

Thursday Afternoon, November 13, 2014

Plasma Science and Technology
Room: 308 - Session PS+SE-ThA

Atmospheric Pressure Plasma Processing; Fundamental and Applications

Moderator: Richard van de Sanden, DIFFER, Stefan Welzel, FOM Institute DIFFER

2:20pm **PS+SE-ThA1 Insights into the Chemistry of Atmospheric Pressure Plasma Deposition Processes**, *Fiorenza Fanelli*, Institute of Inorganic Methodologies and Plasmas - National Research Council, Italy, *P. Bosso, A.M. Mastrangelo, F. Fracassi*, University of Bari 'Aldo Moro', Italy **INVITED**

Over the last decade there have been considerable advances in the utilization of atmospheric pressure cold plasmas for thin film deposition. Intense research efforts have been made to develop a large variety of processes which exploit different types of atmospheric pressure discharges for the direct and remote deposition of thin films from monomers in gas, vapor and aerosol form [1]. However diagnostic studies of the plasma chemistry and mechanistic investigations of thin film growth are still scarce, while being crucial prerequisite for further process optimization. The research should be addressed to detect the film precursors, to identify the main reaction pathways (both homogeneous and heterogeneous processes) and to clarify the plasma-surface interaction.

In this contribution, our studies on thin film deposition by dielectric barrier discharges (DBDs) will be presented to provide insights into the chemistry of atmospheric pressure plasma processes. Examples discussed will include the investigation of the role of the monomer chemical structure in the plasma-enhanced chemical vapor deposition of organosilicon coatings from different methylsiloxanes [2], and the study of the influence of air and water vapor feed gas impurities in the deposition of fluorocarbon coatings from argon-hexafluoropropene fed DBDs [3]. Our recent work on the deposition and characterization of organic-inorganic hydrocarbon polymer/ZnO nanoparticles nanocomposite coatings by a DBD fed with helium and the aerosol of a dispersion of oleate-capped ZnO nanoparticles in hydrocarbon solvents will be presented [4]. Results from the plasma jet co-deposition of acrylic acid and ethylene towards water-stable coatings containing carboxylic functionalities will be also shown.

The overall deposition mechanisms will be outlined on the basis of the results from the chemical and morphological characterization of the coatings, the optical emission spectroscopy investigation of the plasma phase, the analysis of the exhaust gas by means of gaschromatography-mass spectrometry. The latter is a powerful *indirect* diagnostic technique of the gas phase which allows the assessment of the monomer depletion and the quali-quantitative determination of stable byproducts formed by plasma activation.

[1] F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naudé, N. Gherardi, *Plasma Process. Polym.*, 9, 1041 (2012).

[2] F. Fanelli, S. Lovascio, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.*, 9, 1132 (2012).

[3] F. Fanelli, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.*, 8, 557 (2011).

[4] F. Fanelli, A. M. Mastrangelo, F. Fracassi, *Langmuir*, 30, 857 (2014).

3:00pm **PS+SE-ThA3 Understanding Charge Transfer Reactions at a Plasma-Liquid Interface**, *Paul Rumbach**, University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University, *D.M. Bartels, D.B. Go*, University of Notre Dame

The interaction of atmospheric-pressure plasma jets with liquids is becoming increasingly important for medical and materials applications. Despite empirical evidence of reactions occurring both in the bulk plasma and liquid phases, a basic understanding of the chemistry, particularly at the interface of the plasma and liquid, remains poorly understood. Previous studies have shown that species produced in the plasma phase such as nitric oxide (NO) and hydroxyl radicals (OH) can solvate in the liquid, yielding products such as nitrous acid (HNO₂) and hydrogen peroxide (H₂O₂) in the bulk solution [1]. In addition, we have recently shown that charge can be transferred from a DC microplasma jet into an aqueous solution to promote electrolytic reduction reactions [2]. However, it remains unclear how these

charge transfer reactions occur and, in particular, if plasma electrons solvate in the liquid before subsequently reducing solution species.

To clarify the role of electrons solvating at a plasma-liquid interface, we have designed and built an experiment to detect solvated electrons using optical absorption spectroscopy. Electrons solvated in aqueous solutions are well known to absorb strongly in the red. Initial models suggest that because of the short lifetime of solvated electrons in aqueous solutions (~1 μs) and anticipated solvation depths on the order 10 – 100 nm, optical absorption will be on the order of one part in 10⁶, making this an inherently challenging measurement. In this presentation, we will give an overview of our experimental method and present preliminary findings on direct measurements of electron solvation.

[1] P. Rumbach, M. Witzke, R. M. Sankaran, and D. B. Go, *J. Am. Chem. Soc.* **135** 16264-16267 (2013).

