Plasma Science and Technology Division
Room 104A - Session PS+PB-MoA

Plasma and Polymers: 'The Legacy of Riccardo d'Agostino and Beyond'

Moderators: Ankur Agarwal, KLA-Tencor, Mohan Sankaran, Case Western Reserve University

1:20pm **PS+PB-MoA-1 Foreword/introduction to the session: "Reflections on the Legacy of Riccardo d'Agostino"**, *P Favia,* University of Barii, Italy

In this contribution I will review the career of Prof. d'Agostino and reflect on his scientific achievements, his extensive network in the field of plasma chemistry, plasma processing of materials and applications, and his role as mentor for several generations of M.Sc. students as well as PhD and postdocs.

1:40pm **PS+PB-MoA-2 Atmospheric Pressure PE-CVD of Drug-containing Nanometric Capsules***, **Pietro Favia**, C Lo Porto, A Treglia,* University of Bari, Italy*; F Palumbo,* CNR Institute of Nanotechnology NANOTEC, Italy

Plasma Enhanced Chemical Vapor Deposition Processes have been investigated by Riccardo d'Agostino and co-workers, and by many of his colleagues, in the late 80s and early 90s, mainly at low pressure, resulting in a large number of publications on the deposition kinetics and on the applications of coatings of different composition and properties. Many other PE-CVD approaches have been developed since then, and the deposition processes have been or are going to be deeply investigated, following the legacy of Riccardo d'Agostino in this field.

In this talk we present a set of data on the direct PE-CVD of nanometric capsules in the plasma phase resulting from Aerosol Assisted (AA) Atmospheric Pressure (AP) PE-CVD processes fed with Helium (carrier), Ethylene (film precursor) and aerosol droplets of solutions of drugs (nancomicyn, gentamicyn, etc). This approach [1, 2, 3] can lead, in certain conditions, to the deposition of thin coatings directly on the droplets of the aerosol, thus leading to the synthesis of drug-containing nanometric capsules, of potential interest for biomedical applications, e.g., as anti-bacterial surfaces [4].

The influence of various plasma parameters on the AA-AP-PE-CVD processes is discussed, as well as some properties of the coatings.

acknowledgements

The mentorship of Prof. d'Agostino is acknowledged by the authors of this contribution, as well as the recognition of his legacy in the field of plasma processing of materials.

references

1. A. Heyse et al, Plasma Proc. Polym. 8, 965 (2011)

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3. Lo Porto et al, Polym. Chem. 8, 1746 (2017)

4. Sardella et al, *Materials* 2017, 9, 515

2:00pm **PS+PB-MoA-3 Ultrathin Metal-Organic Covalent Networks by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD) for Gas Separation Membranes***, **Karen Gleason**, M Wang,* MIT*; N Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; M Creatore, A Perrotta,* Eindhoven University of Technology, The Netherlands, Netherlands*; K Heinze,* Johannes Gutenberg-Universität, Mainz, Germany

Metal-Organic Covalent Networks (MOCN) were synthesized as ultrathin (<100 nm), defect-free and mechanically flexible layers by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD). The low substrate temperature used for iCVD allowed use of thermal sensitive porous poly[1-trimethylsilyl)-1-propene] (PTMSP) as a substrate. Uniform layers were grown over 150 nm diameter substrates and did not delaminate upon mechanical deformation. The resulting robust MOCN/PTMSP composite membranes exhibiting outstanding gas separation performance for multiple pairs of gases. Using zinc (II) meso-tetraphenyl porphphyrin (ZnTPP) as the monomer and tert-butyl peroxide as the initiator, film deposition was achieved at low plasma excitation powers. The nearly unchanged intensity of the Soret bands in the UV-vis spectra confirmed the retention of the 18 pi e- conjugation of the monomer units incorporated into the films. The gas selectivity for the separation of H_2/CH_4 or H_2/N_2 is small (<3) for either the PTMSP base membrane or for thin films of evaporated ZnTPP. However, the gas selectivity for both H_2/CH_4 or H_2/N_2 rises to >500 for the PTMSP/iPECVD ZnTPP composite membrane, exceeding the performance of commercial membranes. Ellipsometric Porosimetry and Density Functional Theory Calculations are consistent with a pore size of ~0.4 nm in the MOCN film. Additionally, iPECVD layers derived from a metal-free porphyrin and from porphyrins containing magnanese (III) and cobalt (III) will be described.

2:20pm **PS+PB-MoA-4 Influence of Energetic Conditions on the Plasma Polymerization of Cyclopropylamine in Capacitively Coupled Discharges***, **Lenka Zajickova**, M Michlicek,* Masaryk University, Czech Republic*; S Hamaguchi,* Osaka University, Japan

Thin films prepared by plasma polymerization of cyclopropylamine (CPA) in capacitively coupled discharges demonstrated their attractive functional properties as a matrix layer in immunosensors or surface modification of synthetic polymers used for a cell cultivation. These bioapplications required tuning the concentration of amine and other bio-active groups together with the film stability in aqueous media. Since the final plasma polymer composition is influenced by the discharge power and the polymer cross-linking can be modified by ion energy flux towards the growing film the investigation of bulk plasma and plasma-surface interactions with respect to the energetic conditions are necessary for fundamental understanding of the overall process. This work puts together the results on the plasma polymer properties with the plasma diagnostics by mass and ion spectrometry, optical emission spectroscopy and retarding field energy analyzer placed at the substrate position. The experiments are complemented by the molecular dynamic simulations of the film growth.

2:40pm **PS+PB-MoA-5 Electrochromic Investigation of PEDOT Film Deposited by Plasma Radicals Assisted Polymerization *via* CVD***, **Bianca Rita Pistillo**, G Lamblin, J Polesel-Maris, K Menguelti, D Arl, D Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Quite recently conducting polymer have been introduced into a broad range of organic electronic devices in place of analogous inorganic semiconductors, owing to their numerous merits as flexibility, low cost and lightweight over their forerunners. Similarly to inorganic material, also conducting polymer display electrochromism. The oxidation or reduction of these films is usually associated with reversible ion insertion and extraction across an electrochromic material/electrolyte interface with complementary electron transfer across the electrochromic material/electrode interface. In the last years, the study and implementation of organic electrochromic materials (OEM) into devices had a tremendous growth also because of their relatively narrow absorption band in displaying diverse and clear colour. [T.T. Steckler et al. J. Am. Chem. Soc. 2014, 136, 1190] There are many interesting applications of OEM such as smart windows, flexible displays, electrochromic fibres, etc. One of the most attractive ones is Poly(3,4-ethylenedioxythiophene) (PEDOT) with its derivatives. PEDOT changes its colour from dark blue/purple, in its reduced state, to light blue, in the oxidised state with very low applied switching potential. Plasma Radicals Assisted Polymerization via Chemical Vapour Deposition (PRAP-CVD) has been developed at Luxembourg Institute of Science and Technology as an efficient alternative to conventional vapour-based processes of conductive thin films as PEDOT. [D. Lenoble, Controlled radical assisited polymerization, Lux. 91934, 2013] This process is based on the concomitant but physically separated injection of low-energy oxidative radical initiators and vaporized monomer species into a reactor where temperature and pressure are finely controlled. [B.R.Pistillo et al. J. Mater. Chem. C 2016, 4, 5617] A few advantages of making the process completely dry include the possibility of processing solvent-sensitive substrates such as paper, overcoming the effects of rinsing on the underlying films in the case of multilayer structures. Moreover, PRAP-CVD allows the deposition of highly conformal coatings, which accurately follows the geometry of the underlying substrate independently from its nature, enlarging the application of PEDOT as OEM. In this work, we present the investigation of electrochromic properties of PRAP-CVD PEDOT films. The behaviour of films was compared with the data in the literature revealing a faster switching time compared to other vapour-based processes reported. The range of switching potential with limited electrochemical degradation of the thin electrochromic film was also investigated by the means of UV-visible spectroelectrochemistry.

3:00pm **PS+PB-MoA-6 Initial ZnO Crystallite Formation by Plasma Enhanced ALD***, **Alberto Perrotta**, J Pilz, A Coclite,* Graz University of Technology, Austria

ZnO is a wide direct bandgap semiconductor, extensively studied as thin film because of its unique optical, electrical, and piezoelectric properties. Its crystalline structure and degree of crystallinity have a crucial impact on the material characteristics and a particular crystallographic texture may be beneficial for gaining optimized piezoelectric properties or enhanced velocities in surface acoustic wave devices. Therefore, the possibility to control the preferred crystallographic orientation in ZnO thin films has been often investigated.

