## Plasma Science and Technology Division
## Room 315 - Session PS+AS-MoA

### Plasma Chemistry and Catalysis

**Moderators: Michael Gordon**, University of California at Santa Barbara, **Floran Peeters**, LeydenJar Technologies, Netherlands

**1:40pm PS+AS-MoA-1 Study of Plasma-Catalyst Surface Interactions for Nitrogen Oxidation**, *Michael Hinshelwood, Y. Li, G. Oehrlein,* University of Maryland College Park

Cold atmospheric pressure plasma is a promising tool for enhancing thermal catalysis for nitrogen fixation through $NO_x$ formation. Reactive species generated in the plasma are thought to stimulate reactions at the catalyst surface, but the specific interactions are not well understood. We use a plasma-catalysis setup that enables study of such interactions by infrared spectroscopic methods [1]. In this work the formed species of $N_2$-$O_2$ interactions in plasma and over a $Pt-Al_2O_3$ catalyst are analyzed. An $N_2/Ar$ gas stream is flown through an atmospheric pressure plasma jet (APPJ) to the heated catalyst in a confined chamber, and unexcited $N_2$ or $O_2$ gas can also be admitted downstream from the plasma source to the catalyst surface. Catalyst surface species are analyzed using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase species exiting the catalyst bed are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). Plasma power, catalyst temperature and $Ar/N_2$ flow are varied to investigate plasma-catalyst interactions. Bare $Al_2O_3$ is additionally analyzed as a reference material to isolate the effects of the catalyst from the support. Results reveal multiple interactions on the catalyst surface. Downstream gas FTIR shows a slight increase (40%) of total $N_xO_y$ species upon heating the catalyst from 25 °Cto 350 °C suggesting an increase in reactive nitrogen or oxygen species. Additionally, $N_2O$decreases upon heating while $NO_x$ densities rise. The catalyst also promotes oxidation of NO to $NO_2$ compared to the support-only case at 350 °C, a known feature of platinum catalysts.DRIFTS data reveals that the $Al_2O_3$ support acts to store $NO_x$ species below 450 °C through the formation of surface nitrites and nitrates, necessitating the use of long exposure times. Correlations of downstream FTIR and DRIFTS data will be presented to untangle various interactions and isolate the processes resulting in plasma catalysis. We thank B. Bayer, Dr. A. Bhan and Dr. P. J. Bruggeman for helpful discussions. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under award number DE-SC0020232.

**2:00pm PS+AS-MoA-2 Investigation of the Interaction Between Non-Thermal Plasma Activated Nitrogen and Metal Surfaces**, *Garam Lee, C. Yan, W. Schneider, D. Go, C. O'Brien,* University of Notre Dame

Non-thermal plasma (NTP)-assisted catalysis has recently gained substantial interest in the heterogeneous catalysis field for enhancing catalytic activity and/or selectivity, as well as for enabling chemical transformations that neither plasma nor catalysis could deliver individually. Despite the promise, the influence of NTP activation of molecules on reactivity at a catalytic surface remains primitive. Here, we report observations of the products and reactivity of plasma-activated nitrogen ($N_2$) species exposed to polycrystalline Ni, Pd, Cu, Ag, and Au surfaces using a newly-designed multi-modal spectroscopic tool that combines polarization-modulation infrared reflection-absorption spectroscopy (PM-IRAS), mass spectrometry (MS), and optical emission spectroscopy (OES), combined with density functional theory (DFT) models to rationalize those observations. Observations and models indicate that NTP activation provides access to metastable surface nitrogen species that are inaccessible thermally. Those metastable species are characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), temperature-programmed desorption (TPD), and temperature-programmed reaction (TPR) with hydrogen ($H_2$) to produce ammonia ($NH_3$). Models and observations highlight dependence of this reactivity on the identity of the metal surface. Taken together, results shed light on the role of NTP activation on promotion of surface reactivity.

**2:20pm PS+AS-MoA-3 Long-Term Degradation of PTFE in a Low Temperature Oxygen Plasma**, *Tobias Wagner, T. Zeller, M. Rohnke, J. Janek,* Institute of Physical Chemistry, Justus Liebig University Giessen, Germany

Atomic oxygen (AO) is the most common gas species in the Low-Earth-Orbit (LEO) and responsible for material degradation of the outer shell of satellites and spacecrafts within this space region. As the LEO is also essential for commercial space flights, the degradation process of materials exposed to AO needs to be better understood in order to prevent possibly devastating material failure. Due to its properties, low temperature oxygen plasmas are suited for material degradation studies taking place on earth instead of quite expensive space studies. Here we focus on the long-term degradation of Polytetrafluoroethylene (PTFE), which is often employed on the outside of spacecrafts and therefore exposed to AO. Up to date, there is no complete understanding of the degradation process on the molecular level, which is necessary for materials improvement and new materials development.

