Monday Afternoon, October 31, 2011

Plasma Science and Technology Division
Room: 202 - Session PS+BI-MoA

Multiphase (Liquid, Solid, Gas) and Biological Related Plasmas
Moderator: A.M. Coclite, Massachusetts Institute of Technology

2:00pm **PS+BI-MoA1 Atmospheric-Pressure Microplasmas for Novel Electrochemical Applications**, *S.W. Lee*, *R.M. Sankaran*, Case Western Reserve University
Plasmas formed at sub-millimeter spatial scales operate stably and close to non-thermally at atmospheric pressure and are a source of ions, electrons, and other electronically excited states at ambient conditions. Overall, these features make microplasmas suitable for novel electrochemical applications where gas-phase species (e.g electrons) in the plasma can directly interact with ionic aqueous electrolytes to initiate redox reactions.

In this talk, we will present two approaches to microplasma-based electrochemistry that we have developed for nanoparticle synthesis. In one approach, microplasmas are formed at the surface of a liquid electrolyte and operated similar to an electrochemical cell with the plasma as the cathode and a solid metal immersed in the electrolyte as the anode [1]. Metal cations in solution such as $Ag+$ are electrochemically reduced by the plasma to solid metal, resulting in the formation of metal nanoparticles without any chemical reducing agent. Alternatively, thin films of metal cations dispersed on a polymer are electrochemically reduced by a rastered microplasma [2]. This configuration allows microscale patterns of metal nanoparticles to be produced without the need for lithography. Recently, we have extended our patterning method to the reduction of metallopolymers which are novel molecular structures that can be used as a template for metal ion and metal particle formation [3]. This strategy has enabled patterns of metal nanoparticles to be prepared which are beyond lithographic limits. We will discuss our experimental techniques in detail, as well as the properties of the nanoparticles as assessed by UV-Visible absorbance spectroscopy, X-ray diffraction, and transmission electron microscopy.

1. C. Richmonds et al., Appl. Phys. Lett. 93, 131501 (2008).
2. S. W. Lee et al., Adv. Func. Mater., doi:10.1002/adfm.201100093
3. S. W. Lee et al., in preparation.

2:20pm **PS+BI-MoA2 Water Containing Non-Equilibrium Atmospheric Pressure Plasmas**, *P.J. Bruggeman*, Eindhoven University of Technology, the Netherlands **INVITED**
During the last decade water containing non-equilibrium atmospheric pressure plasmas have received a continuously increasing attention in view of their potential in biomedical, environmental, chemical synthesis and material processing applications. This evolution coincides with a strong need for improved diagnostics to enable us to unravel the complex physics and chemistry of water containing plasmas. Both discharges containing a liquid water phase and only water in the vapor phase will be addressed in this contribution.

We will give an overview of the physical and chemical properties of these discharges. The main plasma parameters such as the electron density, gas and electron temperature will be presented and the complications of the interpretation of the diagnostics to obtain these plasma parameters will be discussed. Water containing discharges produce high radical densities such as OH, which is a key radical in several applications. Due to the often high electron density of these discharges recombination reactions are very important not only for radical production but also to explain the optical emission of these discharges. Key differences between liquid water containing discharges and more conventional gas discharges will be discussed.

References:
P. Bruggeman and C. Leys, Non-thermal plasmas in and in contact with liquids (topical review paper), J. Phys. D: Appl. Phys., 42 (2009) 053001

P. Bruggeman, D.C. Schram, M.A. Gonzalez, R. Rego, M.G. Kong and C. Leys, Characterization of a direct DC-excited discharge in water by optical emission spectroscopy, Plasma Sources Sci. Technol. 18 (2009) 025017

T. Verreycken, A. F. H. van Gessel, A. Pageau and P. Bruggeman, Validation of gas temperature measurements by OES in an atmospheric air glow discharge with water electrode using Rayleigh scattering, Plasma Sources Sci.Technol. 20 (2011) 024002

P. Bruggeman, F. Iza, D. Lauwers and Y. Aranda Gonzalvo, Mass spectrometry study of positive and negative ions in a capacitively coupled atmospheric pressure RF excited glow discharge in He-water mixtures, J. Phys. D: Appl. Phys. 43 (2010) 012003