Atomic layer deposition (ALD) offers the possibility to study in detail the growth of ZnO, due to its layer-by-layer nature and sub-nm thickness control. The initial growth of ZnO adopting diethylzinc (DEZ) and water and its impact on the crystallographic texture of the resulting thin films shed light on the growth mechanisms and the influence of the substrate nature on the in-plane and out-of-plane crystal orientations.

However, thin films deposited with plasma enhanced ALD are known to show several differences when compared to thermal ALD. Therefore, for ZnO thin films the growth mechanism and initial crystallite formation may be greatly influenced by the use of plasma. In this contribution, the initial growth of direct plasma ALD ZnO grown on Si (100) is investigated. DEZ and pure oxygen plasma are adopted during the process. The first 20 cycles of growth are analysed using synchrotron light grazing incidence X-ray diffraction (GIXD), X-ray reflectivity (XRR), and spectroscopic ellipsometry (SE). The influence of substrate temperature ranging from 25 °C to 250 °C on the crystal growth and crystal orientation are studied. A closed layer was obtained within 7 cycles as measured by XRR for all the temperature explored, suggesting island growth of the ZnO. However, GIXD showed no crystalline texture forming at this stage. An amorphous intermixed interface between the native SiO_2 and the growing layer was found, with a density in between pure SiO_2 and ZnO. Irrespective of the deposition temperature, the first crystal structure was measured at around 3 nm, with a preferential out-of-plane orientation transiting from (100) at room temperature to (002) at 250 °C. The first crystallographic seeds were found to largely determine the final microstructure of thicker films.

3:40pm **PS+PB-MoA-8 On Fluorocarbons and Fish: Creating a Global Impact on Generations of Plasma Chemists***, **Ellen Fisher**,* Colorado State University

Plasma processing represents a powerful approach to modification of a range of substrates with an array of chemistries and morphologies. One of the most useful plasma processing tools is that of plasma polymerization for thin film formation. Arguably, the work of Riccardo d'Agostino and his coworkers over numerous decades, especially in the arena of fluorocarbon film deposition, has significantly enhanced our understanding of plasma polymerization and influenced countless additional studies around the globe. Here, we will detail how d'Agostino's work based in Bari, Italy inspired a range of studies of various fluorocarbon systems that have been performed over more than 2 decades in one laboratory nearly 6000 miles away. Despite the foundational data provided by d'Agostino's early examination of plasma polymerization processes, the remaining paucity of data regarding the fundamental, molecular-level mechanisms that drive fluorocarbon and hydrocarbon plasma polymerization begged further examination. Combining a range of spectroscopy techniques, materials characterization tools, and plasma-surface interface studies has yielded another generation (or two) of insight. This presentation will focus on film deposition studies utilizing multidimensional substrates (e.g. membranes, scaffolds, nanomaterials), and the connections between d'Agostino's pioneering plasma polymerization work and our more recent studies relevant to a range of value added products, including blood-contacting devices, sensors, tissue engineering, and separation technologies.

4:00pm **PS+PB-MoA-9 DIRECT and Remote Surface Functionalization using Atmospheric Pressure Dielectric Barrier Discharges***, **Francesco Fracassi**,* University of Bari, Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; F Fanelli,* Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; V Armenise, A Uricchio, R d'Agostino,* University of Bari, Italy, Italia

The utilization of atmospheric pressure dielectric barrier discharges (DBDs) for the surface modification of materials is a very interesting and actual topic. In recent years, efforts have been directed toward the development of a large variety of processes which exploit different DBD configurations and electrode geometries. This contribution describes DBD-based deposition and treatment processes which are potentially of interest also for environmental applications. The processes are performed on polyurethane (PU) foams, i.e., three-dimensional porous substrates which can be quite uniformly surface functionalized by DBDs, since, under suitable experimental conditions, the discharge ignites both outside the foam and throughout its entire porous structure. Three experimental strategies are utilized: i) direct treatment and deposition in parallel plate DBD; ii) direct aerosol-assisted deposition in parallel plate DBD; iii) remote deposition of thin films containing carboxylic acid groups with DBD jet.

The direct treatment is performed by feeding the DBD with He-O_2 mixtures in order to form carboxyl groups on the polyurethane surface. The treated foams are able to adsorb heavy metals from water solutions and can be regenerated (release of adsorbed heavy metals) through immersion in concentrated sodium chloride solution. However, the treated foams suffer ageing in water and, therefore, at the second reuse the amount of adsorbed metals decreases. A water-stable surface containing carboxyl groups is obtained with the DBD jet fed with helium-acrylic acid-ethylene mixtures (remote thin film deposition). No morphological and chemical modifications of the deposits are detected also after 72 h of immersion in water.

When the parallel plate DBD is fed with He-C_3F_6 mixtures, the deposition of fluoropolymer thin films occurs on both the exterior and interior of the foam. The treated foams are superhydrophobic and oleophilic, simultaneously, with potential application for the separation of oil from polluted water, since they selectively adsorb oil, while repelling water.

The direct aerosol-assisted deposition in parallel plate DBD is utilized to prepare hybrid organic-inorganic nanocomposite coatings composed of a hydrocarbon polymer and ZnO or TiO_2 nanoparticles. Under appropriate deposition conditions, it is possible to obtain multifunctional coating characterized by superhydrophobicity, superoleophilicity as well as by the peculiar photocatalytic properties of the utilized nanoparticles. The application of the treated foams for oil-water separation and for the photocatalytic degradation of organic pollutants in water is currently under investigation.

4:20pm **PS+PB-MoA-10 Quest for Durable Low-index Optical Coatings: From Plasma Polymerized Fluorocarbons to Hybrid Organic-inorganic and Nanostructured Films***, L Martinu, **Jolanta Klemberg-Sapieha**, O Zabeida,* Ecole Polytechnique de Montreal, Canada

Low (n less than about 1.55@550nm) and ultra-low refractive index materials (n less than 1.38@550nm) are of particular interest in the context of enhanced optical performance of interference filters (IF, including anti-reflective coatings). In addition, for many years now, there has been a lot of effort to develop such low and ultra-low index films with multifunctional characteristics making them suitable for the applications of IF on plastic and flexible substrates. This includes a necessity to better understand and optimize the thermo-mechanical properties (hardness, Young's modulus, adhesion, thermal expansion coefficient), surface energy (hydrophobicity), and possibly provide complementary functionalities (color, electrical conductivity, etc.). This presentation provides an overview of the progress in the field outlined above, starting with the work performed jointly with Professor Riccardo d'Agostino. In the first part, we describe the main optical, mechanical and dielectric characteristics of plasma polymerized fluorocarbons and related metal-doped plasma polymers. In the second part, we introduce hybrid organic-inorganic (SiOCH) materials that are shown to combine high mechanical resistance of ceramics with high elasticity of polymers. We demonstrate, that the refractive index of such films can vary from 1.50 to 1.53, while the extinction coefficient is kept below 10-4. At the same time, the hardness-to-Young's modulus ratio, H/E, is substantially increased (to 0.16) compared to 0.08 for pure SiO2), a result that is well correlated with the increased resistance to crack formation and propagation. Such layers, incorporated in multilayer structures on plastic substrates, provide significantly enhanced optical and mechanical stability in environments involving large temperature and humidity excursions. In the third part, we explore the characteristics of a new category of hybrid SiOCH thin films prepared by glancing angle deposition (GLAD) using electron beam evaporation of SiO2, in the presence of an organo-silicone precursor. The resulting layers are shown to exhibit n as low as 1.2, high elastic rebound and high hydrophobicity, and better mechanical properties than their inorganic counterparts. Their performance is discussed in terms of their anisotropy assessed by the nanostructure-based spectroscopic ellipsometry model. Finally, we demonstrate successful implementation of the ultra-low index material in a complete IF stack.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+NS+PB+SS-TuM-1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices***, **Y. Shirley Meng**,* University of California San Diego*; Y Yang,* University of California at San Diego **INVITED**

Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

8:40am **PC+AS+BI+NS+PB+SS-TuM-3 An *In situ* Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces***, **James De Yoreo**,* Pacific Northwest National Laboratory **INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered.Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation.Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate.The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

9:20am **PC+AS+BI+NS+PB+SS-TuM-5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface***, F Geiger, **Ariana Gray Be**,* Northwestern University **INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

11:00am **PC+AS+BI+NS+PB+SS-TuM-10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS***, **Meng Jia**,* University of Delaware*; A Broderick, J Newberg,* University of Delaware

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently “greener and safer” compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction, and electrochemical window. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts (ΔBE/ΔE) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a ΔBE/ΔE value of less than one. Upon introducing water vapor, forming an IL/water mixture, the ΔBE/ΔE approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM-11 Role of Air Gas at the Interface between Water and Graphite Surfaces***, **Ing-Shouh Hwang**,* Institute of Physics, Academia Sinica, Taiwan, Republic of China*; C Yang, C Fang,* Institute of Physics, Academia Sinica,Taiwan, Republic of China, Taiwan, Republic of China*; Y Lu,* Institute of Physics, Academia Sinica, Taiwan, Republic of China*; H Ko,* Institute of Physics, Academia Sinica,Taiwan, Republic of China, Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water interface. The work clearly shows the crucial role of gas molecules at hydrophobic/water interfaces and has broad implications in diverse research fields.

