Plasma Science and Technology
Room 201 ABCD W - Session PS-WeM

Plasma Catalysis and Surface Interactions

Moderators: Sumit Agarwal, Colorado School of Mines, USA, **Mohan Sankaran**, University of Illinois at Urbana-Champaign

8:00am **PS-WeM-1 The Impact of Plasma Enhancement Gasses on Hydrogen Superpermeation Through Palladium Alloy Metal Foil Pumps***, **Caroline Hufnagel**, Vitor Camacho,* Colorado School of Mines*; Thomas Fuerst,* Idaho National Laboratory*; Doug Way, Colin Wolden,* Colorado School of Mines

The fusion reaction between the hydrogen isotopes deuterium and tritium is the most likely path to enabling fusion energy. The efficient processing of the tritium is critical to the plant operation for fusion energy systems. Metal foil pumps (MFPs) are the leading technology for direct internal recycling (DIR) of hydrogen isotopes from the plasma exhaust in future fusion plants. MFPs rely on the concept of superpermeation, where H atoms generated by a plasma directly absorb into the metal foil, rapidly diffuse, and desorb downstream. To date, studies of superpermeation have predominantly employed pure hydrogen. In practice the plasma exhaust may contain significant levels of plasma enhancement gasses (PEGs, i.e. Ar, Ne, Kr).These inert gasses have metastable states that can enhance plasma density and stability.In this work, we systematically study the impact of PEG addition on the hydrogen superpermeation performance of PdCu and PdAg MFPs operated at low temperature (< 200 °C). In the case of argon, flux enhancements of up to 60% relative to pure H_2 plasma were observed, with the optimal concentration range being 5-10 % Ar.Performance correlated with the optical emission of the atomic H, and benefits were more appreciable on PdAg than PdCu.Beyond 15% addition plasma enhancement benefits were offset by dilution.Interestingly, the level of permeation enhancement improved with increasing DIR fraction, and potential reasons for this phenomenon are discussed.

Depending on programming this may be a better fit in PS8: Sustainability and Plasmas

8:15am **PS-WeM-2 The Impact of Contaminants on Superpermeation Through Palladium Alloy Metal Foil Pumps***, Chao Li,* Marathon Fusion*; Caroline Hufnagel,* Colorado School of Mines*; Thomas Fuerst,* Idaho National Laboratory*; Vitor Camacho, Doug Way, **Colin Wolden**,* Colorado School of Mines

The fusion reaction between the hydrogen isotopes deuterium and tritium is the most likely path to enabling fusion energy. The efficient processing of the tritium is critical to the plant operation for fusion energy systems. Metal foil pumps (MFPs) are the leading technology for direct internal recycling (DIR) of hydrogen isotopes from the plasma exhaust in future fusion plants. MFPs rely on the concept of superpermeation, where H atoms generated by a plasma directly absorb into the metal foil, rapidly diffuse, and desorb downstream. To date, studies of superpermeation have predominantly employed pure hydrogen. Though undesired, inevitably MFPs will be exposed to unintentional contaminants such as carbon and oxygen, with consequences for long term durability. In this work, a combination of surface analytical techniques (Auger, XPS) and superpermeation experiments were employed to understand the impact of common contaminants.The critical nature of clean surfaces is first demonstrated through compression experiments using asymmetrically prepared PdCu MFPs. Contamination degrades performance, inhibiting both absorption of superthermal hydrogen on the feed surface and recombinative desorption on the permeate surface, with the latter being more detrimental. Next, sputter-cleaned MFPs were placed in a chamber that had been pre-contaminated with carbon. Upon plasma ignition, the superpermeation rate initially increased before rapidly declining to zero. The initial increase suggests that very small (submonolayer) contamination levels are perhaps beneficial, but would be difficult to control.O_2 plasma exposure could largely restore the performance of carbon-contaminated PdAg MFPs, but proved detrimental to PdCu. Surface analysis techniques are employed to understand the differences between the two alloys.