[2] M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, *J. Phys. D: Appl. Phys.* **45** 442001 (2012).

3:20pm **PS+SE-ThA4 A Novel Atmospheric Pressure Plasma Application for Fuel Tank Inerting**, *Matthew Price, A. Srivastava*, Interspace, Inc.

Aircraft fuel tanks have traditionally been protected from ballistic threats caused from explosive vapors by filling the area above the fuel with suppressant foam or inert gas. More recently fuel tank inerting systems have been developed for commercial transport aircraft. Inert gas is the preferred method since foam is heavy, reduces fuel tank capacity and is expensive to maintain. Current solutions consist of Onboard Inert Gas Generation Systems (OBIGGS) to reduce oxygen content in fuel tanks through the use of nitrogen-air separators. These membrane-based separators require high-powered pumps to flow air through small pores in the membranes. OBIGGS systems are bulky and too power hungry to be practical for smaller aircraft with multiple fuel tanks and limited electrical power. INTERSPACE has developed an innovative and efficient inerting system that does not rely on a pre-stored inerting agent or bleed air and is scalable to support multiple independent tanks. The system requires minimal electrical power and is capable of inerting to trace oxygen concentration levels without contaminating the fuel.

Our solution uses a getter material to readily sequester oxygen as surface oxides. A non-thermal, atmospheric pressure plasma then combines hydrocarbons in the tank with the getter to reduce the oxide and reverse the process to form water vapor. No consumable inerting product is used. Experimental data shows the getter absorbs 20 times its volume in oxygen before saturation. Scaling up this reaction would inert a 500 gallon fuel tank in 11.4 minutes with one liter getter at standard temperature and pressure conditions. Time-to-inert decreases at higher altitudes due to lower pressure. Time-to-inert curves were calculated for the typical aircraft flight envelope based on this model. We have successfully demonstrated the feasibility of our inerting system in a laboratory environment. Our inerting system is highly selective to oxygen, and eliminates the membranes and high power pumps used in existing systems. The next step will be to evaluate a prototype system through demonstration testing on the replica of a military aircraft fuel tank system. A customized plasma source will be developed optimized in size and weight competitive with aircraft applications.

4:00pm **PS+SE-ThA6 In Situ Diagnostic Studies of CO₂ containing Dielectric Barrier Discharges**, *Stefan Welzel*, FOM Institute DIFFER; Eindhoven University of Technology, Netherlands, *F. Brehmer*, Eindhoven University of Technology; AFS GmbH, Germany, *B.L.M. Klarenaar*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM Institute DIFFER; Eindhoven University of Technology, Netherlands, *R. Engeln*, Eindhoven University of Technology, Netherlands

Carbon dioxide will be a key enabler for the integration of renewable energy into a future CO₂ neutral energy system as well as into chemical industry. The application of non-equilibrium plasmas offers a promising route to overcome the initial energy-demanding CO₂ dissociation step. Through subsequent hydrogenation of the CO produced, gaseous or liquid hydrocarbon(ate)s are synthesised. Dielectric barrier discharges (DBDs) are known as useful tools in plasma-assisted gas conversion. The main objective was to unravel main reaction mechanisms in CO₂ containing DBDs through combination of several *in-situ* diagnostic techniques.

Optical emission spectroscopy, (infrared) absorption spectroscopy along with rotational Raman scattering were employed to study the CO₂ conversion and deduce gas temperatures in mid-frequency (kHz) driven DBDs at elevated pressures. To study the kinetics of CO formation the DBD was additionally operated in pulsed mode. Absolute densities of CO, O₂ and O₃ were established downstream the plasma reactor. The CO yield

* Coburn & Winters Student Award Finalist

was typically below 5% for gas flow rates that would allow reasonable throughput. The generally weak emission of electronically excited species (CO_2^+ , CO) was monitored during individual AC cycles. Additionally, phase- and time-resolved signals of ro-vibrational absorption lines of CO and CO_2 in their (electronic) ground state were detected by quantum cascade laser absorption spectroscopy. In contrast to emission, the CO absorption remained constant throughout individual AC cycles. The modulation of CO absorption signals during pulsed operation can be successfully modelled by considering the power density of the DBD, the reactor wall and gas temperatures (up to 550 K), and the residence time of the gas along with the reactor geometry.

The results suggest electron-impact CO_2 excitation and ionisation followed by potentially surface enhanced recombination. The stoichiometric $\text{CO}:\text{O}_2$ ratio is described by a uniform trend as function of the number of charges transferred during the residence time of CO_2 in the active plasma zone.