[1] H.-C. Ko, W.-H. Hsu, C.-W. Yang, C.-K. Fang, Y.-H. Lu, I.-S. Hwang, *Langmuir***32**, 11164 (2016)

[2] Y.-H. Lu, C.-W. Yang, and I.-S. Hwang, *Langmuir***28**, 12691 (2012).

[3] Y.-H. Lu, C.-W. Yang , C.-K. Fang, H.-C. Ko, I.-S. Hwang, *Sci. Rep.***4**, 7189 (2014).

[4] C.-K. Fang, H.-C. Ko, C.-W. Yang , Y.-H. Lu, I.-S. Hwang, *Sci. Rep.* 6, 24651 (2016).

11:40am **PC+AS+BI+NS+PB+SS-TuM-12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry***, **Musahid Ahmed**, O Kostko,* Lawrence Berkeley National Laboratory **INVITED**

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.[1] I will follow up with very recent results on association of water with “hydrophobic” naphthalene & “hydrophilic” glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample’s electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams[2] that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its’ implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).[3] A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.[4]

[1] T. Stein, B. Bandyopadhyay, T.P. Troy, Y. Fang, O. Kostko, M. Ahmed, M. Head-Gordon, PNAS (2017), DOI 10.1073/pnas.1616464114

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Plasma Science and Technology Division
Room 104C - Session PS+PB-TuM

Plasma Medicine

Moderator: Deborah O'Connell, University of York, UK

8:00am **PS+PB-TuM-1 Lessons from Tesla for Plasma Medicine***, **David Graves**,* University of California at Berkeley

It can be argued that plasma medicine originated with Nikolai Tesla in the late 19th century when he showed that one could pass large quantities of high frequency currents through a human body with no apparent damage. [1, 2] Tesla interpreted the significant sensations he experienced following exposure to these currents as being potentially valuable therapeutically. Tesla's work inspired much more extensive investigations over a period of several decades by numerous other researchers, on both the physics and biomedical effects of these currents. Researchers such as Arsene d'Arsonval and Paul Oudin in France and Frederick Strong in the United States, among others, were important pioneers. These early pioneers had a surprisingly modern view of some aspects of the therapeutic mechanisms of high frequency currents that clearly overlap with recent results. The perspective of this community was that the most important physiological effects are associated with the high frequency currents rather than the gas phase plasma. Some early work, such as the analgesic effects of dielectric barrier air plasma on tissue, is not well known today. [3] The range of afflictions that early practitioners treated successfully is remarkable. This body of work, in some cases almost 130 years old, has important lessons for current investigations into plasma medicine. Observations from Tesla and other early practitioners suggests that high frequency currents are potentially important and plasma medicine researchers should probably pay more attention to them.

[1] F.F. Strong, High Frequency Currents, Herman Company, New York, 1908.

[2] S.H. Monell, High Frequency Electric Currents in Medicine and Dentistry, WR Jenkins, New York, 1910.

[3] P. Oudin, Application therapeutique locale des courants de haute frequence en gynecologie, Archives d'électricité médicale, 287, 10 juin, 1910.

8:20am **PS+PB-TuM-2 Characterization of a Helium Atmospheric Pressure Plasma Jet by Measuring the Total Yield of Reactive Species in Real Time***, **Ek Adhikari**, V Samara, S Ptasinska,* University of Notre Dame

Recently, we performed in-situ measurements of reactive oxygen species of a helium atmospheric pressure plasma jet (APPJ) using an acidified ferrous sulfate solution (Fricke) as a sample. The total yield of reactive species reached to or originated in the solution corresponds to the amount of the yield of Fe^{3+} from reactions that transform Fe^{2+} into Fe^{3+} during plasma irradiation. The measurements indicated that the number of reactive species formed in the plasma jet is proportional to the applied pulse voltage and repetition frequency. However, there is a decrease in the yield of Fe^{3+} per pulse for an increase in the frequency. For higher frequencies, there is not enough time to complete all reactions before the next pulse arrives to the sample. Whereas, for lower frequencies, this yield is higher due to the relatively longer time period necessary for reactions to complete. Further, the flow rate of feed gas and treatment distance, which is the distance between the sample and glass capillary, have a minor effect on the formation of reactive species, but the yield of Fe^{3+} gradually decreases for a treatment distance longer than 20 mm. Moreover, we calculated the yield of Fe^{3+} in a very short time (equivalent to time period used in the experiment), and compared with the experimental results. The yield of Fe^{3+} formed within 15 s of plasma irradiation was also compared with the fractions of plasma induced DNA damage level under similar experimental conditions.

8:40am **PS+PB-TuM-3 Dry Etching of Patterned Medical Grade Titanium Alloys***, **Eitan Barlaz**, J Mettler, D Ruzic,* University of Illinois at Urbana-Champaign

We report on the development of a plasma etch process for Ti-6Al-7Nb, an alloy of titanium common for performance biomedical implants due to its excellent mechanical properties and corrosion resistance. The process uses the same chlorine and oxygen chemistry common to etches of pure titanium, with added ion bombardment to remove reaction products with low volatility and to ensure minimal texturing of the surface. The process is capable of etch rates in excess of 50 nm/min in 50 mTorr of Argon and 20 mTorr of CCl_4 using 50 W of RF power and a negative sample bias of > 500 Volts. Due to the need to produce irregularly shaped geometries, relative etch rates are reported for a variety of features including through holes and posts on representative parts. Plasma diagnostics including Langmuir and radical were applied to the process to compare the efficacy of both inductively coupled and surface wave plasma sources over large part sizes.

9:00am **PS+PB-TuM-4 Electron Temperature And Plasma Density Of Ar Plasma In Atmospheric Pressure Micro-DBD***, **Pradoong Suanpoot**, J Sornsakdanuphap,* Maejo University Phrae Campus, Thailand*; B Ghimire, Y Hong,* Plasma Bioscience Research Center, Republic of Korea*; G Cho,* Charged Particle Beam and Plasma Laboratory, Republic of Korea*; E Choi,* Plasma Bioscience Research Center, Republic of Korea

A model based on plasma propagation velocity has been recently developed to estimate the electron temperature (T_e) of atmospheric pressure μ-DBD plasma. In this work, we have extended this model to calculate T_e for plasma generated with Ar gas. Plasma has been generated by input discharge voltage of 2.7 kV at driving frequency of ≈ 45 kHz. A high-speed single-frame intensified charged coupled device (ICCD) has been used to observe the space and time-resolved discharge images and estimate the value of plasma propagation velocity (u_g). The value of u_g for Ar plasma has been obtained in the range of 6.2´10^3 m/s. The electron temperature has been calculated for this plasma. The average electron temperature has been found to be about 1.18 eV and the average plasma density has been found to be about 3.62×10^{14} cm^{-3} for Ar plasma. Our results obtained with modified convective-wave packet model can be a new contribution to plasma medicine.

Keywords: Atmospheric-pressure μ-DBD plasma, Ar plasma, plasma propagation speed, electron temperature, plasma density

9:20am **PS+PB-TuM-5 Plasma Immunotherapy of Cancers**, ***Vandana Miller***, *A Lin, P Ranieri,* Drexel University*; A Snook,* Thomas Jefferson University*; A Fridman,* Drexel University **INVITED**

Non-thermal plasmas are currently being developed as an alternative therapy for cancer. Local application of plasma to tumors *in vivo* has led to reduced tumor size and increased life expectancy of treated animals.[1] The body's immune system plays a vital role in the control of cancer.[3] In fact, cancer immunotherapy, the control of cancer by employing components of the patient's own immune system, is emerging as an appealing strategy.[3] New approaches being explored include increasing the immunogenicity of tumor cells by inducing immunogenic cancer cell death (ICD).[4] ICD of cancerous cells has been demonstrated with certain chemotherapeutic drugs and through physical methods such as X-ray therapy and UVC.[5, 6] Cells undergoing ICD express damage associated molecular patterns (DAMPs) which assist immune responses that may mediate systemic elimination of cancer.[4] We have demonstrated that non-thermal plasma is a good candidate for cancer therapy via immunomodulation by:

direct effects on immune cells[7, 8] and

indirect effects of cancer cell ICD.[8]

The role of plasma augmentation on the immune system, based on our *in vitro* and *in vivo* studies, will be discussed as a potential modality for clinical application in cancers. *In vivo* studies using Balb/c mice inoculated with subcutaneous CT26 colorectal cancer cells, treated with nspDBD plasma showed DAMP signal expression and recruitment of immune cells in the local tumor environment. Furthermore, there was development of a systemic, tumor-specific immune response. This demonstrates that plasma elicits ICD locally, in the treatment area, which leads to beneficial host immune responses both locally and systemically. The clinical potential of plasma cancer immunotherapy will be discussed and the challenges to address will be identified for further development of this technology. Results from a small clinical trial will also be presented.