8:30am **PS-WeM-3 Elucidating Complex Interactions in Non-Thermal Plasma-Assisted Reactions on (Supported) Porous Catalysts***, **Michele Sarazen**,* Princeton University **INVITED**

Reactions such as dry reforming of methane (DRM) and ammonia synthesis are significant targets for renewable electricity driven manufacturing, given their current dependence on fossil fuels. Plasma-assisted catalysis, which aims to activate reactants near bulk ambient temperature and pressure, is one of these approaches. While plasma alone can activate these molecules, it is often unselective, requiring a catalyst to tailor the selectivity to desired products. Further, plasma-assisted catalysis can demonstrate synergistic effects due to the interactions of the plasma discharge on the catalyst and vice versa. However, effective catalyst design is limited by the lack of fundamental understanding of these plasma/catalyst interactions during reaction. In this work, we demonstrate the use of a dielectric barrier discharge (DBD) plasma, in part interfaced with a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reaction chamber, for ammonia synthesis, DRM, and related chemistries on various oxide supports (with metal nanoparticles). We elucidate impacts of surface species and porosity/functionality of porous oxide supports on plasma properties, catalytic activity, therefore the energy yield of DBD-assisted catalysis, which is required for implementation.

9:00am **PS-WeM-5 in Situ/Operando Diagnostics of Liquids and Catalysts in Contact with Plasmas***, Kasidapa Polprasarn, Dihya Sadi,* Laboratoire de Physique des Plasmas (CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Sorbonne Université), France*; Darwin Kurniawan,* Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan*; Thomas Orrière,* Institut PPRIME (CNRS, Université de Poitiers, ISAE-ENSMA), France*; Pankaj Pareek,* Faculty of Mathematics, Physics, and Informatics, Comenius University, Slovakia*; Francesca Caielli, Karthik Thyagajaran,* Institut PPRIME (CNRS, Université de Poitiers, ISAE-ENSMA), France*; Mario Janda,* Faculty of Mathematics, Physics, and Informatics, Comenius University, Slovakia*; Wei-Hung Chiang,* Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan*; Olivier Guaitella, **David Pai**,* Laboratoire de Physique des Plasmas (CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Sorbonne Université), France **INVITED**

Plasma interactions with liquids and solids are at the core of plasma electrochemistry (PEC) and plasma-assisted catalysis (PAC), respectively. To address the need for direct measurements in the plasma-liquid and plasma-catalyst interfacial regions, respectively, we employ an *in situ*/*operando* approach using multiple diagnostic techniques to study a range of physical and chemical properties at plasma interfaces. The centrepiece of this platform is *in situ/operando* spontaneous Raman microspectroscopy. For a PEC batch reactor in pure water, this technique revealed that the concentrations of aqueous H_2O_2 and NO_3^- at a depth of a few tens of microns from the plasma-liquid interface are greater than in the bulk liquid [1].We have also successfully performed *in situ/operando* Raman on an electrospray reactor [2]. Here, we will present two case studies of changes to Raman spectra observable only in the presence of plasma. First, for PEC in air plasma-water systems at atmospheric pressure, we will focus on the spectral profile of the –OH stretch band of water and of probe molecules such as NO_3^-. Analysis of –OH stretch indicates that the plasma disrupts the hydrogen bonding network of water. To assist in pinpointing the cause, we will examine the broadening of the N-O symmetric stretch mode (v_1) of NO_3^- at less than 20 µm depth from the plasma-liquid interface. Second, we will present a study of a PAC reactor consisting of a low- to medium-pressure CO_2 plasma in contact with CeO_2 as a catalyst [3]. Tracking of the first- and second-order optical phonons of CeO_2, as well as O-O bonds in superoxides, yields information on thermal effects and oxygen vacancy formation. Besides Raman spectroscopy, additional *in situ/operando*diagnostics have been employed when monitoring the synthesis of graphene quantum dots by PEC reactors [4]. We tracked their production via photoluminescence (PL) and UV-VIS absorption spectroscopies. Both the PL and absorption signals achieve their peak intensity not at the interface but at a depth of several millimeters. This aligns with liquid flow field measurements by particle image velocimetry, which indicate the presence of a low-velocity zone at this depth.

References

[1] D. Z. Pai, Journal of Physics D: Applied Physics **54**, 355201 (2021).

[2] P. Pareek, S. Kooshki, P. Tóth, and M. Janda, Chemical Engineering Journal **493**, 152583 (2024).

[3] C. A. Garcia-Soto, E. Baratte, T. Silva, V. Guerra, V. I. Parvulescu, and O. Guaitella, Plasma Chemistry and Plasma Processing 1 (2023).