4:20pm **PS+SE-ThA7 Effect of the Nature of the Plasma Gas on the Resulting Chemistry of Atmospheric Plasma Deposited Coatings and of Plasma Treated Gases**, *D. Merche, N. Vandencastele, A. Ozkan, J. Hubert, François Reniers*, Université Libre de Bruxelles, Belgium

In atmospheric plasma processes, the use of a main gas, usually considered as inert, to sustain the plasma is common. Nitrogen, argon and helium are the most regularly used gases. If the nature of the gas has a strong influence in the breakdown discharge voltage (due to Paschen Law), it also leads to plasmas which are optically and electrically different. This has drastic consequences on the chemistry and structure of plasma deposited coatings and on the chemistry of plasma treated gases. In this study, we compare, and try to explain, the results obtained on different topics using either argon or helium as main plasma gas.

All experiments have been conducted in dielectric barrier discharge reactors, powered with sinusoidal AFS generators, operating at frequencies lower than 40 kHz. For all the studies the reactors have been pumped down to evacuate contaminations and then backfilled with the plasma gas (Ar or He). The precursor is then injected in the DBD through the appropriate flow of the carrier gas.

Internal chemistry of coatings :

Through a combined XPS, FTIR and SIMS study, it is shown that the degree of cross-linking, the branching and the number of insaturations of plasma-polymerized polystyrene or sulfonated polystyrene (for fuel cell applications) is higher with argon than with helium, whereas the density of aromatics exhibits the opposite behavior.

Surface roughness of coatings

Similarly, for all the organic coatings synthesized by a dielectric barrier discharge (PS, CFx from C_6F_{12} , PA), the roughness, determined by AFM is always higher with argon than with helium.

Conversion of CO_2 by DBD

Finally, the conversion rate of CO_2 into CO in atmospheric plasma conditions (DBD), is higher when argon is the main plasma gas than with helium.

It is suggested that all these effects are strongly related to the plasma operating mode and to the energy distribution inside the plasma.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency

4:40pm **PS+SE-ThA8 Diagnostics of an Atmospheric-Pressure dc Glow Plasma in Contact with Solution: Insight into Plasma-Liquid Interaction**, *Koichi Sasaki*, Hokkaido University, Japan **INVITED**

The interaction between an atmospheric-pressure plasma and a liquid attracts much attention in conjunction with plasma-aided medical treatments and plasma-assisted agriculture. Major interests are the production and the transport of OH radicals in plasmas in contact with liquids. In this work, we examined the spatial distribution of the OH radical density in the gas phase of a dc glow plasma produced between a stainless-steel nozzle as the anode and electrolyte of NaCl solution as the cathode by laser-induced fluorescence (LIF) imaging spectroscopy. We were careful about the influence of collisional quenching and the rotational temperature in deducing the spatial distribution of the OH radical density from the LIF images.

The maximum rotational temperature was approximately 3000 K, which was observed in the plasma column in contact with the electrolyte surface. The frequency of collisional quenching was also high in the contacting region to the electrolyte surface, suggesting that the dominant quencher of the excited state of OH was water vapor. The absolute density of water vapor was evaluated from the quenching frequency and the rate coefficient of collisional quenching. It was found that the partial pressure of water vapor was more than five times higher than the saturated vapor pressure of water at room temperature.

The OH radical density was high in the neighboring region to the electrolyte surface, suggesting that water vapor produced from the electrolyte is the parent of OH radical. However, the peak of the OH radical density was separated from the electrolyte surface, and also the OH radical density on the electrolyte surface was not zero. It is noted that, if OH radicals are not reactive on the electrolyte surface, the decrease in the OH density toward the electrolyte surface would not be observed. On the other hand, if OH radicals are too reactive in the gas phase, the OH radical density on the electrolyte surface would become zero (Note that the production of OH in the cathode sheath is negligible), and in this case we cannot expect the interaction of OH radicals with the electrolyte. The axial distribution of the OH density observed in this work indicates that the electrolyte surface interacts with OH radicals as their sink. In other words, OH radicals are lost on the electrolyte surface. A possibility of the loss process is recombination to form hydrogen peroxide and water. In addition, we can also expect the transport of OH radicals into the inside of the electrolyte.

5:20pm **PS+SE-ThA10 Absolute Measurements of Short Lived Reactive Species in Cold Atmospheric Pressure Plasmas**, *Deborah O'Connell, K. Niemi, J. Dedrick, S. Schroeter, J. Bredin, A. West, E. Wagenaars, T. Gans*, University of York, UK

Low temperature plasmas are emerging as an exciting development for therapeutics. The unique properties of cold non-equilibrium plasmas have enormous potential in disease therapeutics and plasma pharmacology as drug alternatives. Applications of these plasmas include surface sterilization and bacterial decontamination, biofilm inactivation, antimicrobial treatment in food preservation, wound healing, to cancer treatment.

