Monday Morning, November 7, 2016

Plasma Science and Technology
Room 104D - Session PS+SE-MoM

Atmospheric Pressure Plasma Processing

Moderator: Lorenzo Mangolini, University of California Riverside

9:00am **PS+SE-MoM3 Fundamental Characterization of a Low Frequency, Ambient Air, Plasma Jet Discharge***, **Vladimir Milosavljevic**,* Dublin Institute of Technology, Ireland*; L. Scally, J. Lalor, P.J. Cullen,* Dublin Institute of Technology

Plasma discharge in open air has charged species, energetic photons, active radicals, and also a low degree of ionization gas. Interaction of such plasma with surfaces has been a subject of intense study for many decades. In particular, an atmospheric jet plasma system used to solve surface preparation problems. The biggest advantages of such a system are: high density plasma in contrast to corona discharge, no electrical current or filamentary streamers in the plasma jet, broad material application capability, simple host automation integration, low environmental impact, and low thermal load allows low melting point polymers to be treated. Despite the widespread usage of plasma jet technology, it remains largely unknown whether atmospheric plasma maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. In this work optical spectroscopy was used as a diagnostic method due to its non-intrusive nature. In additional to this, surface metrology based on a measurement of the water contact angle (WCA) and surface energy was also engaged.

In this study a high pressure (6 bar) atmospheric plasma jet system, which operates with ambient air chemistry, was employed. The plasma jet operated at a frequency of 60 Hz and used a pencil type beam applicator. The low operation frequency makes this system significantly different from a vast majority of other plasma jets. Namely, at low frequencies (<50 kHz) ions and electrons both oscillate and therefore both contributed in interaction with surfaces. At high frequencies (>50 kHz) heavy ions cannot follow switching fields and therefore only electrons oscillate while ions are relatively stationary which has a huge impact on the plasma sheath dynamics.

The polymer used in this work was polyethylene terephthalate (PET) and was widely used in a variety of industries from food packaging to the electrical, electronics, and biomedical industries. PET could be easily thermally damaged at relatively low temperatures and so a delicate balance must be reached where surface activation of the polymer was maximised, while thermal damage was prevented. The level of polymer surface activation was evaluated based on changes to the WCA of PET samples after plasma treatment. A direct correlation was obtained between the polymer WCA changes and the OES measurement. This correlation may indicate that OES peak intensities can be used as an indicator of the treated polymer WCA, without the need for conventional off-line metrology.

This work was a funded by SFI under the PlasmaGrain project.

9:20am **PS+SE-MoM4 CO_2 Splitting by Dielectric Barrier Discharge at Atmospheric Pressure: Understanding the Influence of Electrical Regimes and Electrical Configurations***, **Alp Ozkan**, T. Dufour,* Université Libre de Bruxelles, Belgium*; A. Bogaerts,* University of Antwerp, Research group PLASMANT, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) are commonly used to generate cold plasmas at atmospheric pressure. In this experimental work, a flowing tubular DBD is used for the CO_2 splitting into O_2 and CO. The influence of the frequency (from 16 to 28 kHz), the power (from 30 to 100 W), the role of the barrier thickness (2.0, 2.4 and 2.8 mm), the kind of dielectric material (alumina, mullite, pyrex, quartz), and the effect of a pulsed AC discharge (so-called burst mode) are investigated on the filamentary behavior of the plasma and on the CO_2 conversion, by means of mass spectrometry measurements correlated with electrical diagnostics. Their influence on the gas and electrode temperature is also evidenced through optical emission spectroscopy and infrared imaging. A new methodology is developed to investigate the microdischarge properties. For this purpose, electrical measurements, based on a numerical method, are carried out to explain the conversion trends and to characterize the microdischarges through their number (N_{md}), their lifetime (L_{md}), their intensity (i_{pl}) and the induced electrical charge (Q_{pl}) for a given analysis time. These extracted data are usually underestimated or poorly described in literature.