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11:00am **PS+PB-TuM-10 Hydroxyl Radical Footprinting with Plasma-Induced Modification of Biomolecules (PLIMB): A Novel Tool for Protein Structural Analysis**, ***Faraz Choudhury***, *D Benjamin, B Minkoff, J Blatz, M Sussman, J Shohet,* University of Wisconsin-Madison

The protein-therapeutic industry, typified by anti-cancer proteins like Herceptin, has accelerated the need to be able to analyze the 3-dimensional structure of proteins in solution. Mass spectrometry is widely used for this. This has generated a need for new types of probes that covalently label protein solvent-accessible sites. Two common ones rely upon the creation of and covalent modification with highly reactive hydroxyl (OH) radicals. The first, fast photochemical oxidation of proteins (FPOP), generates hydroxyls from H_2O_2 via laser photolysis, and the second, synchrotron X-ray beam exposure, produces OH radicals via direct radiolysis of water. These techniques suffer from issues such as: a reaction times that are potentially too long to correctly measure protein structure or the necessity to add chemicals. Furthermore, both are cumbersome & expensive, either by accessing a synchrotron or building an instrument to perform FPOP. As a result of a collaboration at the interface of plasma physics and biochemistry, we developed a technique that generates µsecond bursts of OH radicals, using a surface-barrier discharge, for labeling proteins at solvent-accessible amino acid side chains. We call this Plasma-Induced Modification of Biomolecules (PLIMB). PLIMB does not require chemical additives, circumvents the issues associated with reaction timescale, and ultimately costs far less. Using a model protein in solution, cytochrome C, the protein was modified in a dose-dependent fashion in only a lightly buffered water-based solution, demonstrating that the system can generate OH radicals capable of labeling proteins without additional reagents. In addition, only discrete peptides within the protein are modified. Perturbing protein structure via digestion prior to plasma exposure significantly increases the observed covalent modification, suggesting that conformational structure is maintained during exposure. Experiments with myoglobin, a second protein, also revealed distinct regions of modification despite examining in depth the entirety of the protein's sequence. Mapping the oxidized peptides to myoglobin's crystal structure reveals that all of these peptides fall within the same face of the protein, suggesting the preservation of a higher-order structure under the solution conditions described. These experiments suggest that PLIMB provides a means of efficaciously generating microsecond bursts of OH radicals while providing a low cost and readily accessible means of probing the conformation of proteins in solution using mass spectrometry. We envision PLIMB being useful in a wide range of biological, medical and pharmaceutical fields.

11:20am **PS+PB-TuM-11 Biological Effects of Plasma-Irradiated Organic Molecules in Plasma- Treated Liquids**, ***Kenji Ishikawa***, *Y Hosoi, D Kanno, Y Kurokawa, H Tanaka, M Mizuno, F Kikkawa, M Hori,* Nagoya University, Japan

Selective killing of cancer cells incubated in non-equilibrium atmospheric pressure plasma (NEAPP)-activated medium (PAM) has been reported.[1] This antitumor effect revealed by involvement of reactive oxygen and nitrogen species (RONS) in PAM.[2] The effect was also found in plasma-activated lactate in Ringer's solution (Lactec), so called as PAL.[3] We found that the cancer cells incubated in the PAL received lesser oxidative stress than that of the PAM.[3] A cause of intracellular oxidation with respect to the RONS reactions has been studied by nuclear magnetic resonance (NMR) analysis of organic substances in the Lactec solution.

From the NMR measurements, reactive organic acids, that is, plasma activated lactate (LA) involved pyruvic acid (PA) and acetic acid (AA)-like components in the PAL were detected. The plasma activated organic acids act potentially as antitumor agents other than RONS.

Furthermore, NEAPPs irradiated to fullerenol. The plasma irradiated fullerenol demonstrated a cytotoxic effect on cells. The PF was modified by the plasma irradiation, arising carbonyl groups, ether bonds, and intercalated nitrate anion. Endocytosis of the PF induced to apoptotic cell death and generated intracellular RONS on cells cultured in the PF-added cell culture medium.

1 mL of fullerenol-added water (1.6 mM) was irradiated by the NEAPP (Ar 2 slm) for 3 min. Precipitates of the PF were collected by drying water at 70°C for 1 hr. The collected PF dissolved again into 50 µM of cell culture media (DMEM). 5×10^3 of HeLa cells were cultured for 24 hr in the PF-added DMEM and the same amount (50 µM) of fullerenol-added DMEM, respectively. Cell viability was evaluated by the MTS assay. Caspase activation and fullerenol permeation of the cell membrane were observed by fluorescent microscopy.

Although the viability of the fullerenol-added DMEM remained at a constant of 110 %, the HeLa cell viability decreased to 70 %, when the cells were incubated in the PF-added DMEM. The cells showed caspase 3/7 activation. The PF activate the caspase cascade pathway to induce apoptosis and permeation of the fullerenol into the cells. Therefore, the fullerenol properties were modified by the plasma-irradiation to enhance the cytotoxicity of PF.

Acknowledgments This study was supported by KAKENHI 24108002.

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11:40am **PS+PB-TuM-12 OH-Radical Generation in an Atmospheric-Pressure Plasma Discharge for use in Three-Dimensional Protein Structural Analysis*, Joshua Blatz*,** *B Minkoff, F Choudhury, D Benjamin, J Shohet, M Sussman,* University of Wisconsin-Madison

Atmospheric-pressure plasma discharges are well-known to generate OH radicals when interacting with water. However, the use of radicals created in this way for protein footprinting is virtually non-existent. Here, we describe a novel technique which utilizes a dielectric-barrier plasma discharge to oxidize proteins in solution. These oxidation events are quantified using mass spectrometry and allows us to determine the exterior domain and solvent accessibility of a protein.

To generate the plasma a high-voltage A.C. signal is applied to a needle electrode in close proximity to the surface of the liquid sample. This causes the gas to breakdown and form the plasma. These plasma discharges have been measured to be on the order of microseconds which prevents the protein from cleaving. During plasma exposure the sample is cooled to maintain temperature and prevent denaturation.

Protein bovine serum albumin was exposed to plasma. Labeling of the exterior domain was found in a manner consistent with other protein structural analysis techniques. Additionally, initial measurements have been collected which indicate that by changing various electrical, physical, and chemical parameters the technique may still be optimized. This could lead to greater OH-radical generation, reduced sample heating, and reduced pH change.

In addition to the consistent initial results and optimization potential there are many advantages it holds over competing techniques. It can be built inexpensively and on a space-limited benchtop. There are no necessary chemical additives which may interfere with the results and there seems to be no limit to the size of the protein which can be treated. All the samples are treated in liquid solution so they are free to move as they would *in vivo*.

