

Plasma Science and Technology Division

Room 21 - Session PS+AS+SE-MoM

Atmospheric Pressure Plasmas

Moderators: Olivier Guaitella, Ecole Polytechnique - CNRS, France, Seiji Samukawa, Tohoku University, Japan

8:20am **PS+AS+SE-MoM-1 Study of Atmospheric-pressure kHz Multi-jet Plasma System**, *Vladimir Milosavljevic, J Lalor, L Scally, P Cullen*, Dublin Institute of Technology, Ireland

Non thermal plasmas can be generated in laboratory conditions using generic, readily available and easily sourced components. Examples include glass tubing, copper or stainless wire electrodes, metal mesh, plastic enclosures, and step-up transformer based power supplies. Such sources, although effective, may not offer optimised conditions or efficiencies. In many cases they may not sustain extended operation due to excess thermal and electrical breakdown. Second-generation laboratory apparatus and scaled up designs involve selected materials, custom machined components, electrodes based on calculated requirements, and suitably designed or sourced power supplies. These assemblies will offer a more accurate theoretical and empirical view of the plasma performance. The inclusion of a material selection software tool for the rational selection of engineering materials can provide detailed information relating to the mechanical thermal and electric properties. Developing a non-thermal atmospheric plasma source involves three important factors for material selection. Firstly the application and operating conditions of the design needs to be examined; is it to be handheld, exposed to ambient air or contained in an enclosure. For many plasma sources, certain polymers offer an ideal material, for other configurations, composites or metals may be best. Secondly, does the source need to facilitate a controllable environment in which to generate the plasma, in other words, is it necessary to purge or evacuate the enclosure in order to accurately control the gas chemistry, if this is the case, a choice of material for this housing and containment area must be considered. The third factor is the material selection for the conducting elements, namely the cables, electrodes and grounding components. Typical electrode metals include copper, aluminium, brass and stainless steel.

In this work 12 circular plasma jets are presented. They are designed and built in-house, and power up with a single phase generator of 10-30 kV, at 10-100 kHz that powers up to 2 kW. Voltage-current measurements and optical emission spectroscopy (OES) are applied for optimization of transient discharges operated for several different gas chemistry at atmospheric pressure. The influence of applied voltage, frequency, gas flow rate and gas chemistry in relation with the OES signal, plasma plume formulation, gas velocity and electrical properties of plasma jets are the objectives of this study.

This work was funded under the 'PlasmaGrain' project funded by the SFI, Republic of Ireland.

8:40am **PS+AS+SE-MoM-2 Synthesis of Nitrates by Atmospheric Microplasma Over Water : Effect of the Experimental Parameters and Intermediate Species**, *Nicolas Maira, C De Vos, F Reniers*, Université Libre de Bruxelles, Belgium

Nowadays, nitrates are used mainly as fertilizers in agriculture. They are produced by the combination of the Haber-Bosch and Ostwald process. Industry, throughout the years, has increasingly optimized the energetic yield of this synthesis. Nevertheless, this method requires the use of a hydrogen source, essentially extracted from fossil fuel. Moreover, nitrates synthesized in colossal plant factories have to be shipped to the end-user. However, in 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, the same philosophy as for the ozone process is applied: taking advantage of the composition of natural air in order to synthesize nitrates directly in a solution [1]. The mechanism of formation of nitrates using an atmospheric microplasma discharge operating in air or in argon in an open air environment is investigated. The effect of the treatment time, the discharge current and power, the water surface – capillary distance, and the solution pH on the formation of nitrogen oxides in the gas phase and in solution is studied. 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).

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 (NO_2^-) and nitrates (NO_3^-). The reaction mechanism involves the formation of gas phase NO, as evidenced by OES. It is known that the synthesis of nitrates is pH-dependent [2]. In an acidic solution with a pH below 3, the formation of nitrates is favored whereas a higher pH allows the formation of nitrites which are oxidized in nitrates after the treatment. The transformation of nitrites into nitrates after plasma synthesis is monitored by IC during time and seems to follow a logarithmic trend. The performed experiments allow the determination of the amount of energy required to form a mole of nitrate in this set-up.

[1] Fridman A. *Plasma Chemistry*, Cambridge University Press, **2008**, 382-398

[2] Machala Z., Tarabova B., Hensel K., Spetlikova E., Sikurova L., Lukes P. Formation of ROS and RNS in water electro-sprayed through transient spark discharge in air and their bactericidal effects, *Plasma Processes and Polymers*, **10**, 649-659, **2013**.

9:00am **PS+AS+SE-MoM-3 Plasma Catalysis for CO_2 and CH_4 Conversion at Atmospheric Pressure**, *A Ozkan, S Chorfi, L Brune, T Visart de Bocarmé, François Reniers*, Université Libre de Bruxelles, Belgium

The field of plasma-catalysis, i.e. combining a plasma process and a catalyst, either inside the plasma or in its post-discharge is gaining importance for the conversion of CO_2 and CH_4 mixtures. Indeed, the combination of plasma and catalysis could not only increase the conversion of these gases, but also orient the reaction(s) towards the synthesis of valuable molecules.