3:00pm **PS+BI-MoA4 Mechanism of Au Nanoparticles Formation in Solution Plasma**, *M.A. Bratescu*, *O. Takai*, *N. Saito*, Nagoya University, Japan
The Solution Plasma Processing (SPP) has been developed in our laboratory to synthesize nanoparticles and to improve surface properties of carbon nanomaterials by decorating with different nanoparticles or binding functional groups on the surface. The purpose of the present study is to investigate the mechanism of the Au nanoparticles (NP) formation in the SPP and to correlate the SPP properties with the Au NPs characteristics (morphology, size and surface functionalization). The investigation was conducted by changing the solution pH, using the same surfactant and keeping the same processing parameters.

The Au NPs were synthesis in an aqueous solution of 1 mM $HAuCl_4 \cdot 3H_2O$ used as precursor, 1 mM hexadecyltrimethylammonium chloride (CTAC) used as surfactant, and NaOH used to adjust the solution pH (3.2, 6.5 and 11.2). The plasma was produced by using a pulsed high voltage (HV) power supply with the peak voltage and current of 2 kV and 1 A, respectively and the pulse width of about 1 μs. Plasma was characterized by optical emission spectroscopy (OES). The OES gives information about the presence of the relative number densities of the radicals as H, OH, O, and O_2 and from these data the electron temperature and density were evaluated.

On surface, in high vacuum environment, the Au NPs were characterized by Transmission Electron Microscopy (TEM), Secondary Ion Mass Spectrometry Time of Flight (SIMS - ToF) and X-rays Photoelectron Spectroscopy (XPS). In solution, as prepared, the Au NPs were characterized by UV-visible spectroscopy and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy.

The size of the synthesized Au NPs depends on the initial pH of the solution. In a low pH solution, the particle size was around 15 – 20 nm diameter and in a solution with a higher pH value than 6, the NPs diameter was found to be 2 – 5 nm. The negative SIMS-ToF measurements reveals the presence of the Au^-, $AuCl^-$ and AuN^- ions in the solution with a pH 3 and AuO^- in a solution with pH 11. In a solution before plasma processing, with a low pH value the negative ions Au_2Cl^- and $Au_3Cl_2^-$ were detected, which can suggest an initial agglomeration of Au atoms in solution. The binding functional groups on the Au NPs are confirmed by the XPS analysis.

The correlation among information of the Au NPs morphology, the binding atoms on Au surface, plasma electron temperature and density and the formation of the Au complexes, during the Au NPs synthesis will be presented and discussed.

3:40pm **PS+BI-MoA6 Pulsed Plasma Studies of 2-chloro-p-xylene**, *I.C. Estrada-Raygoza*, *G. Padron-Wells*, *P.L.S. Thamban*, *L.J. Overzet*, *M.J. Goeckner*, University of Texas at Dallas
Chemical vapor deposited parylene-C is widely used for applications ranging from biomedicine to microelectronics. In our work, we use 2-chloro-p-xylene (2ClpX) as a precursor to deposit plasma polymerized Parylene C. Here we report data aimed at determining the dissociacion mechanisms of the 2ClpX in the plasma. Specifically that data is from: in situ Fourier transform infrared spectroscopy (FTIR); plasma optical emission spectroscopy (OES); and electron beam OES. The main dissociation products are HCl, methane and acetylene. We also observe atomic and molecular hydrogen and chlorine, HCl ion, CH and the characteristic broad aromatic band in the 300 nm region. Both frequency and duty cycle have a strong effect in 2ClpX dissociation. When the pulse period is smaller than the diffusion time, the discharge behaves as continuos wave system, independent of the duty cycle used. When the pulse period is much larger than the diffusion time, the discharge behaves different and very little break up of the monomer is detected. When the pulse period is similar to the diffusion time, then the effect of duty cycle is considerable. This work is supported in part by NSF (Grant CBET- 0922962), Verity Instruments and CONACYT Grant 170201.