[4] D. Kurniawan, F. Caielli, K. Thyagajaran, K. K. Ostrikov, W.-H. Chiang, and D. Z. Pai, Nanoscale **16**, 15104 (2024).

9:30am **PS-WeM-7 Catalytic Deconstruction Product Tunability Through Atmospheric Air Plasma Pre-Treatment*, Aunic Goodin,*** North Caroline State University*; Tridip Das,* California Institute of Technology*; Shashwata Chakraborty, Sujoy Bepari, Debasish Kuila,* North Carolina Agricultural and Technical State University*; William Goddard,* California Institute of Technology*; Steven Shannon,* North Carolina State University

The large amount of waste plastic produced is becoming a more prominent concern, as production of single use plastic continues to increase. Catalytic deconstruction is viewed as one potential method for deconstruction of waste plastics into usable material. In this work, we use an atmospheric pressure air plasma to pre-treat polypropylene, to better facilitate reaction with the catalyst. It has been found that this pre-treatment can tune the products of the catalytic deconstruction to change the distribution of products as needed.

Plasma treatment is performed in a sealed vial with a rubber septum cap. A steel hypodermic needle is used to both deliver synthetic air and apply a high voltage in a pin-to-cup configuration. The grounding cup is made up of a copper pipe soldered to a copper plate. The vial is placed the copper “cup” with the whole assembly surrounded with a 3D printed holder to prevent arcing from the high voltage to ground. A second hypodermic needle is then used to allow air to escape. Treatments range from 15-120 minutes at 30-40 kV (6-34 W), a frequency of 450 Hz, and a flow rate of 0-400 SCCM.

The catalyst used was a ZSM-5/SBA-15 composite catalyst, with the ZSM-5 added into the SBA-15 structure during its production. This was reacted with an equal ratio of catalyst to plastic at 400 °C with a constant flow of 1.5 SCCM of N_2. This treatment was continued until products were no longer detected using gas chromatography mass spectrometry (GC/MS).

The best total conversion of 94% was observed with a 30 kV treatment for 30 minutes, at a flow rate of 110 SCCM, with a major product of propene (66%). The major product, as well as overall product distribution can be changed by performing the plasma treatment under different voltage, time, and flow rate.

Molecular dynamics simulations have shown the mechanism of the plastic degradation in plastic to be due to a reaction with ozone. Ozone measurements were taken to investigate different conditions. The plasma and product plastics will be further investigated through MALDI-TOF and OES measurements to better understand the conditions needed to produce specific products. The mechanism can then be better illuminated to understand how this could be applied to catalytic deconstructions with different scaled up or different plasma systems.

Through variations in plasma pre-treatment, catalytic deconstruction can be tuned to produce different product distributions. While this cannot shift the total distribution of products, it could increase the viability of catalytic deconstruction despite market fluctuations.

This material is based upon work supported by U.S. Department of Energy (DOE) no. DE-EE0009945.

11:00am **PS-WeM-13 Gas-Phase Plasma Synthesis as a Method for Producing Nanomaterials with Special Properties*, Hartmut Wiggers,*** University of Duisburg-Essen, Germany **INVITED**

Gas phase synthesis has been an established process for the production of functional nanoparticles for decades. The manufacturing processes used are dominated by flame processes, whereby mostly oxide materials are produced. However, with the increasing use and storage of renewable energies for industrial processes, there is a growing need for new types of materials that can often no longer be produced using flame-based processes alone. Gas-phase plasma synthesis offers new possibilities here, as an essential prerequisite of flame processes – the use of a reactive gas mixture consisting of fuel and oxidizer – is not required, which opens up access to oxide-free materials in particular. At the same time, plasma processes can be operated over a wide pressure and temperature range, which can be used for setting specific temperature-time profiles.

Microwave and ICP plasma processes are particularly suitable for the production of high-purity materials in technically relevant quantities, as the coupling of energy into the gas phase process is contactless. Using the example of selected materials based on carbon (especially few-layer graphene, FLG) and silicon, it is shown how specific materials for applications in the field of energy conversion and storage as well as for catalysis can be produced using plasma processes. Starting from the first steps of nanoparticle formation, possibilities are shown to further develop the synthesis up to the production of functional composite materials as well as single-atom catalysts.