This paper will present first the main factors that influence the conversion and the energy efficiency for the reduction of CO_2 using an atmospheric pressure dielectric barrier discharge. Second, an alumina supported catalyst will be added between the electrodes and its effects on the conversion of pure CO_2 , pure CH_4 and CO_2/CH_4 mixtures will be presented. Ni, Co, Cu have been tested, as well as various loadings of Ni.

The conversion is studied by atmospheric mass spectrometry, and the chemical identification of the end products was obtained either by mass spectrometry or gas chromatography.

It is shown that the frequency, the pulse mode, the dielectric nature and thickness strongly influence the conversion and energy efficiency of the reaction, whereas the residence time and the power injected into the discharge modify the conversion[1]. An increase in the Ni loadings leads to an increase in conversion of both CO_2 and CH_4 . If CO and H_2 , starting molecules for more complex organic chemistry, are always the main products of reaction, C2, C3 and C4 molecules, oxygenated or not are also detected. The effect of the nature of the catalyst on the relative amounts of these molecules is discussed.

[1] : A. Ozkan, A. Bogaerts, F. Reniers, J. Phys. D: Appl. Phys. **50** (2017) 084004, doi:10.1088/1361-6463/aa562c

9:20am **PS+AS+SE-MoM-4 Aluminium Surface Plasma Treatment at Atmosphere Pressure**, *Lucia Bonova, I Shchelkanov, C Ahn, S Chaudhuri, D Ruzic*, University of Illinois at Urbana-Champaign

Plasma surface treatment at atmosphere pressure is a fast growing industry. Among other applications, surface treatment of metals for adhesion and corrosion resistance improvement has attracted widespread interest. Being operated at atmosphere pressure, various types of plasma discharge devices provide efficient, cheap and large scale processing capabilities. In this area, surface treatment of aluminium for surface properties modification is of great interest as it can decrease steps in process for final coating deposition, reduce usage of harmful chemical reagents, which in their turn require costly dispose procedures, and increase functional coatings performance.

The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device and a method for multicomponent metal coatings deposition at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. The device is capable of coating deposition from a solid metal state and from gas carried precursors as well as composites with processing gas like ZrO. These capabilities make ECAP a very flexible tool for gradient coating deposition for surface functionalization and adhesion improvement. In this gradient coating, the alumina facing materials is gradually replaced with a second layer material with perfect adhesion for final functional coating.

Current work discusses several methods, which were used to improve aluminium surface wettability and adhesion to an epoxy. As a fundamental

experiment, we have conducted the simple treatment on aluminium plate by ECAP which operated with feedstock gas of evaporated H₂O and He. It shows remarkable enhanced epoxy adhesion on aluminium sample against the control condition. System configuration for roll-to-roll applications and broad area coatings/cleaning are also discussed.

9:40am **PS+AS+SE-MoM-5 The Role of Bulk Liquid Transport Processes in the Plasma-Liquid Interfacial Chemistry**, *Selma Mededovic Thagard, M Vasilev, D Bohl, P Conlon*, Clarkson University **INVITED**

Plasmas formed directly in and contacting a liquid are powerful sources of reactive radicals, ions and high-energy electrons and have been successfully used to sterilize water and fruit juices, purify water, synthesize materials and nanoparticles, and for applications in plasma medicine, electrical transmission, and polymer surface treatment. Nevertheless, despite the obvious versatility in processing capabilities, the optimization and broader application of electrical discharge plasmas in and contacting a liquid have been limited due to a general lack of understanding of the underlying physical and chemical processes occurring at the plasma-liquid interface. Despite the significant progress that has been made towards understanding interfacial chemistry of plasmas----- in the last decade or so (especially for air plasmas contacting water), relative contributions of plasma processes such as formation and diffusion of reactive species and bulk liquid processes such as electrohydrodynamic flow to interfacial dynamics have not been yet determined.

This work investigates the extent to which bulk liquid processes, primarily bulk liquid composition and plasma-induced electrohydrodynamic flow control the rates of chemical reactions at a plasma-liquid interface. We have determined the efficacy of the plasma process for treatment of a wide range of different compounds and used the results of this investigation to construct a model to predict the approximate treatability of any compound based on just a few of the compound's physical properties. Experiments with different initial bulk liquid concentrations of non-surfactant and surfactant compounds have also been performed to investigate how interfacial compound concentration affects its removal rate. Particle Image Velocimetry has been used to quantify the surface velocity of a liquid as a function of its chemical composition.