12:00pm **PS+PB-TuM-13 Plasma-Surface Interaction at Atmospheric Pressure: From Mechanisms with Model Polymers to Applications for Sterilization*, Pingshan Luan*[1]**, *G Oehrlein,* University of Maryland, College Park

Cold atmospheric plasma (CAP) produces many types of chemically reactive species and is capable of modifying materials at atmospheric pressure. Studying plasma-surface interaction (PSI) at such pressure has been challenging due to the small mean-free-path (< 100 nm) which prohibits the method of using independently controlled beams of ions/neutrals. In the past few years, we developed an alternative approach of studying PSI at atmospheric pressure using well-controlled source-ambient-sample systems and comprehensive characterization techniques. First, we characterized and compared a few types of CAP sources such as atmospheric pressure plasma jet (APPJ) and surface micro-discharge (SMD). We found that the dominant reactive species generated by different CAP sources can be dramatically different. By tuning source operating parameters, we were able to manipulate the dominant reactants generated by these sources. Second, by controlling the gaseous environment wherein PSI took place, we could suppress certain unwanted interactions of plasma species with the ambient and regulate the delivery of reactive species to material surfaces. Lastly, we used polymers with representative functional groups to study the effect of reactive species on certain surface moieties. Due to the multi-phase nature of PSI, we integrated many characterization techniques in our study, including that of plasma/gas phases such as optical emission spectroscopy (OES), Fourier transform infrared spectroscopy (FTIR) and UV absorption, and that of material surfaces such as X-ray photoelectron spectroscopy (XPS), attenuated total reflection (ATR) FTIR and Ellipsometry. To our knowledge, the perpendicular electric field enhanced ATR-FTIR was used for the first time to study plasma processed polymer films less than 10 nm-thick. Combined with XPS, these techniques provide rich chemical information of both surface and subsurface modifications. By correlating plasma/gas phase with surface/subsurface measurements, we showed the dominant effect of a few types of reactive species such as O, OH and N_2O_5 on materials. We also provided evidence showing the competition between etching and surface modification during plasma treatment. Besides, we extended our investigation to studying the CAP-induced bacterial membrane damage, which might help understand the sterilization mechanism of CAP. We gratefully acknowledge funding from National Science Foundation (PHY-1415353) and US Department of Energy (DE-SC0001939). We thank Andrew J. Knoll, Elliot A. J. Bartis, V. S. S. K. Kondeti, Peter J. Bruggeman, Andrea Gilbert, Rohan Tikekar and David B. Graves for collaborations.

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

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

Moderators: Jeffrey Fenton, Medtronic, Inc., Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA-1 Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications***, **Andreas Thissen**, P Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; M Kjaervik, W Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

ACKNOWLEDGEMENTS: This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA-3 Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo***, **Jeffrey Fenton**, B Theilacker, A Belu, B Tischendorf,* Medtronic **INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA-7 Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes***, R Mom, L Frevel,* Fritz-Haber Institute of the Max Planck Society, Germany*; J Velasco-Velez,* MPI CEC Mülheim, Germany*; T Jones, M Plodinec,* Fritz-Haber Institute of the Max Planck Society, Germany*; R Schlögl,* MPI CEC Mülheim, Germany*; **Axel Knop-Gericke**,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one (μ_1) or two (μ_2) iridium atoms. It appears that oxygen is not only a "non-innocent ligand", but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO_2 formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO_2 may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA-9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides***, **Gabor A. Somorjai**,* University of California at Berkeley **INVITED**

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of b-hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; “free OH^-”, liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

5:40pm **PC+AS+BI+EM+NS+PB+SS-TuA-11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface***, **Takehiro Tamaoka**, H Yoshida, S Takeda,* Osaka University, Japan

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well–known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge–shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy (EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

6:00pm **PC+AS+BI+EM+NS+PB+SS-TuA-12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface***, **Angela Silski**, J Petersen,* University of Notre Dame*; R Brown,* Clarkson University*; S Corcelli, S Kandel,* University of Notre Dame

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

Plasma Science and Technology Division
Room 104C - Session PS+PB+SE-TuA

Atmospheric Pressure Plasmas

Moderators: Francois Reniers, Université libre de Bruxelles, Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+PB+SE-TuA-1 Compact, Low Cost Atmospheric Pressure Plasma Jets Driven by Piezoelectric Transformers***, **Michael Johnson**,* National Research Council*; D Boris, L Petrova, S Walton,* Naval Research Laboratory

In order for non-thermal atmospheric pressure plasma technology to be used for applications outside of the laboratory, there is a need to develop low-cost, portable devices that can be used for applications in the field. Constructing portable power supplies that can produce stable, non-thermal plasmas in full density air can be challenging as large electric fields are required to generate breakdown. Piezoelectric transformers are solid state transformers that can produce large gains in voltage, which makes them attractive candidates for plasma production. In this work, a piezoelectric transformer is used to amplify a low voltage AC signal in order to produce an atmospheric pressure plasma jet. Using this approach, plasma jets were generated with input voltages as low as 10 V when the piezoelectric transformer was operated at its resonance frequency (≈ 88 kHz). The electrical and optical characteristics of the piezoelectric driven plasma jet was compared to a plasma jet produced using a conventional high voltage sinewave of comparable operating frequency. Both jets were examined in helium and argon for a variety of different flow rates and operating voltages. The length of the jets were measured to determine if the piezoelectric transformer limited the potential size of the plasma jet. The current carried by the plasma jets were measured along with optical emission spectroscopy to examine the relative characteristics of the jets. Together, the results suggest the piezoelectric material may have influence beyond simple voltage amplification.

This work was supported by the Naval Research Laboratory Base Program. This research was performed while Michael Johnson held an NRC Research Associateship award at the U.S. Naval Research Laboratory.

2:40pm **PS+PB+SE-TuA-2 Process Regimes of Atmospheric Pressure Plasma-enhanced Chemical Vapor Deposition with Source Materials Highly Diluted in Inert Gases***, **SeungJae Baik**, J Jang,* Hankyong National University, Republic of Korea*; H Oh,* Yonsei University, Republic of Korea

Plasma-enhanced chemical vapor deposition (CVD) is appropriate for fast deposition with moderate film quality, but to form high quality materials such as epitaxial thin films, thermal processes at higher temperature are more favorable. High energy particles that are statistically produced in plasma processes are sources of film quality degradation. It has been previously reported that the plasma process at high working pressure, e.g., atmospheric pressure is feasible for epitaxial Si growth; where source gas species are highly diluted in inert gas. Employing a large dilution of source materials opens a new process regime in plasma-enhanced CVD: (1) low damage plasma processing (2) high deposition rate process with controlled powder generation (3) efficient usage of source materials.

We have performed Si thin film deposition processes with silane and hydrogen as source materials highly diluted in He or Ar gases under working pressure close to the atmospheric pressure (up to 700 torr). The new process regimes showing low damage plasma processing, high deposition rate with controlled powder generation, and efficient usage of source materials are experimentally demonstrated in various process conditions. In addition, the impurity incorporation into the film during deposition processes degrades the crytalline quality of the deposited Si thin films, which can be improved by employing plasma electrode pre-coating or pre-deposition cleaning process. Furthermore, the trade-off relation of plasma power and gas flow velocity revealed the process window of polycrystalline thin film deposition, and even epitaxial growth.

Atmospheric plasma-enhanced CVD tool is promising for fast deposition and low damage processing, and moreover, cheaper setup may also be viable via pre-deposition cleaning processes instead of utilizing expensive vacuum facilities.

3:00pm **PS+PB+SE-TuA-3 Plasma-enhanced Chemical Film Conversion (PECFC): Direct, Low-temperature Growth of Solution-processible and Printable Layered Thin Films***, T Liu, **R. Mohan Sankaran**,* Case Western Reserve University

In plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD), the addition of a plasma to dissociate or excite the gas molecules and create active chemical and energetic species can lower the thermal energy required at the substrate to drive thin film nucleation and growth. Here, we show that a similar approach can be used to lower the temperature required to convert molecular precursors deposited from solution onto a substrate to a functional, crystalline thin film which we term plasma-enhanced chemical film conversion (PECFC). We apply this method to layered materials such as hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) whose applications are currently limited by the lack of large-area, low-temperature, direct (substrate independent) growth processes.

Our experimental setup consists of an atmospheric-pressure, planar, dielectric barrier discharge and a cold wall substrate heater. Single molecular precursors for h-BN, ammonia borane, or MoS_2, ammonia tetrathiomolybdate were dissolved in solution and deposited by a variety of methods including dropcasting, airbrush spraying, spin coating, and inkjet printing on different substrates such as silicon (Si), silicon dioxide (SiO_2), and copper. The area of the film was only limited by the current size of our plasma source which is ~2 in^2. After conversion, the films were characterized by X-ray diffraction, micro Raman spectroscopy, atomic force microscopy, scanning electron microscopy, and transmission electron microscopy. We systematically compared thermal and plasma-assisted conversion at the same temperatures, background gas environments, and substrates. For h-BN, our results show that thermal conversion requires a minimum of 800 ^oC to nucleate on SiO_2, but only 650 ^oC with the addition of a plasma. Adding 20% H_2 enables a further 150 ^oC reduction for plasma conversion. For MoS_2, our results show that nucleation is enhanced in the presence of a plasma at the same growth temperature of 500 ^oC and a subsequent annealing step leads to a smooth (<0.2 nm RMS surface roughness) and highly crystalline film. We suggest that plasma species, especially atomic hydrogen (H), are involved in several important surface reaction mechanisms including abstraction of hydrogen, insertion in strained bonds, and radical formation, to enhance grain growth that overall enhance nucleation and growth of crystalline domains. We will also discuss the performance of the PECFC materials in electronic and energy devices.