For the degradation studies, a self-constructed capacitively driven 13.56 MHz RF reactor was used to generate an oxygen plasma for the simulation of LEO conditions. PTFE was characterised in the pristine state and after AO treatment at different times by ToF-SIMS, XPS, SEM and confocal microscopy. During plasma treatment, the samples show a linear mass loss behaviour. ToF-SIMS surface analysis reveal mass fragments like $COF^-$ or $C_3O^+$, which shows a clear chemical reaction of oxygen species with PTFE. The presence of these molecular indicators was verified by XPS, where additional carbon and oxygen species were found after treatment. SEM micrographs showed an inhomogeneous degradation on the surface in the first hours similar to actual LEO exposure. For a complete understanding of the degradation progress, mass spectrometric studies of the plasma composition are carried out in situ. Overall, the results show that the reaction of PTFE with AO is occurring on a chemical rather than a physical path, with the fragmentation of long carbon chains into smaller fragments likely driving the material degradation.

**2:40pm PS+AS-MoA-4 Study of Elastomer Degradation in Processing and Cleaning Plasma Chemistries**, *Nicholas Connolly, D. Barlaz, R. Garza, D. Ruzic, M. Sankaran,* University of Illinois Urbana-Champaign*; N. Kolliopoulos, G. Lunardi,* DuPont Precision Parts & Solutions

Fluoroelastomer (FKM) and perfluoroelastomer (FFKM) materials are used extensively in seals for plasma processing equipment used to manufacture semiconductors. Chamber etching and cleaning processes, particularly those using fluorine chemistry, oxygen chemistry, or a mixture of both, lead to the degradation of the elastomer seals. While most decomposition products are volatile, the recognition of seals as a source of chamber contamination in the form of undesired etch products and particle generation is important for robust semiconductor manufacturing processes. Recent emphasis on coatings and filler materials for elastomer seals makes understanding of decomposition conditions an ongoing effort.

This work investigates the relationship between plasma parameters, including electron temperature, plasma density, and radical densities, and elastomer seal degradation in mixtures of $SF_6/O_2/Ar$ plasmas. Various commercial FKM/FFKM materials will be investigated. Langmuir probe analysis is used to characterize electron temperature and density (predicted $T_e$ of 3 eV and density of $1 \times 10^{17}$ $m^{-3}$), while in-situ thermocouple-based radical probes are used to measure radical densities of oxygen. Efforts towards the development and implementation of an in-situ fluorine radical probe will also be reported. Characterization of the elastomer surface after plasma exposure will be completed using electron microscopy and optical profilometry, as well as testing of mechanical properties of the seals.

**3:00pm PS+AS-MoA-5 Utilizing Optical Spectroscopy to Explore Mechanisms of Plasma-Assisted Catalysis in Model Exhaust Systems**, *Joshua Blechle,* Wilkes University

With increasing concerns over the environmental presence of nitrogen oxides, there is growing interest in utilizing plasma-mediated conversion techniques. Nonthermal plasma-assisted catalysis (PAC) in particular has shown great potential for continued improvements in exhaust abatement. Advances, however, have been limited due to a lack of knowledge in regards to the fundamental chemistry of these plasma systems, and the complexity of the plasma-surface interface. The sheer number of potential catalysts and the variability in exhaust gas composition further exacerbate these issues.

In order to investigate these interactions, a number of inductively-coupled plasma systems were generated from model exhaust precursors (notably, $N_2$ and $O_2$ mixtures). Internal energies of notable diatomic species are determined via optical emission spectroscopy (OES) to explore the trends in energy partitioning with respect to plasma conditions. Repeated measurements in the presence of precious metal (Ag, Pt, and Pd) and alumina surfaces demonstrate a strong vibrational temperature ($T_V$) dependence with respect to applied power (25-200 W) but a somewhat

limited dependence on substrate identity. In addition, very little change in $N_2^*$ and $N^*$ densities are observed, whereas there are significant decreases in both $NO^*$ and $O^*$ densities in the presence of all substrates. A series of composite ($Ag/\gamma$-$Al_2O_3$) catalysts with varying Ag loading are also studied, with $T_v$'s ranging from ~2500-5100 K, with the highest temperatures reached for raw alumina systems, demonstrating a Ag-mediated vibrational quenching.