4:00pm PS+BI-MoA7 Deactivation of Lipopolysaccharide and Lipid A by Ar/H₂ Inductively Coupled Plasma, *E. Bartis,* University of Maryland, College Park, *T.-Y. Chung, N. Ning, J.-W. Chu, D.B. Graves,* University of California, Berkeley, *J. Seog, G.S. Oehrlein,* University of Maryland, College Park

Low temperature plasma (LTP) treatment of surfaces is a promising path toward sterilization of bacteria [1]. Past works have shown plasma-induced degradation of bacteria [2], but little knowledge exists regarding the plasma-induced chemical modifications in biomolecules that result in inactivation since various plasma species, e.g. ions, reactive radicals, and UV/VUV photons may aid in inactivation. Lipopolysaccharides (LPS) are a main component of the outer membrane of gram-negative bacteria and are difficult to remove from surfaces by conventional methods [3]. LPS is made up of a polysaccharide chain and lipid A and lipid A elicits an immune response in animals [1]. Previous studies have found that adding H_2 to an Ar plasma leads to a reduction of infrared bands originating from the aliphatic chains of lipid A, namely C-Hx stretching, C-O, and amide bands [4]. This study aims to distinguish the roles of physical sputtering, chemical attack by H-atoms, and plasma-generated VUV. LPS-coated silicon chips were exposed to LTP (Ar, H2, and Ar/H2 mixtures) to explore the effects of plasma composition/ion energy on the etch rates (ER) and chemical and optical properties of LPS. Real-time in-situ ellipsometry was used to monitor ER and changes in the LPS film's optical density during plasma exposure. The real-time data showed that Ar plasmas create a dense film on the surface that decreases in density with H_2 addition. The films were etched fastest in Ar discharges mixed with ~10% H_2 and were slowest in pure H_2. Since previous work [4] found that adding H_2 to an Ar discharge enhanced sterilization, these results may indicate that chemical modification rather than rapid erosion may be more important for inactivation. After LTP treatment, samples were characterized by vacuum-transfer to x-ray photoelectron spectroscopy (XPS) to measure the chemical modifications taking place in the LPS layer. With XPS, we measured a decrease in the intensity of the C-C/C-H peak, which indicates that the aliphatic chains in lipid A were removed. The N/C ratio increases approximately equally in all discharges, which suggests that gas chemistry does not have a large impact on amides. Complementary studies with Lipid A will be presented as well as results of a VUV optical filter approach used to probe VUV-induced LPS modifications in real time by in-situ ellipsometry while protecting the material against ion bombardment.

[1] A. von Keudell et al., Plasma Process. Polym. 7, 327 (2010)

[2] H. Rauscher et al., Chem. Phys. Chem. 11, 1382 (2010)

[3] E. T. Rietschel et al., FASEB J. 8, 217 (1994)

[4] O. Kylian et al., Plasma Process. Polym. 5, 26 (2008)

4:20pm PS+BI-MoA8 Development of Plasma Treated Mn Induced Nano-arrayed Structures in Sol-gel Derived TiO₂ Matrix for Biosensing Applications, *R.R. Pandey,* Centre for Cellular and Molecular Biology, India, *K.K. Saini,* National Physical Laboratory, India, *M. Dhayal,* Centre for Cellular and Molecular Biology, India

We describe Mn doped TiO_2 nanomaterial-based biosensors modified by high pressure RF plasmas for biosensor applications which activates nanostructure matrix and greatly enhanced enzyme loading capacity for development of high sensitivity biosensors. As a test modal, effects of plasma treatment on a novel potentiometric urea biosensor for selective and quantitative recognition of urea by immobilizing urease onto Ti/urease-imprinted Mn induced TiO_2 film has been studied and monitoring the potentiometric response caused by the immobilized urease/urea reaction system was carried out. These platforms has been characterized by XRD, XPS, FTIR, SEM, cyclic voltametry to determine the changes in structure, surface chemistry and electron transfer characteristics of platforms after plasma treatments and have been correlated with improved response of biosensor.