3:20pm **PS+PB+SE-TuA-4 Plasma-based Remediation of Nanoscale Particulate Matter in Charbroiler Smoke Emissions***, **Sisi Yang**, S Subramanian,* University of Southern California, Los Angeles*; D Singleton,* Transient Plasma Systems*; C Schroeder, W Schroeder, M Gundersen, S Cronin,* University of Southern California, Los Angeles

Recent studies have shown ultrafine particulate matter (UFPM) produced in commercial charbroiling processes represents a serious health hazard and has been linked to various forms of cancer. In this study, we demonstrate a highly effective method for treating restaurant smoke emissions using a transient pulsed plasma reactor based on a nanosecond high voltage pulse generator. We measure the size and relative mass distribution of particulate matter produced in commercial charbroiling processes (e.g., cooking of hamburger meat) both with and without the plasma treatment. Here, the plasma discharge is produced in a 3” diameter cylindrical reactor with a 5-10 nanosecond high voltage (17 kV) pulse generator. The distribution of untreated nanoparticle sizes peaked around 125-150 nm in diameter, as measured using a scanning mobility particle sizer (SMPS) spectrometer. With plasma treatment, we observe up to a 55-fold reduction in total particle mass and a significant reduction in the nanoparticle size distribution using this method. The effectiveness of the UFPM remediation increases with both the pulse repetition rate and pulse voltage, demonstrating the scalability of this approach for treating higher flow rates and larger systems.

4:20pm **PS+PB+SE-TuA-7 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: *In situ* Measurements of Electron Heating in Materials***, **Scott Walton**,* U.S. Naval Research Laboratory*; J Tomko, B Foley,* University of Virginia*; D Boris,* U.S. Naval Research Laboratory*; M Johnson,* National Research Council*; T Petrova,* U.S. Naval Research Laboratory*; A Giri, P Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest since both contribute to the physicochemical changes during plasma-based materials processing. A 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 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 electrons propagate radially from the point of contact. These results, in conjunction with voltage and current measurements, 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.

4:40pm **PS+PB+SE-TuA-8 Surface Activation by Atmospheric Plasma: the Right Technology for the Right Application***, A Ozkan, D Merche, **Francois Reniers**,* Université Libre de Bruxelles, Belgium

Cold atmospheric plasma are widely used for surface activation in many applications. Today, many technologies are available, such as coronas, dielectric barrier discharges (DBDs), remote (or post-discharge) DBDs, torches, operating in the radiofrequency mode, gliding arcs, ……. A wide variety of operating conditions can be found in the literature or on the websites of the manufacturers : AC, DC, kHz range, noble gas or air, high or low power, ….. For the scientist, the lab manager, or the CTO of a company looking for a new, clean, activation technique, the vast list of possibilities, although representing opportunities, may represent a challenge. In this paper, we try to set up a product driven roadmap to help the scientist making the best choice for the plasma technology to implement for his application. Through a few selected examples, all tested in our laboratory equipped with 7 different plasma technologies and 15 reactors, we show which is the best technology for the application of interest. Advantages and drawbacks of each of the tested technologies with respect of the material, the energy consumption, and the time and cost of operation are presented, and discussed in terms of plasma and surface characterization.

The applications chosen addresses a wide range of questions such as:

- which plasma to chose to clean and activate glass substrates (a comparison between torches and in-situ DBDs is proposed)

- atmospheric plasma to grow an oxide layer on aluminium : a comparison between an air operated torch and plasma electrolytic oxidation

- how to activate a macroscopic 3D pre-painted metal piece for further painting using an atmospheric plasma torch. A comparison between 4 torches is presented

- how to activate the surface of selected polymers using DBD, RF torches with different gases

- how to activate surfaces (silicon, polymers, nanotubes) for further grafting of metal nanoparticles

- how to modify PTFE using a torch, what are the side effects, and why.

These examples will be starting points for a more general discussion about methodology, based on the final expectations and the chemistry and physics of each technology.

5:00pm **PS+PB+SE-TuA-9 Aluminum Alloy Surface Cleaning by Atmospheric Pressure Microwave Discharge***, **Lucia Bonova**, W Zhu, A Farrokhpanah, D Krogstad, Z Jeckell, S Chaudhuri, D Ruzic,* University of Illinois at Urbana-Champaign

Aluminum and its alloys are commonly used as lightweight materials in many industrial sectors including aerospace. During the manufacturing process of aluminum, a series of lubricants and additives are used to avoid sticking of layers and prevent degradation or corrosion. The residual hydrocarbon film is typically removed by a chemical chromate process prior to the deposition of an anticorrosive layer. We present an alternate method to remove the hydrocarbons deposited on the aluminum surface by an atmospheric pressure microwave discharge.

The Center for Plasma Material Interaction (CPMI) at University of Illinois has developed novel patented technologies of Evaporative Coatings at Atmosphere Pressure (ECAP) using a 2.45 GHz microwave power to treat the aluminum surface with an air plasma at atmospheric pressure. The cleaning effect of this microwave plasma was analyzed by contact angle measurements, XPS and ATR-FTIR.

5:20pm **PS+PB+SE-TuA-10 Temporal and Spatial Study of a Parallel pin-plate Plasma Reactor***, **Vladimir Milosavljević**, M Gulan, L Scally, P Cullen,* BioPlasma Research Group, Dublin Institute of Technology, Dublin, Ireland

Electrical discharges in gases have demonstrated a wide range of effects for material science and energy applications. Under both laboratory and industrial setups, such electrical discharges can produce a stable plasma. From both fundamental and applied purposes, such gaseous plasmas are well studied, the technology has found many applications. Recent interest has turned to operating such plasma under atmospheric conditions. The main advantage of the plasma discharge at atmospheric pressure over low-pressure plasma or high-pressure plasma, is that no reaction vessel is needed. However, with increasing gas pressures, the stability and reproducibility of the plasma discharge are significantly impacted. For atmospheric pressure, in order to obtain a stable plasma discharge in addition to the electrodes a dielectric barrier is required. The function of this dielectric is to spread the electrical charge throughout the entire electrode in order to create multiple conducting paths for the discharges to occur. This is the foundation of the Dielectric-barrier discharge (DBD). One or both electrodes in DBD could be covered by a dielectric material which serves as an electric polarizer, and helps maintain a low gas temperature. Over the course of its life, for any DBD system, the biggest disadvantage is the dielectric contamination. In most cases, this dielectric is a polymer, and polymers are generally fragile materials. Therefore, developing a plasma system that does not require a dielectric, and has a reproducible and stable electrical discharge at atmospheric pressure would offer new system designs and applications.

This work presents a pulsing plasma system (PPS) which can run at atmospheric pressure under various external parameters. The system has a planar configuration with a bottom (grounded) flat electrode and a top multiple pin electrode (high voltage). The design of this PPS allows several parameters to be modified, such as: discharge frequency (30-125 kHz), duty cycle (1-100%), duty cycle frequency (100-3000 Hz), peak-to-peak voltage (up 60 kV), power (up to 700 W), distance between electrodes (up to 55mm), and treatment time (unlimited). The new plasma system allows an increase in the surface-plasma interaction selectivity and to reduce plasma induced damages to surfaces. The electron properties and gas radical density generated for the system under such control parameters are reported.

This work was funded by the Dublin Institute of Technology and PlasmaLeap Technologies, Ireland.

5:40pm **PS+PB+SE-TuA-11 Plasma-modulated Metamaterials and Photonic Crystals***, **Jeffrey Hopwood**, H Kim,* Tufts University

Metamaterials are periodic assemblies of man-made structures that can mimic naturally occurring materials. By clever design, electromagnetic transmission through metamaterials may have extraordinary properties such as negative refractive index. In this paper we describe the formation of atmospheric pressure argon microplasmas within metamaterials as well as photonic crystals. Microplasma ignition within these materials is initiated by first creating an implicit microwave or millimeter wave resonance within the structure. For example, a vacancy in the artificial crystalline structure can act as a millimeter wave cavity. Incident EM waves excite this resonance and the strong resonant electric field causes gas breakdown.

In general, metamaterials are pre-configured during the design process and exhibit fixed transmission characteristics. The self-initiated plasma, however, dynamically changes the metamaterial. We show that depending on the gas pressure and electron density, microplasma inclusions may act as dielectrics or conductors. Experimentally one observes that the appearance of microplasma causes a change in the material from transparent to reflective, or vice versa. A metamaterial consisting of an array of copper split-ring resonators (3x3x9) is described in terms of the plasma density and its microwave transmission from 1-3 GHz. The appearance of microplasmas quenches the resonance and decouples the resonators from one another; the transmission spectra are radically changed upon de-coupling. In the millimeter wave band, a photonic crystal consisting of alumina rods is shown to support argon plasma at 43 GHz. The transient response of the photonic crystal during pulsed EM radiation and plasma formation is measured and found to act as a power limiting device.