To further explore catalytic behavior, kinetic trends are observed via time-resolved OES, with rate constants determined for both the formation and destruction of relevant excited states. Correlating these data with measured densities and temperatures allows for unique insight into the plasma-surface interface and the mechanisms by which these processes occur. Expanding upon the library of system conditions and increasing the complexity of the exhaust gas model will serve as a foundation for improved design and implementation of PAC methods.

**3:20pm PS+AS-MoA-6 Gasification of Carbon and $CO_2$ Into CO at Low Vacuum Through Combined Plasma and Heating Exposure**, *Edwin Devid,* DIFFER, Netherlands*; R. Van de Sanden,* DIFFER & EIRES, Netherlands*; M. Gleeson,* DIFFER, Netherlands

Atmospheric $CO_2$ concentrations still continue to rise in 2020 [1] and are threatening the goals of the Paris Agreement [2]. By activating $CO_2$ through plasma, $CO_2$ is reduced into CO where CO is not only a high-value chemical for the chemical industry but also allow to store renewable electricity into chemical energy via an intermittent way at the cost of $CO_2$ consumption. Currently, mere $CO_2$ dissociation through non-thermal inductively coupled Radio Frequency (RF) plasma is not economically viable to obtainboth high $CO_2$ conversion and energy recovery efficiencies [3,4].

In this experiment, $CO_2$ dissociation by plasma is assisted by the co-reactant carbon. Through this co-reactant, additional processes will take place that aids the $CO_2$ dissociation into CO. In low vacuum (~1.3 mbar $CO_2$), carbon is heated (till 1000 K, in a quartz tray) while being exposed to $CO_2$ plasma. This process gives increased yields of CO where $O_2$ gas is consumed by the dominating process: $2C + O_2 –> 2$ CO. No evidence of the gas phase back reaction $CO+ 1/2O_2 –> CO_2$ is observed. By usage of isotopic carbon[13] and modeling of the mass spectrometric data, the different processes operating (i.e. $2C + O_2 –> 2$ CO versus $CO_2 –> CO+ 1/2O_2$ and $CO_2 + C –> 2$ CO) are disentangled. Under a buildup ~1.3 mbar $CO_2$ atmosphere plus combined plasma and heat exposure upon the carbon gives, with increasing temperature a steeply rising of emitted CO at the cost of declining $O_2$ and $CO_2$. From the isotopic carbon is determined that after plasma and heat exposure: the surface color, surface area and pore volume has been changed. In addition the sample mass is reduced (carbon consumption up to 36% gravimetrically), confirming that carbon is consumed.

This potentially opens a new way toward $O_2$ removal during $CO_2$ dissociation processes by combining plasma with heating of carbon to generate a clean $CO_2/CO$ stream. If the carbon is of a biogenic origin, the process as a whole is sustainable and fossil free CO is generated. Other additional processes that aid to further increase the CO yield (like reverse Boudouard reaction: $CO_2 + C –> 2$ CO) help to find ways for industry to reach higher CO yields by both increasing the $CO_2$ conversion and the consumption of $O_2$ through the presence of carbon via non-thermal plasma.

[1] IPCC, *Climate Change 2022,* P. R. Shukla et al., Cambridge University Press, Cambridge, NY, USA.

[2] C. Streck et al., Journal for European Environmental & Planning Law, (2016). 13. 3-29.

[3] R. Snoeckx and A. Bogaert, Chem. Soc. Rev., 46, (2017).

[4] Wolf, A. J. et al., The Journal of Physical Chemistry C, 124, 31, (2020), 16806-16819

**4:00pm PS+AS-MoA-8 Investigation of Oxygen Permeation Enhancement with He/$O_2$ Plasma and SOEC Interaction**, *Xingyu Chen,* Dutch Institute for Fundamental Energy Research, China*; F. Peeters, F. Smits, W. Bongers, R. van de Sanden,* Dutch Institute for Fundamental Energy Research, Netherlands

High temperature solid-oxide electrolysis cells (SOECs) using oxygen-selective conducting membrane in combination with plasma has shown high conversion efficiencies in nitrogen fixation and $CO_2$ conversion, which provides a promising method for renewable energy usage and gas conversion. But the underlying kinetics and limiting rates of the plasma-assisted oxygen conducting membrane remain not clear. The plasma-activated species (e.g., by plasma-excitation, dissociation and ionization) may promote the reduction kinetics on the ion-conducting membrane surface. The effects of plasma-induced surface charging and local fields on the exchange kinetics may also play a significant role in the improvement of the oxygen permeation fluxes of the ion-conducting membrane. To understand the interaction of the plasma and the oxygen-conducting membrane, we develop a dedicated plasma-SOEC reactor to investigate the plasma enhanced oxygen permeation mechanism.