Non-equilibrium plasmas, operated at ambient atmospheric pressure and temperature, are very efficient sources for highly reactive neutral particles e.g. reactive oxygen and nitrogen species (RONS) (such as atomic oxygen, atomic nitrogen, hydroxyl radical, superoxide, singlet delta oxygen, nitrogen oxides), charged particles, UV-radiation, and electro-magnetic fields. Individually many of these components have been implicated in therapeutics. RONS are known to play a crucial role in biological systems, such as signalling, and generating oxidative damage to a variety of cellular components, which can ultimately lead to cell death. Plasmas have the advantage of delivering these simultaneously providing potentially superior processes.

Transport of the plasma components to the target is complex. In the core plasma production region a large, but defined, number of species can be created (including for example O, N, NO, O_2^-). As the plasma interacts with ambient air new reactions and components are formed. Upon interaction with either humidity or liquid layers on biological samples new species of varying lifetimes can be created (e.g. OH, H, H_2O_2 , ONOO $^-$). Energy dissipation at these interfaces is important and to date unclear.

In order to understand the chemical kinetics and plasma-liquid-biological interaction mechanisms measurements of the relevant RONS are key. Measurements and simulations under this atmospheric pressure environment are challenging, primarily due to the multi-phase (solid, liquid, gas and plasma), strongly non-equilibrium with large gradients (e.g. in electric field), high collisionality, thus requiring extremely high temporal (picosecond to nanosecond) and spatial (microns) resolution.

Two advanced optical diagnostic techniques are applied, and will be presented, to measure absolute radical densities: Pico-second two-photon absorption laser induced fluorescence (ps-TALIF) and high-resolution synchrotron VUV absorption spectroscopy will be presented. Radicals measured in an atmospheric pressure plasma operated in helium with varying admixtures of oxygen, nitrogen and water vapour will be presented.

5:40pm **PS+SE-ThA11 Recent Progress in the Diagnostics of Microwave Discharges for Optimization of CO_2 Dissociation**, *Tiago Silva, N. Britun, T. Godfroid, R. Snyders*, University of Mons, Belgium

The increase in global emissions of carbon dioxide (CO_2) due to fossil-fuel combustion and other energy-related human activities is strongly related with the global warming issue. Due to this effect, the study of CO_2 dissociation process is a highly demanding topic, which requires attention and efficient solutions. Among the proposed strategies, one possible way to limit CO_2 emission is to use plasma technology to break the CO_2 molecule into oxygen (O) and carbon monoxide (CO), which can be later used for production of valuable chemicals, e.g. for the fuel synthesis (syngas).

Recently, energy-efficient powerful plasma-chemical systems have been developed based on microwave plasmas. These discharges are often generated using electromagnetic waves in the range of 300 MHz to 10 GHz, and can operate over a wide range of conditions of pressure and power. In particular, microwave surfaguide discharges (MSGD) where the gas flow in the discharge tube is perpendicular to the waves propagation, are proven to be good solution for an efficient molecular dissociation of di- or multi-atomic species [1].

In this work, the recent results on CO₂-containing MSGD operating at 0.9 GHz and 2.45 GHz in pulsed and continuous regimes are presented. The plasma is sustained in CO₂ and CO₂+N₂ flowing gas mixtures in a quartz tube crossing a copper waveguide. The microwave discharges are characterized in terms of various plasma parameters using various optical emission spectroscopy (OES) methods. In particular, the characteristic plasma temperatures, such as the gas temperature (via CO rotational spectra), and vibrational temperature (via N₂ vibrational bands) are determined as a function of time at different axial positions along the gas flow in the discharge tube. The CO₂ conversion rate in the discharge volume, along with the measurements of plasma energetic efficiency of such conversion is performed by means of optical emission actinometry. The results of the time- and space- resolved OES measurements demonstrate a non-uniform dissociation rate of CO₂ along the gas propagation direction in the discharge. As a result, the dissociation degree can be substantially modified by varying the power balance and the composition of the gas mixture [2]. In addition, in order to get a complete picture of the process, gas chromatography measurements were performed in the post discharge region. The obtained integrated results allow better understanding the μ wave plasma-based dissociation of CO₂.

[1] T. Godfroid, J. P. Dauchot and M. Hecq, *Surf. Coating Technol* **174-175** 1276-1281 (2003)

[2] T. Silva, N. Britun, T. Godfroid, R. Snyders *Plasma Sources Sci. Technol* **23** 025009 (2014)

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