4:40pm PS+BI-MoA9 Growth Promotion of Bread Yeast using Atmospheric Pressure Dielectric Barrier Discharges, *S. Kitazaki, K. Koga, M. Shiratani,* Kyushu University, Japan, *N. Hayashi,* Saga University, Japan

Nonthermal atmospheric pressure plasmas have been employed for biomedical processing applications, because they provide high density radicals at a low gas temperature [1]. Recently, nonthermal atmospheric pressure plasmas as well as low pressure plasmas have been employed for growth promotion of plant cells [2,3]. In this study, we have developed a scalable atmospheric dielectric barrier discharge (DBD) device for biomedical processing in a large area and have applied the device to growth promotion of bread yeast. The device consisted of 20 electrodes of a stainless rod of 1 mm in outer diameter and 60 mm in length covered with a ceramic tube of 2 mm in outer diameter. The electrodes were arranged parallel with each other at a distance of 0.2 mm. The dry yeast was set at 1 mm under the electrodes. The discharge voltage and frequency were 10 kV

and 10 kHz, respectively. The plasma treatment was carried out in the air. The treatment duration T_{on} was 50, 100 and 150 s. After the treatment, yeast was suspended in 0.5 ml yeast extract peptone dextrose (YPD) medium and agitated with a vortex mixer. 1 μl of sample was mixed with 99 μl YPD medium in a micro well plate and cultivated using a shaking incubator at 30 °C. To obtain growth curve of yeasts time evolution of 660 nm light absorbance of the samples was measured with a micro plate reader. For the control, the absorbance is almost constant until t = 15 hrs after the beginning of the cultivation, which corresponds to the lag phase, and then it exponentially increases with t, the exponential growth phase. For yeast with the plasma treatment, the absorbance increases from t = 0 hrs. At t = 10 hrs, the maximum absorbance for T_{on} = 150 s is 6.6 times as high as that for the control. From t = 10 to 15 hrs, the gradient of the absorbance becomes gradual. After t = 15 hrs, the absorbance increases exponentially with t. The plasma treatment reduces the lag phase of yeast growth and enhances the growth rate. The growth promotion tends to be enhanced with increasing T_{on} from 50 to 150 s. The growth promotion, therefore, depends on the dose of radicals produced by discharge plasmas.

[1] M. G. Kong, M. Keidar, and K. Ostrikov, J. Phys. D: Appl. Phys. 44, 174018 (2011).

[2] S. Kitazaki, D. Yamashita, H. Matsuzaki, G. Uchida, K. Koga, and M. Shiratani, Proc. IEEE TENCON 2010, 1960 (2010).

[3] Y. Akiyoshi, A. Nakahigashi, N. Hayashi, S. Kitazaki, T. Iwao, K. Koga, and M. Shiratani, Proc. IEEE TENCON 2010, 1957 (2010).

5:00pm PS+BI-MoA10 Plasma Deactivation of Pyrogenic Biomolecules: Vacuum Ultraviolet Photon and Radical Beam Effects on Lipid A, *T.-Y. Chung*, N. Ning, J.-W. Chu, D.B. Graves,* University of California, Berkeley, *E. Bartis, J. Seog, G.S. Oehrlein,* University of Maryland, College Park

Conventional medical instrument sterilization methods are generally ineffective in completely removing harmful biological residues [1]. Biomolecules such as proteins and other pyrogens from bacterial residues are particularly resistant to elevated temperature and are not easily removed by conventional procedures [2, 3]. For example, the presence of lipopolysaccharide (LPS) in host tissue or blood circulation could lead to a generalized sepsis syndrome including fever, hypotension, and respiratory dysfunction and may lead to multiple organ failure and death [4]. Low temperature plasma is a promising technique for sterilization/deactivation of surgical instruments or medical devices, but its effectiveness against such targets is incompletely understood [5]. In this study using a vacuum beam system, we chose lipid A, the major immune-stimulating region of LPS, as a model biomolecule to study. Lipid A consists of a β-1,6-linked D-glucosamine (GlcN) disaccharide carrying two phosphoryl groups. This structure is attached to multiple acyl chains by ester or amide linkage [6]. After vacuum ultraviolet (VUV) photon exposure, loss of CH_2/CH_3, C=O ester, and P=O absorption peaks were observed by ex-situ transmission Fourier transform infrared (FTIR) spectroscopy, but the C=O amide absorption peak was only mildly affected. Monitoring photolysis products from lipid A films by in-situ mass spectrometry, we observed cracking patterns similar to those of alkanes/alkenes with a carbon number ~11-13. This result suggests that VUV photons remove phosphate groups and break ester linkages leading to desorption of acyl chains. Endotoxicity of lipid A is known to be primarily determined by the number and length of acyl chains as well as the phosphorylation state and the disaccharide backbone [6]. The present results therefore indicate that plasma-generated VUV reduces the endotoxicity of lipid A, in support of the hypothesis of Rossi et al. [7]. We report the effects of VUV and radical (H, O) exposures on endotoxicity based upon chemical structural change in Lipid A. Synergism of various beams is compared with plasma exposures and corresponding molecular dynamic (MD) simulations.