In this contribution, we will present the experimental results of the enhancement of the oxygen permeation fluxes owing to the presence of the oxygen radicals and electrons from He/ $O_2$ low pressure (~1 Torr) plasma. Langmuir probe measurements and optical emission spectrometry and actinometry will determine the plasma properties (electron density, electron temperature and O radical densities etc.) and provide inputs for the plasma-kinetic modelling of the plasma bulk and wall region. The characterizations of the SOEC with different plasma conditions and membrane temperature are conducted to determine the pumping rates (current density) of the oxygen permeation process. Ultimately, the plasma effects on SOEC performance will be quantified, and novel insights into the ion-conducting rate-limiting kinetics will be discussed.

**4:20pm PS+AS-MoA-9 Application of Plasma-Liquid Chemistry to Carbon-Carbon Bond Formation via Pinacol Coupling Reaction**, *Scott Dubowsky, J. Wang,* University of Illinois at Urbana-Champaign*; N. Üner,* Middle East Technical University, Turkey*; J. Moore, M. Sankaran,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas in contact with liquids have attracted interest for various chemical applications including the degradation of organic pollutants,[1] conversion of abundant feedstocks,[2,3] and more recently, organic chemistry.[4] Compared to other chemical approaches, plasma-liquid chemistry does not require a catalyst material, is electrified, and produces unique reactive species such as solvated electrons, one of the strongest chemical reducing species.[5]

We present an application of plasma-liquid chemistry to the building of carbon-carbon bonds via the well-known Pinacol coupling reaction. In this organic reaction, a carbonyl group is reduced, typically by an electron donating catalyst such as magnesium, to form a ketyl radical anion species. A pair of these ketyl groups then react to form a vicinal diol, which in the presence of a proton donor such as water, leads to the final diol product. Here, we show that the Pinacol coupling reaction is successfully carried out at a plasma-liquid interface without any catalyst. Our study was performed with a direct-current (DC) powered plasma operated in a previously reported electrochemical setup and primarily focused on methyl-4-formylbenzoate (MFB) as the substrate. For an initial concentration of 0.12 M and a constant operating current of 2.3 mA, the yield of the Pinacol product increased with time from 6.1% after 1 h to 34% after 8 h, while the faradaic efficiency correspondingly decreased from 85.7% to 54.2%. Based on nuclear magnetic resonance (NMR) spectroscopy, methyl 4-(dimethoxymethyl)benzoate and 4-(methoxycarbonyl)benzoic acid were also generated as side products. By carrying out scavenger control experiments, we show that the vicinal diol is produced by solvated electron reduction. Finally, we have extended the application of plasma-liquid chemistry to Pinacol coupling of several other aromatic aldehydes and ketones to emphasize its generality.

References:

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4:40pm **PS+AS-MoA-10 Understanding Temperature Inhibition of Methane Conversion in DBD Plasma Using Electrical Characterization and Optical Emission Spectroscopy**, *Ibukunoluwa Akintola*, *G. Rivera-Castro, J. Yang, J. Hicks, D. Go,* University of Notre Dame

Non-thermal plasmas (NTPs) produce highly reactive chemical environments made up of electrons, ions, radicals, and vibrationally excited molecules. These reactive species, when combined with catalysts, can help drive thermodynamically unfavorable chemical reactions at low temperatures and atmospheric pressure. We are particularly interested in the direct coupling of light hydrocarbons (e.g. methane) and nitrogen to produce value-added liquid chemicals (e.g. pyrrole and pyridine) in a plasma-assisted catalytic process. In order to effectively create these plasma catalytic systems, it is imperative that there is a fundamental understanding of the plasma-phase chemistry alone. While there have been many studies on nitrogen ($N_2$) and methane ($CH_4$) plasmas, there is limited understanding on how changing operating conditions (i.e. feed ratio, plasma power, operating temperature) affect the plasma properties and ensuing plasma chemistry. In this work, we characterize the plasma using electrical measurements and optical emission spectroscopy (OES) and analyze the chemical products using gas chromatography to understand the effects, if any, of varying plasma parameters on product formation. Relevant electrical properties and thermodynamic information such as electron density, vibrational and rotational temperatures, as well as the presence of key plasma species (C-N, C-H, $N_2$) are compared to relevant products formed during plasma-alone reactions. Results show that different operating conditions lead to changes in energy partitioning in the reaction. Specifically, an increase in temperature leads to a reduction in methane conversion which appears to have an inverse relationship with the vibrational temperatures of C-H species in the plasma.