6:00pm **PS+PB+SE-TuA-12 Generation of Large-Volume Transient Glow Discharge Plasma by an External Fast Ionization Wave (FIW) from a Plasma Jet***, **Hamid Razavi**, M Laroussi,* Old Dominion University

A non-thermal transient glow discharge can be generated remotely in a nonconductive low–pressure chamber by an external guided fast ionization wave (FIW). We used an atmospheric-pressure LTP jet (APLTPJ) as an external source of FIW to transfer the enhanced electric field at the wavefront to a reduced–pressure Pyrex glass chamber with no electrical connection to the chamber [1]. Here, we study on the interaction of FIW with a dielectric surface which forms the wall of the low-pressure system.

In this study, key characteristics of the transient diffuse plasma are discussed. Plasma parameters were measured by Langmuir probe and APLTPJ electrical measurements were done to elucidate the operational mechanisms of the FIW as an igniter of a reduced pressure glow discharge plasma. It is shown that the transient discharge in the low-pressure chamber generates a bulk plasma with negative potential due to the nonconductive boundary. We also used Optical emission spectroscopy (OES) to show the physical and chemical characteristics of the APLTPJ plasma and the transient glow discharge plasma. It is shown that the glow discharge plasma is capable of producing second and third ionized nitrogen and oxygen atoms (OII, NII, and NIII). Fast images were taken by an intensified CCD to study the launching and propagation phases of both APLTPJ plasma and the transient reduced pressure glow discharge plasma as well as the incidence of the guided FIW on a dielectric surface.

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Plasma Biology, Agriculture, and Environment Focus Topic
Room Hall B - Session PB-TuP

Plasma Biology, Agriculture, and Environment Focus Topic Poster Session

PB-TuP-1 Detection of Metallic Ions in Solution Using Optical Emission Spectroscopy of Plasma Driven by Bipolar Pulsed Power Sources, ***Ching-Yu Wang***, *C Hsu,* National Taiwan University, Taiwan, Republic of China

Detection of metallic ions in solution using optical emission spectroscopy in plasmas offers advantages including simultaneous detection of multiple elements, minimization of cross-element interference, and rapid detection. In this work, plasma ignited in metallic-salt-containing-solution using bipolar pulsed DC power is studied. The goal is to understand how the modulation of the bipolar pulsed power influences the plasma optical emission of metallic elements. A power source that provides asymmetric bipolar voltage pulses of a duration between 10 µs to 100 ms with an amplitude up to ±1 kV is used. Plasma is ignited inside the gas-phase formed in the solution. The gas phase composes of water vapor, oxygen, and/or hydrogen through joule heating and/or electrolysis. The plasma behavior and therefore the optical emission are greatly influenced by the width, polarity, and amplitude of the bipolar pulses. Voltage and current probe are used to conduct electrical analysis; optical emission spectrometer and photo multiplier tube are used to perform time-averaged optical emission spectroscopy and time-resolved emission intensity, respectively.

While using repetitive 7500µs-widelow voltage pre-pulses followed by 100 µs-wide 600 V pulses to ignite plasma in solution consisting of 0.1 M HNO_3, 500 ppm Pb, and 250 ppm Na, we observe a low peak current with the application of the pre-pulse. The intensities and ratios of H, Pb, and Na emission lines are varied with different polarity and amplitude of the pre-pulse. The above observations show the modulation of the voltage pulses greatly influences the plasma behavior and therefore its optical emission. This work provides an effective way to tailor the plasma behavior and its optical emission, which could potentially be used as a strategy to obtain more reproducible and sensitive detection of metallic ion in water for analytical purposes.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

PC+AS+BI+EM+NS+PB+SS-TuP-1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water, ***Pitambar Sapkota***, *S Ptasinska,* University of Notre Dame; *A Cabrera,* Instituto de Física, Pontificia Universidad Católica de Chile, Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H_2O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of $CuFeO_2$ and $CuFe_{1-x}Ga_xO_2$ composites were exposed to various H_2O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

PC+AS+BI+EM+NS+PB+SS-TuP-2 Interfacial Water in Silicon-based Catalytic Motors, ***Jordi Fraxedas***, *K Zhang, B Sepulveda, M Esplandiu,* Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *X Garcia, J Llorca,* Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain; *V Perez-Dieste, C Escudero,* Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt4+ species and then the reduction of Pt2+ species, which increases the metallic character of the surface.

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[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

PC+AS+BI+EM+NS+PB+SS-TuP-3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study, ***Yufei Ni***, *F Zaera,* University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H_2 pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(−)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine.The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its anime moiety, and not through the aromatic ring as commonly believed.

PC+AS+BI+EM+NS+PB+SS-TuP-4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst*, Sonal Singhal,* *A Shukla,* IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152^0, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

PC+AS+BI+EM+NS+PB+SS-TuP-5 Thermally Driven Solid-solid Li^+ Transfer into Nanostructured TiO_2*, Tiffany Kaspar, T Varga,* Pacific Northwest National Laboratory*; D Shapiro,* Advanced Light Source, Lawrence Berkeley National Laboratory*; A Martinez, Y Shin, K Han, M Lee, S Thevuthasan, V Murugesan,* Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO_2) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 $mAhg^{-1}$. Furthermore, nanostructured TiO_2 anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO_2, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO_2 nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li^+ transfer to, and intercalation in, TiO_2 nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO_2 nanoparticles during Li^+ intercalation. Our results indicate that thermally driven solid-solid Li^+ transfer to TiO_2 has occurred, and altered the TiO_2 structure at the edges of the agglomerated nanoparticles.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

Novel Approaches and Challenges of Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+EM+PB+SS-WeM-1 Probing Chemical Species and Potential Profiles of Electrified Interfaces*, Ethan J. Crumlin,*** Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/liquid electrochemical interface. In particular, I will discuss how we were able to probe the potential drop within the electrochemical double layer (EDL) as well as the potential of zero charge under polarization conditions. This unique approach was accomplished by measuring spectral changes observed in both the electrolyte (water) and a neutral spectator probing molecule (pyrazine). By combining these experiments with numerical simulations provided the ability to discern the shape of the electrochemical double layer profile as a function of both electrolyte concentration and applied potentials. Extending beyond the EDL, I will highlight some of our recent investigations into both the oxygen evolution reaction on a platinum electrode as well as a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

8:40am **PC+AS+BI+EM+PB+SS-WeM-3 Observation of Electron Transfer in Riboflavin Reduction by In Situ Liquid SIMS*, Rachel Komorek,*** *X Yu, Z Zhu, X Yu,* Pacific Northwest National Laboratory

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials. Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram. Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

Key words: in situ liquid SIMS, SALVI, riboflavin reduction, electrochemistry, electron transfer

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9:00am **PC+AS+BI+EM+PB+SS-WeM-4 Electrowetting of Liquid Drops Revisited by XPS*, Sefik Suzer,*** *P Gokturk, B Ulgut,* Bilkent University, Turkey

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO_2/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency (10^{-2} – 10^{5} Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

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9:20am **PC+AS+BI+EM+PB+SS-WeM-5 Probing Interfaces in Heterogeneous Catalysts at Atomic Scale: Current and Emerging STEM Techniques*, Miaofang Chi,*** Oak Ridge National Laboratory **INVITED**

Chemical reactions take place on the surfaces and interfaces of heterogeneous catalyst systems. Depending on the phase of the reactant, the reactive interfaces include those between solid-gas, solid-liquid, and triple-phase interfaces of solid-gas-liquid. At these interfaces, the catalyst provides active sites where the reactants are adsorbed, activated, and converted to new chemical species that are eventually released from the catalyst surface. The ability of catalysts in promoting these reactions is determined by the surface binding energy, which can be modified by tuning the interfacial atomic arrangements or by forming new interfaces, e.g., forming core-shell structures. Understanding the formation of these interfaces during synthesis and their structural and chemical evolution during operation are important to the rational design of future high-performance catalysts. Probing these dynamically evolving interfaces at a sufficient spatial resolution, however, presents many challenging. Recent work on elucidating the formation and the operation mechanisms of interfaces in precious metal-based heterogeneous catalysts using *in situ* atomic-scale scanning transmission electron microscopy (STEM) techniques will be discussed. Several emerging STEM-based methods, such as vibration spectroscopy and atomic-scale differential phase contrast imaging that are currently under development within the microscopy community will be introduced, and their prospective influence on future studies to design functional interfaces in heterogeneous catalysts will be discussed.

