasma system designed for use in surface treatment and modification applications. The system was developed in-house to meet the specific technological needs, and includes detailed information on the design and operating parameters of the system. The new plasma system allows an increase in the plasma-surface interaction selectivity and reduces plasma induced damages to the surface. The innovative design of our plasma system led to the development of unique plasma parameters that are not currently available on the market. Specifically, the system allows for precise control of plasma temperature, density, and composition, which are essential for effective plasma treatment of a range of materials. These unique parameters were designed with the goal of simplifying plasma treatment in industrial applications such as surface modification, cleaning, and sterilization, where precision and efficiency are critical factors for success. The system creates a plasma discharge in gap from 5 to 60 mm in space of hundreds of cm^2. The plasma source is based on a pulse resonance circuit which allows the creation of high voltage pulses with the ability to control and reduce a current of the plasma discharge. The study also includes different setting of plasma source to control the ion flux, the ion energy and the plasma chemistry. Plasma pulsing allows new domains of ion energy and radical fluxes to be reached, thereby extending the operating range of plasma generators. The plasma diagnostics in this work include the absorption spectra of oxygen and nitrogen based molecules and their dependence on the process parameters such as duty cycle, discharge frequency, pick-to-pick voltage, etc.

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