5:00pm **PS+AS-MoA-11 Optimization of $CO_2$ Dissociation Efficiency and Conversion in Vortex-Stabilized Microwave Plasmas by Effluent Nozzles**, *Cas van Deursen,* DIFFER, Netherlands*; H. van Poyer,* DIFFER, Belgium*; Q. Shen,* DIFFER, China*; W. Bongers,* DIFFER, Netherlands*; F. Peeters,* Technical University of Eindhoven, Netherlands*; F. Smits, R. van de Sanden,* DIFFER, Netherlands

Efficiency and conversion in a reverse vortex microwave plasma utilized for $CO_2$ dissociation are enhanced by considering and optimizing the thermal trajectory of the plasma effluent using a Laval nozzle. The nozzle is used to mix the cold, unconverted gas at the edges of the tube with the hot, dissociated gas in the middle of the flow and to force the gas to accelerate, thereby cooling the effluent. The temperature trajectory of the gas is determined by measuring the gas temperatures of the plasma core and the afterglow using OES and the gas exiting the Laval nozzle using a thermocouple. The effects of the nozzle on the size of the plasma is determined using OES and plasma imaging. The effects of different nozzle diameters on the temperature trajectory and conversion and efficiency are compared to the baseline configuration. Measurements show significant improvements in energy efficiency at close to atmospheric pressures (500 – 900 mbar), especially for higher flows (12 – 18 slm). Results are discussed and explained on the basis of simulations. Options for further improving reactor efficiency and conversion are also discussed.

# Author Index

## Bold page numbers indicate presenter

— A —
Akintola, I.: PS+AS-MoA-10, **3**
— B —
Barlaz, D.: PS+AS-MoA-4, 1
Blechle, J.: PS+AS-MoA-5, **1**
Bongers, W.: PS+AS-MoA-11, 3; PS+AS-MoA-8, 2
— C —
Chen, X.: PS+AS-MoA-8, **2**
Connolly, N.: PS+AS-MoA-4, **1**
— D —
Devid, E.: PS+AS-MoA-6, **2**
Dubowsky, S.: PS+AS-MoA-9, **2**
— G —
Garza, R.: PS+AS-MoA-4, 1
Gleeson, M.: PS+AS-MoA-6, 2
Go, D.: PS+AS-MoA-10, 3; PS+AS-MoA-2, 1
— H —
Hicks, J.: PS+AS-MoA-10, 3
Hinshelwood, M.: PS+AS-MoA-1, **1**
— J —
Janek, J.: PS+AS-MoA-3, 1

— K —
Kolliopoulos, N.: PS+AS-MoA-4, 1
— L —
Lee, G.: PS+AS-MoA-2, **1**
Li, Y.: PS+AS-MoA-1, 1
Lunardi, G.: PS+AS-MoA-4, 1
— M —
Moore, J.: PS+AS-MoA-9, 2
— O —
O'Brien, C.: PS+AS-MoA-2, 1
Oehrlein, G.: PS+AS-MoA-1, 1
— P —
Peeters, F.: PS+AS-MoA-11, 3; PS+AS-MoA-8, 2
— R —
Rivera-Castro, G.: PS+AS-MoA-10, 3
Rohnke, M.: PS+AS-MoA-3, 1
Ruzic, D.: PS+AS-MoA-4, 1
— S —
Sankaran, M.: PS+AS-MoA-4, 1; PS+AS-MoA-9, 2
Schneider, W.: PS+AS-MoA-2, 1

Shen, Q.: PS+AS-MoA-11, 3
Smits, F.: PS+AS-MoA-11, 3; PS+AS-MoA-8, 2
— U —
Üner, N.: PS+AS-MoA-9, 2
— V —
van de Sanden, R.: PS+AS-MoA-11, 3; PS+AS-MoA-8, 2
Van de Sanden, R.: PS+AS-MoA-6, 2
van Deursen, C.: PS+AS-MoA-11, **3**
van Poyer, H.: PS+AS-MoA-11, 3
— W —
Wagner, T.: PS+AS-MoA-3, **1**
Wang, J.: PS+AS-MoA-9, 2
— Y —
Yan, C.: PS+AS-MoA-2, 1
Yang, J.: PS+AS-MoA-10, 3
— Z —
Zeller, T.: PS+AS-MoA-3, 1