[1] R. L. Baxter et al., J. Hosp. Infect. **63**, 439 (2006)

[2] T. Nakata, J. Parenter. Sci. Technol. **47**, 258 (1993)

[3] L. Moesby et al., Eur. J. Pharm. Sci. **26**, 318 (2005)

[4] J. Cohen, Nature **420**, 885 (2002)

[5] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

[6] C. Erridge, E. Bennett-Guerrero, and I. R. Poxton, Microbes Infect. **4**, 837 (2002)

[7] F. Rossi et al., New J. Phys. 11, 115017 (2009)

---

* Coburn & Winters Student Award Finalist

5:20pm PS+BI-MoA11 Charge Transfer Reactions at the Plasma-Liquid Interface, *M. Witzke, C. Richmonds, B. Bartling, S.W. Lee, J. Wainright, C.-C. Liu, R.M. Sankaran*, Case Western Reserve University

Electrochemical reactions are normally studied at the interface of a solid metal electrode and an aqueous ionic electrolyte. A smaller number of experiments exist, dating back to more than 100 years ago[1], of plasmas formed at the surface or inside of liquids to initiate electrochemical reactions at the interface of a plasma electrode and a liquid electrolyte. Despite this long history, reactions at the plasma-liquid interface remain poorly understood. Plasmas that are formed at low pressures require liquids with extremely low vapor pressure, limiting previous studies to ionic liquids (i.e. molten salts)[2]. In addition, plasmas are characterized by a complex environment (e.g. ions, electrons, UV, etc.) which has made it difficult to differentiate charge-transfer reactions from other non-faradaic reactions such as radical generation and chemical dissociation.

We have recently developed a novel microplasma source that allows a non-thermal, atmospheric-pressure plasma to be stably formed at the surface of aqueous ionic electrolytes[3-5], facilitating fundamental study of charge-transfer reactions at the plasma-liquid interface. Electron transfer reactions between the plasma and the liquid are studied by using the well-known ferricyanide-ferrocyanide redox couple. The electrochemical reduction of ferricyanide is monitored by UV-vis absorbance spectroscopy and cyclic voltammetry. We find that ferricyanide is indeed reduced by the plasma, confirming that charge transfer reactions can occur at the plasma-liquid interface. The rate of ferricyanide reduction is found to depend on the discharge current, which controls the electron flux delivered to the surface of the solution. By comparing the (discharge) current to the amount of ferricyanide reduced, we obtain a reduction efficiency of ~1%. To address the relatively low efficiency, we have measured the potential at the plasma-liquid interface to determine whether the potential is high enough for water electrolysis and measured hydrogen generation by mass spectrometry. In this talk, we will present our overall methodology and discuss these results in detail.

1. J. Gubkin, *Ann. Phys.* **32**, 114 (1887).

2. S. Z. El Abedin, M. Polleth, S. A. Meiss, J. Janek, and F. Endres, *Green Chemistry* **9**, 549 (2007).

3. C. M. Richmonds and R. M. Sankaran, *Appl. Phys. Lett.* **93**, 131501 (2008).

4. W-H. Chiang, C. Richmonds, and R. M. Sankaran, *Plasma Sources Sci. Technol.* **19**, 034011 (2010).

5. F-C. Chang, C. Richmonds, and R. M. Sankaran, *J. Vac. Sci. Technol. A* **28**, L5 (2010).

Authors Index

Bold page numbers indicate the presenter