10:40am **PS+AS+SE-MoM-8 Efficiency of Electrolytic Reduction of Aqueous Metal Salts to Metal Nanoparticles at a Plasma-Liquid Interface**, *S Ghosh, Ryan Hawtof*, Case Western Reserve University; *P Rumbach, D Go*, University of Notre Dame; *R Akolkar, R Sankaran*, Case Western Reserve University

Electrolytic cells with a plasma serving as one or both of the electrodes eliminate the solid metal and allow electrochemical reactions to be carried out at a gas-liquid interface. This is particularly beneficial for the synthesis of metal nanoparticles from metal salts since the deposition of a thin film onto the electrode is avoided. However, because of the complexity of the plasma and the resulting interfacial reactions, the mechanism for metal nanoparticle formation remains unknown.

Here, we designed experiments to understand the mechanism of the reduction of silver nitrate (AgNO₃) to silver (Ag) nanoparticles by a previously reported atmospheric-pressure, direct current microplasma operated as the cathode. We applied a well-known methodology in electrodeposition to assess the faradaic efficiency whereby the mass of the synthesized material is compared with the theoretical amount of mass estimated from the charge injected into solution. A faradaic efficiency of 100% would indicate that all the charge is going towards the desired reduction of Ag cations to solid Ag, $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$, whereas an efficiency less than 100% would suggest that there are side reactions, most probable of which is the second order recombination of (solvated) electrons to form hydrogen gas and hydroxide ions, $\text{e}^-_{(\text{aq})} + \text{e}^-_{(\text{aq})} + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-_{(\text{aq})}$.

We find that at a relatively high AgNO₃ concentration in the bath, the faradaic efficiency depends weakly on the current, reaching values of 100% at 2 mA and decreasing to slightly less than 100% at 6 mA. To corroborate these measurements, the mass change of a Ag foil anode which oxidizes in solution by the reverse of the cathode reaction, $\text{Ag}^0 \rightarrow \text{Ag}^+ + \text{e}^-$, was compared and found to yield slightly lower efficiencies, but with the same overall trend. At constant current and varying AgNO₃ concentration in the bath, the faradaic efficiency was found to drastically decrease to less than 100%. We interpret these results as follows. The kinetics of the primary reactions, Ag⁺ reduction and second order recombination, depend on the respective rate constants which are similar (3.7 x 10¹⁰ M/s and 5.5 x 10⁹ M/s) and the reactant concentrations. At low current or high AgNO₃ concentration, the rate of Ag⁺ reduction is higher than second order recombination and the faradaic efficiency approaches 100%. Conversely,

the rate of second order recombination is higher than Ag⁺ reduction at high current or low AgNO₃ concentration, lowering the faradaic efficiency. A reaction model was developed to support these interpretations.

11:20am **PS+AS+SE-MoM-10 Amorphous Indium Zinc Oxide (IZO) Semiconductor Films Grown by Atmospheric Plasma-Enhanced Spatial ALD for Application as High-Mobility Channel in Thin Film Transistors**, *A Illiberi, I Katsouras, S Gazibegović, B Cobb, E Nekovic*, TNO-Holst Centre, Netherlands; *W van Boekel, C Frijters*, TNO-Solliance, Netherlands; *J Maas*, TNO-Holst Centre, Netherlands; **Fred Roozeboom**, TNO-Holst Centre & Eindhoven University of Technology, Netherlands; *Y Creighton*, TNO-Solliance, Netherlands; *P Poodt*, TNO-Holst Centre, Netherlands; *G Gelinck*, TNO-Holst Centre & Eindhoven University of Technology, Netherlands **INVITED**

Less than a decade ago, InGaZnO has been reported as a new Amorphous Oxide Semiconductor (AOS) channel material replacing conventional amorphous silicon (a-Si:H) for application in thin-film transistor (TFT) circuits in display back panels [1]. Among these, indium zinc oxide (IZO) is emerging as the most promising AOS candidate for next-generation displays based on oxide TFTs because it combines a very high electron mobility with excellent optical transmission and thermal stability [2,3].

We have grown InZnO thin films by plasma-enhanced spatial atomic layer deposition (s-ALD) [4,5] and these layers have been manufactured into oxide TFT and ring oscillator devices which outperform the state-of-the-art. We will describe the growth of InZnO at atmospheric pressure and high deposition rates (~ nm/sec) starting with a short explanation of the basics and the advantages of this novel deposition technique including the use of a special atmospheric plasma source design of the so-called Surface Dielectric Barrier Discharge (SDBD) type [6]. Next, we will show that by varying the ratio of the trimethyl indium and diethyl zinc chemical precursor vapors, the In/(In+Zn) ratio of the film can be accurately tuned over the entire composition range from zinc oxide to indium oxide. TFT test devices with an In/Zn ratio of 2:1 show very high field-effect mobility exceeding 30 cm²/V.s (Fig. 1), excellent thermal (Fig. 2) and bias stress stability. We will further demonstrate the scalability of the IZO TFTs by fabricating 19-stage ring oscillators operating at 200 kHz which outperform the state-of-the-art.

This superior electrical performance, in combination with the intrinsic advantages of spatial ALD demonstrate the great potential of this atmospheric plasma concept for application in commercial manufacturing of low-cost and large-area AOS-based electronics.

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