It is shown that, when the applied power is modified, the conversion depends mostly on the Q_{pl} and not on the effective plasma voltage ($V_{pl,eff}$). Similarly, a better conversion is observed at low frequencies, where a more diffuse discharge with a higher $V_{pl,eff}$ than at higher frequency is obtained. Moreover, increasing the barrier thickness decreases the capacitance while preserving the electrical charge. As a result, the voltage over the dielectric (V_{diel}) increases and a larger N_{md} is generated, which enhances the CO_2 conversion. Furthermore, changing the dielectric material of the barrier, while keeping the same dimensions, also affects the conversion. The highest CO_2 conversion and energy efficiency are obtained for quartz and alumina. From the electrical characterization, we clearly demonstrate that the most important parameters are the somewhat higher $V_{pl,eff}$ (yielding a higher electric field and electron energy involved in CO_2 dissociation) for quartz, as well as the higher plasma current (thus larger electron density) and the larger N_{md} (mainly for alumina due its higher roughness, but also for quartz due to its higher V_{diel}). Finally, a comparison between DBD ignited in burst mode and pure AC mode is achieved. Decreasing the duty cycle from 100% (pure AC mode) to 40% leads to a rise in the conversion due to a larger N_{md} and a higher voltage.

9:40am **PS+SE-MoM5 Effect of Structural Variations of the Monomer on the Fast Synthesis of Highly Oxygenated Coatings in an Argon DBD***, **Jérémy Mertens**, F. Reniers,* Université Libre de Bruxelles, Belgium

The use of atmospheric plasma DBD for the synthesis of organic coatings has recently become more and more popular. Their unconventional polymerization pathways allow the synthesis of brand new polymers with specific properties which are strongly dependent on the chemical structure of the injected monomer[1,2].

The goal of this research is the development of an intermediate coating presenting a high surface energy with an important deposition rate in order to improve the adhesion of a resin on aluminum by DBD. Because of their initial structure, anhydrides are seen as ideal candidates for the synthesis of such films. We here present how small variations in their chemical structure can affect their behavior in the discharge and the chemical properties of the coatings. Firstly, the influence of the C/O ratio in the injected monomer is investigated by the use of acetic, propionic and butyric anhydride. The addition of double bonds in the initial structure of the precursor is then studied using isobutyric and methacrylate anhydride. Surface analyses such as infrared spectroscopy (IRRAS), X-Ray Photoelectron spectroscopy (XPS) and stylus profilometry showed that highly oxygenated coatings could be synthesized when the C/O ratio of the injected monomer was decreased. Nevertheless, high deposition rates could only be reached with the addition of double bonds in the structure of the monomer. By combining these observations with oscilloscope and mass spectrometry measurements of the discharge, a fragmentation/recombination polymerization is suggested for the non-conventionally polymerizable monomers. On the contrary, a mainly radical propagation through the double bonds is proposed for the methacrylate anhydride. The amount of carboxylic components on the surface can be tuned by the addition of an Ar-O_2 post-treatment but is limited by the degradation of the films that leads to the formation of oxidized volatile compounds.

This work was financially supported by the Walloon Region (FLYCOAT project n°131847) and by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

[1] J. Hubert & *al.*, *Journal of Materials Research,* **2015**, 30, 21, 3177-3176

[2] A. Batan & *al., Plasma Processes and Polymers,* **2013**, 10, 857-863

10:00am **PS+SE-MoM6 Quantitative Study of Plasma Electrochemical Reduction of Aqueous Metal Salts***, S. Ghosh, A. Aube, R. O'Toole, R. Hawtof, **R.Mohan Sankaran**,* Case Western Reserve University

The possibility of combining ionized gases and ionic solutions to initiate electrochemical reactions in solution with a plasma electrode has been explored for over 100 years. Recently, this idea has been the basis of numerous reports of metal nanoparticle formation when aqueous solutions of metal salts are exposed to a plasma. While this approach has been successfully demonstrated by a range of plasma sources and experimental conditions, the chemistry behind the reactions between plasma and solution species is highly complex and remains poorly understood.