11:30am **PS-WeM-15 Interaction of Etching Plasmas with Polyurea Films deposited by Molecular Layer Deposition for Surface and Sidewall Passivation*, Wallis Scholl,*** Colorado School of Mines*; Thorsten Lill, Mingmei Wang, Wenyu Zhang, Harmeet Singh,* Lam Research Corporation*; Sumit Agarwal,* Colorado School of Mines **INVITED**

Molecular layer deposition (MLD) is a vapor-phase process of alternating surface reactions which can be used to grow organic and hybrid organic-inorganic films. MLD films have several potential applications in semiconductor processing, including as conformal coatings or as a protective layer during plasma etching. However, the use of MLD in practical applications is hindered by the complexity of the growth mechanism. Some bifunctional molecules will react to the film surface with both of their functional groups, thereby consuming reactive sites and lowering the growth per cycle (GPC). Molecules can also be added to the film through physisorption to the growth surface, which adds new reactive sites to the film. Further, we have found that different MLD precursors can have different rates of double reaction and physisorption. Molecule chain length, flexibility, and hydrogen bonding must be carefully considered when selecting an MLD chemistry, as they all affect the film growth. The physisorption contribution to film growth can also be promoted by lowering the deposition temperature, which results in an increase in GPC. However, films with a high degree of physisorbed material can be unstable, as this weakly physisorbed material can later diffuse out.

In this work, toluene diisocyanate (TDIC) and ethylene diamine (ED) were used as precursors for MLD of polyurea, which was grown on top of a SiO_2 starting surface. The films were then exposed to a HF plasma to evaluate their interactions with reactive plasma. During initial HF exposure, only the MLD film was etched, while the underlying SiO_2 was protected. As plasma exposure continued, eventually removal of the MLD film stopped and the SiO_2 was selectively etched. The length of the SiO_2 etch delay was found to be highly dependent on the morphology of the MLD film; films with a higher degree of interconnectivity were better able to prevent F from diffusing through the film to access the SiO_2. For example, depositing at a higher deposition temperature, which reduces physisorption into the film, resulted in a higher etch resistance. Ion bombardment was also found to increase film interconnectivity, thereby preventing SiO_2 etch. Additionally, we deposited MLD films on high aspect-ratio (HAR) trenches to evaluate the film conformality. While the analogous process of atomic layer deposition (ALD) requires very high doses to provide necessary diffusive flow into the trench, we found that during MLD of polyurea, films are deposited conformally using the saturation doses for a flat surface. We’ve attributed this to film reconstruction during MLD, which includes migration of physisorbed molecules through the film.

12:00pm **PS-WeM-17 Characterization and Operation of a 2-D Plasma Reactor for Methane Pyrolysis***, Huseyin Ozturk, Andac Yagiz Kaya,* ***Necip Berker Uner,*** Middle East Technical University, Turkey

Methane pyrolysis is breaking the C-H bonds of methane in an O_2-free atmosphere. This process can synthesize H_2 directly from natural resources along with solid carbon with no carbon dioxide emissions. Using an atmospheric plasma for methane pyrolysis is attractive since the process is fully electrified, is completely intermittent with very rapid turn-on/off times and requires no consumables. However, the number of plasma reactors demonstrated for methane pyrolysis is very limited, and the application of chemical reaction engineering fundamentals to the design and operation of these reactors is currently absent in literature.

This talk focuses on the design and characterization of a unique, 2-dimensional, gliding arc (GA) plasma reactor for conducting methane pyrolysis at atmospheric pressure to produce carbon black and hydrogen. The GA is a *warm* plasma, and it combines high-temperature thermal conversion with non-equilibrium electron-impact chemistry. The reactor flow was confined to be unidirectional such that nearly all the gas was put in contact with the GA, thereby increasing flow utilization in the reactor, as verified by computational fluid dynamics. This resulted in improvements on the experimentally measured residence time distribution, and GA formation was visually and electrically analyzed in the confined flow geometry under direct-current excitation. Temperature measurements and heat transfer modeling indicated that the thermal efficiency of the reactor can be made to be as high as 50%, meaning that half of the electrical energy was converted to heating the gas, whereas the rest was dissipated into the ambient through the reactor body. This presentation will elaborate on CH_4 conversion, as well as continuous collection and ex-situ characterization of the carbon product, primarily through Raman and FTIR spectroscopy. The effect of using argon in the mixture and the influence on reactor materials to CH_4 conversion and H_2 selectivity will also be presented.

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