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11:00am **PC+AS+BI+EM+PB+SS-WeM-10 From 2D to Advanced 3D Surface Functionalization using Self-limiting Reactions in the Fluidized Bed Reactor Technology*, Didier Arl,*** *T Da Cunha, N Adjeroud, K Menguelti, M Gerard, D Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

The integration of novel functional nanomaterials like high specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

Plasma Biology, Agriculture, and Environment Focus Topic
Room 104A - Session PB+BI+PC+PS-WeA

Plasma Agriculture & Environmental Applications

Moderator: Deborah O'Connell, University of York, UK

2:20pm **PB+BI+PC+PS-WeA-1 Pulsed Power Applications for Farming and Food Processing***,* ***Koichi Takaki****,* Iwate University, Japan **INVITED**

High-voltage and plasma are useful in several stages in agriculture, fishery and food processing including contribution to the food safety. Pulsed high-voltage produces intense high-electric field which can cause some biological effects such as stress response (stimulation) and electroporation. Types of pulsed power that also have biological effects are caused with gas discharges and water discharges which include reactive species such as ROS and RNS. We developed repetitively operated compact pulsed power generators with a moderate peak power for the agricultural applications.

The pulsed repetitive discharge were used for promoting growth of the vegetables and fruits. The growth rate of the vegetables and sugar content in the strawberry harvested after the cultivation increased by the plasma irradiation to the hydroponic solution [1] . The plasma was irradiated in the drainage water for 10 and 20 minutes each day. The leaf size of the plants increased with plasma treatment time. Number of colony forming units (CFU) of *R. solanacearum* in the liquid fertilizer decreased from 10^7 to 10^2 CFU/mL using the discharge plasma treatment [2]. Seedlings with discharge plasma treatment were relatively healthy; in contrast, all seedlings in the positive control wilted and died from infection of *R. solanacearum* after 12 days. The yielding rate of Shiitake mushroom (*L. edodes*) was also improved with the high-voltage stimulation in fruit-body formation phase [3] .

Electrostatics effect were used for keeping freshness of not only agricultural products [4, 5], but also marine products [6] . In postharvest phase of agriculture, keeping freshness in storage house and in transportation container is important. The electrostatic effects can contribute to remove airborne bacteria and fungi spore from the storage house and container [4] . This removal contributes to reduce the infection risk with fungi and bacteria. Some kinds of fruit and vegetable emit the ethylene gas which accelerate a degradation of other kind fruits and vegetables. The plasma can contribute the ethylene removal via oxidization reaction [5] . The AC electric field induces a conformational change of protein. This technologies can contribute to extend the freshness of marine products [6] .

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2. T. Okumura *et al.,* Plasma Medicine, **6** (2017) 247.
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6. T. Okumura *et al.,* Jpn. J. Appl. Phys., **55** (2016) 07LG07.

3:00pm **PB+BI+PC+PS-WeA-3 Stimulus Control on Organisms Using Pulsed Power Technology***,* ***Douyan Wang****, T Namihira,* Institute of Pulsed Power Science, Kumamoto University, Japan **INVITED**

Pulsed power is instantaneous ultra-high power with high energy density (10^5-10^7J/m^3). By controlling and utilizing it in a narrow space and an instantaneous time, phenomena and reactions that are not attained by conventional and ordinary methods can be achieved. For instance: electromagnetic field, discharge plasma, shockwaves, intense light emission, etc. By selecting or combining some of these physical phenomena, it is able to control the degree of output performance. Bioelectrics refers to the use of pulsed power, powerful pulsed electric or magnetic field for extremely short periods of time, non-thermal plasmas in gases or liquids and shock waves, in order to give novel physical stresses to biological cells, tissues and/or organisms as well as bacteria. Bioelectrics is an interdisciplinary academic field over physics, chemistry, biology, medical science, agriculture, environmental, mechanical and electrical engineering, and is expected to open up new science and technology.

By controlling the degree of electrical stimulations using pulsed power, it is possible to either inactivate biological targets or keep them alive and activate their functions. Examples of inactivation are given as: sterilization of liquids, treatment of algae and marine harmful organisms, growth inhibition of plants. On the other hand, more delicate stress control enables the activation of living organisms such as transcriptional activation of genes, substance transduction into cells, growth enhancement of plants. Both direct and indirect stimuli are useful. Here, aerial, liquidus and edaphic environmental control are examples of the indirect stimulus.

4:20pm **PB+BI+PC+PS-WeA-7 Synthesis of Nitrates by Atmospheric Microplasma in Aqueous Solution***,* ***Nicolas Maira****, F Reniers,* Université Libre de Bruxelles, Belgium

For many years, cold atmospheric plasma techniques have been used for a large variety of applications such as surface modification, film deposition, nanoparticles synthesis or pollutants degradation. One of their main advantage is the possibility to work with a gaseous, liquid or solid phase. In this study, the plasma water treatment is investigated for a potential application in agriculture. When water solutions are treated by plasma, in air environment, several reactive oxygen and nitrogen species (RONS) are generated [1,2]. The main RONS are hydrogen peroxide (H_2O_2), nitrites (NO_2^-) and nitrates (NO_3^-). Nitrates are one of the most essential molecules for plants because, together with ammonium, they represent an important source of nitrogen which is mandatory for DNA, RNA, enzymes, chlorophyll, ATP and many other molecules. For some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, a DC atmospheric microplasma system is used for the investigation of the formation mechanism of NO_3^- in water. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

Firstly, the influence of the inner diameter of the microplasma stainless steel needle is investigated (internal diameter of 0,76 mm, 0,50 mm and 0,20 mm). The amount of NO_x^- (NO_2^- and NO_3^-) synthesized varies with the diameter and the shape of the plasma is different for a larger internal diameter. Furthermore, the total amount of NO_x^- formed in a solution shows a linear trend with the total charge injected into the plasma with, however different slopes for nitrites and nitrates.

The oxidation mechanism of NO_2^- to NO_3^- is then explored and the influence of other reactive species on this mechanism is then studied. Indeed, it is known from the literature that H_2O_2 may play a role in the process for different atmospheric plasma systems [2]. The formation of oxygenated water and its role as an oxidant is highlighted in the microplasma system. Therefore, the amount of H_2O_2 synthesized by microplasma is compared to other plasma systems. The nature of the atmosphere above the solution is modified in order to determine the species formed in the gaseous phase and their respective influence.

The authors would like to thank the financial support of NITROPLASM (EOS Project 30505023)

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[2] Judée F. *et al. Water Research* 133, 47-59, **2018**.

5:00pm **PB+BI+PC+PS-WeA-9 Design Considerations for Plasma-based Water Purification Reactor Scale-up***,* ***John Foster****, S Mujovic, J Groele, J Lai,* The University of Michigan-Ann Arbor **INVITED**

Plasma-based water purification has been proven viable in laboratory demonstration experiments, highlighting its effectiveness at the removal of contaminants of emerging concern and at disinfection. While these small scale experiments bolster the promise of plasma based advanced oxidation, translating demonstration experiments to practice has proven challenging. A chief challenge is the scale up of plasma-based methods to a viable water treatment technology that is both robust and usable at treatment flow rates of interest. Presented here is an attempt to frame the scope of the challenge, the current state of the art in plasma water purification, and scale up design considerations both from plasma science and engineering standpoints. The objective here is to summarize key challenges to scale-up and implementation as well as elaborate on approaches to achieving a high throughput plasma-based water treatment system. Two illustrative reactor examples amenable to scale up are highlighted along with associated performance data. The pathway from bench-top demonstration of plasma-based systems to piloting and ultimately to the reduction of the technology to practice is also elaborated upon.

5:40pm **PB+BI+PC+PS-WeA-11 Radicals and Ozone Generated in Ar/He and Ar/He/H_2O Plasma by using Atmospheric Pressure Plasma Jet Systems and their use in Methylene Blue Degradation**, *J Hsieh, **YiJinWei Wei,*** Ming Chi University of Technology, Taiwan, Republic of China*; C Li,* National Yang Ming University, Taiwan, Republic of China

Optical emission spectroscopy (OES) and UV absorption spectrometry were first used to gather information about the excited species present near/in the plasma plume generated using Ar/He and Ar/He/H_2O gases with an atmospheric pressure plasma jet (APPJ). Afterward, the APPJ system was used to study its efficiency in degrading methylene blue as a function of radical and ozone density. According to the results, it was found that the degradation of methylene blue was directly related to the ozone concentration and, perhaps, OH radical density. Additional moisture may be used to control the ratio of ozone and OH radical density, resulting in the variation of degradation rate. Complete degradation of MB can be achieved in 80 seconds.

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