Here, we report quantitative studies of the reduction of aqueous metal salts by a plasma electrode to better understand the reaction kinetics and thermodynamics, analogous to conventional electrochemistry. Kinetic studies were performed by measuring the rate and efficiency of the reduction of a metal salt, silver nitrate. Analogous to weight measurements in electrodeposition of metal thin films, we developed a methodology to measure the mass of the final product, silver (Ag) nanoparticles, by separating the agglomerated particle powder. The reduction efficiency was defined as the actual amount of reduced Ag compared to that predicted by Faraday's law based on the plasma current. We find that in ambient air, the faradaic efficiency for silver nitrate reduction is approximately 80%, and, curiously, the efficiency increases to >100% in a closed reactor cell with an Ar ambient. We interpret these results as follows. Assuming that the chemistry in solution is driven by electrons from the plasma which are directed into solution and can solvate, in ambient air, there is a decrease in the electron flux to the solution because of electron attachment processes involving O_2 gas. Removing air with ambient Ar increases the electron flux and, thus, increases the faradaic efficiency. The surprising efficiency of more than 100% most probably results from an autocatalytic effect whereby reduced Ag (Ag^0) also reduces Ag^+, a mechanism that has been previously reported in radiolytic synthesis of Ag nanoparticles. The thermodynamics of the reduction process was probed by studying a series of metals which have different reduction potentials including copper, iron, and zinc. Successful reduction of the corresponding metal salts for these metals suggests that solvated electrons, which are one of the strongest reducing species, are involved. We will also discuss the respective reduction rates and efficiencies of these metals as compared to Ag.

10:40am **PS+SE-MoM8 LDPE Modified by an Ar/H_2O Dielectric Barrier Discharge: Correlation between Texturization, Wettability and Grafting of Oxygen***, **Stéphanie Collette,*** Université Libre de Bruxelles, Belgium*; P. Viville,* Université de Mons, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

In the literature, some studies focus on the use of H_2O in plasma discharges because of its potential high reactivity. However, is also known to destabilize plasmas. In this study, the reactivity of water at the interface between the plasma and the surface of the low density polyethylene (LDPE) was investigated. LDPE is chosen as polymer because of its high capacity to be functionalized.

In the first part of this project, we study the water reactivity in atmospheric plasma by injecting H_2O vapor in the discharge of a dielectric barrier discharge, supplied with Ar as carrier gas. OES evidenced the production and the consumption of Ar, O, OH, and N_2 species. They can be quantified as a function of the H_2O flow rate and the treatment time in order to have a better understanding of the reactivity. Some chemical reactions occurring within the discharge can be highlighted. To characterize the discharge itself, current measurements are performed and a high speed camera is used to observe the changes of the discharge (number and size of the streamers).

In the second part of this research, LDPE surfaces exposed to water-containing plasma are characterized by XPS. The measurements of the O 1s peak reveal a strong increase of oxygen from 0% to 16%. XPS Depth profiles evidence the diffusion of O in the subsurface. These results have been compared with WCA measurements expressed as a function of time. Between 0 and 30 s, a strong decrease in the WCA is observed (from 100° to 63°) and can be linked to the rise of the O% (from 0% to 13%). After 30 s, the WCA rapidly decreases to 43° which seems inconsistent with the very slow increase of the O% (almost no rise) observed by XPS. In parallel, AFM measurements show a texturization of the treated LDPE, as the surface roughness increases from 27 nm to 75 nm. The effect observed after 30 s of treatment can be explained by the Wenzel equation:

$\text{Cos } \Theta_{app} = r \cos \Theta$

Indeed, the "r" factor in the Wenzel corresponds to the roughness ratio defined as the ratio of true area of the solid surface to the apparent area. Cos Θ can be linked to the polar component of the surface energy and therefore to the oxygen concentration at the surface. The roughness and the oxygen content increase simultaneously with time and the combination of these two factors lead to obtain a higher Cos Θ_{app}. Indeed, the texturization and the grafting of oxygen are correlated by the use of the Wenzel equation thereby allow the understanding of the large decrease of WCA.

This work is supported by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

11:00am **PS+SE-MoM9 Particle-free Fabrication of Stretchable, Electrically Conductive Features by Atmospheric-Pressure Plasma Reduction of Metal-Ion-Containing Polymer Films***, **Souvik Ghosh**[*], P.X.-L. Feng, C.A. Zorman, R.M. Sankaran,* Case Western Reserve University

Stretchable electrically conductive patterns are an importance class of materials for emerging electronic applications. A relatively well-established approach for their fabrication is printing metal nanoparticle inks on elastomeric polymers to combine the high electrical conductivity of metals with the large mechanical deformability of polymers. However, nanoparticle-based inks have organic-based solvents and contain organic capping molecules to stabilize the nanoparticles, limiting the conductivity of as-printed features and requiring high temperature sintering (>200 °C) to remove the organics, which is not compatible with most polymers. Moreover, the printed metal nanoparticle film may not be well-integrated with the polymer, compromising conductivity at large deformation.

Here, we report a plasma-based approach to producing electrically-conductive metallic features at the surface of polymer films that eliminates the need for nanoparticle inks and has the potential to better integrate metals and polymer. In general, metal salts are initially mixed with a polymer and cast as a thin film. The films are then exposed to a plasma which results in reduction of the metal ions to metal nanoparticles. By using an atmospheric-pressure microplasma jet and rastering the metal-ion-containing polymer film, the reduction is localized and two-dimensional patterns of metal nanoparticles are fabricated.

We initially focused our study on films prepared from silver nitrate ($AgNO_3$) and polyacrylic acid (PAA) which is known to cross-link with metal cations. After exposure to the microplasma, films were characterized by X-ray diffraction (XRD) which confirmed crystallinity from the presence of peaks corresponding to face-centered cubic silver (Ag). Further materials analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) revealed that microplasma reduction leads to nanoparticle formation only at the surface of the film. The bulk resistivity of the patterned features was determined by two-point probe measurements and reached values as small as ~1 mΩ-cm.

To obtain stretchable films, two approaches were explored. First, PAA-Ag thin films were cast on top of polydimethylsiloxane (PDMS) - an elastomer, and reduced by the microplasma. Second, we extended our process to a rubber polymer (styrene-isoprene-styrene) (SIS) which could be mixed with silver trifluoroacetate to be reduced and form Ag in a single polymer layer. Results for the resistivity as a function of the strain in the various material systems will be presented, as well as a working model for the role of the plasma in the reduction of the metal in the polymer and its final morphology.

11:20am **PS+SE-MoM10 Plasma Polymerised 4-vinyl Pyridine Films with High Charge Density Synthesised in Atmospheric Roll-to-Roll System***, **Hindrik de Vries,*** FOM institute DIFFER, Netherlands*; W. van Baak, S.A. Starostin,* FUJIFILM Manufacturing Europe B.V., Netherlands*; M.C.M. van de Sanden,* FOM institute DIFFER, Netherlands

Nowadays plasma polymerisation is considered as an attractive tool to synthesise ultra-thin organic functional coatings. In this contribution we report for the first time the synthesis of PP thin 4-vinylpyridine containing films synthesised in a roll-to-roll set-up in an atmospheric pressure plasma enhance chemical vapour deposition (AP-PECVD) reactor using low cost nitrogen gas. The general details of the reactor and plasma parameters were described elsewhere [1]. Specific of the present work is the use of a variable short pulse trains. Nitrogen was used as a carrier gas admixed with a variable flow of argon to control the vaporisation rate of 2 monomers: 4-vinylpyridine (4-VP) and divinylbenzene (DVB) to enable copolymerisation reaction. The film properties were tuned by varying the power per injected precursor molecule and the mixing ratio of the 2 monomers. The films were characterized on thickness (spectroscopic ellipsometry), adhesion (tape test), roughness (interferometric microscopy), and wettability (water contact angle). The microstructure of the 4-VP films was assessed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS). The fixed charge was characterised by zeta potential measurements. Film analysis showed that the main feature (pyridine group) was preserved although newly formed peaks in the ATR-FTIR spectrum indicate partial dissociation of the 4-VP. Pulse parameters as well as the DVB [2] flow were studied to improve cross-linking of the film. Zeta potential measurements confirmed the presence of positive charge at the surface. Subsequently, the films were quaternized

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[*] **Coburn & Winters Student Award Finalist**

leading to a further enhancement of the fixed charge on the surface. Recent results will be highlighted and recommendations for further improvement of the atmospheric plasma processing will be discussed.

[1] S.A. Starostin et al. *Plasma Process. and Polym.* 12, no. 6 (2015): 545–54.

[2] R. Yang et al. *Advanced Materials* 26, no. 11 (2014): 1711–18.

11:40am **PS+SE-MoM11 Plasma-Surface Interactions in Atmospheric Pressure Plasmas: *In Situ* Measurements of Local Excitations in Thin Films***,* ***Scott Walton****,* Naval Research Laboratory*; B.M. Foley,* University of Virginia*; D.R. Boris, E.D. Gillman, S.C. Hernández,* Naval Research Laboratory*; A. Giri,* University of Virginia*; Tz.B. Petrova, G.M. Petrov,* Naval Research Laboratory*; P.E. Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physicochemical changes associated plasma-based materials processing. The unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure the electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the excited electrons propagate radially from the point of contact. These results, in conjunction with plasma characterization, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

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