DOE Center for
Predictive Control of Plasma Kinetics:
Multi-Phase and Bounded Systems

9th Annual Meeting

May 17-18, 2018
Bethesda North Marriott Hotel and Conference Center
Bethesda, MD
Participating Institutions

We gratefully acknowledge the funding from
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## Schedule

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- **Valery Godyak (University of Michigan)**  
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- **Michael Lieberman (University of California-Berkeley)**  
  *Nonlinearity, Hysteresis, and Symmetry-Breaking in High Frequency CCP’s*

- **Ed Barnat (Sandia National Labs)**  
  *Advancing Diagnostics to Interrogate Plasma Environments*

- **Igor Adamovich (Ohio State University)**  
  *Electric Field and Excited Species Measurements in Ns Pulse Discharges*

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|            | *Kinetic Modeling of Non-Equilibrium Plasmas for Modern Applications* |  |  
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**Moderator:** Kraig Frederickson

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Abstracts
Oral Presentations
Maximizing the Plasma Contact Area at the Plasma-Liquid Interface

John E. Foster, Selman Mujovic and Joseph Groele
The University of Michigan (jefoster@umich.edu)

The key driver of plasma-induced reactivity in liquid water is the plasma-liquid interface. The contact area between the plasma and the water ultimately determines the treatable throughput; thus, understanding the physics and chemistry of the plasma-liquid interface is key to optimizing plasma water reactors. The plasma-liquid interface is the thin, reactive interfacial zone formed between the gas phase plasma and the liquid water. The reactive zone is not a distinct boundary in that it includes the supersaturated vapor layer above the liquid as well as a thin layer within the liquid where the chemistry can be driven far from equilibrium. Here, species produced in the gas phase can diffuse into solution. These species include reactive oxygen and nitrogen species, such as hydroxyl, hydrogen peroxide, superoxide and NOx. Incident UV can also drive the production of OH in solution via the detachment of OH⁻. Recombination of OH in solution produces hydrogen peroxide. The incident electrons solvate only to ultimately decompose water molecules on a microsecond time scale to also produce OH. The longer-lived species, such as hydrogen peroxide and ozone, can diffuse deeper into solution, ultimately forming OH, which in turn can attack contaminants within the bulk.

Herein describes test and design considerations for the development of an efficient, high throughput plasma-based water reactor that maximizes the plasma liquid contact area. Here, we consider ground rules for determining the apparatus’s efficiency. This consideration is important in that it should be done in a way that allows for direct comparison with conventional water treatment systems. Characterization of effectiveness is also important. For example, to assess dose in conventional water treatment systems, so-called batch or jar tests are utilized. The feasibility of utilizing this approach to assess dose in plasma reactors will be discussed as well. The importance of optimizing both contact time and contact area is then discussed from the context of the plasma-liquid interface. Ultimately, the key to optimizing plasma-based water purification systems lies in understanding the source chemistry taking place in the gas phase, at the plasma-liquid interface, and subsequent mass transport processes into the bulk solution that follow. We discuss two example sources that have the capacity for high throughput applications currently being researched at the University of Michigan.
Atmospheric pressure plasmas in air produce reactive oxygen and nitrogen species (RONS) that can have beneficial biological effects, including antibacterial and antifungal applications [1]. The biological effects of plasma treatment often occur through a liquid interface and this has led to the use of plasma-activated water (PAW) or plasma-activated medium (PAM) as a way to deliver plasma-generated species to surfaces. [2] We report extending this idea to a perfluorocarbon liquid compound that has been extensively used in other biomedical applications.

The first step in plasma-liquid interactions is the solvation of RONS in the liquid phase. Increasing RONS solvation should increase the exposure of materials in contact with the liquid phase. Application of a perfluorocarbon solvent prior to plasma treatment can enhance the antifungal effects of a plasma on \textit{T. rubrum} toenail fungus by raising the log reduction of fungi, even on the side of the nail not in direct contact with the plasma effluent [3]. Presumably, this is related to the enhanced solvation of RONS by perfluorocarbons, but the mechanism of treatment improvement has not been explored. We are currently studying the ability of perfluorodecalin (PFD) to enhance the solvation of plasma-produced RONS and the mechanisms by which PFD enhances plasma treatment of porous membranes and other surfaces.

Using a jet from a plasma-based ozone generator operated in air and incident on a 1.2mL cuvette of liquid, experiments were performed to investigate the solvation of O\textsubscript{3} with UV-vis spectrometry. These experiments showed the PFD easily dissolving an order of magnitude more O\textsubscript{3} than water (cf. Fig. 1). Fourier Transform Infrared Spectrometry (FTIR) experiments with a surface micro-discharge (SMD) in air have also shown that the rise time for N\textsubscript{2}O in the gas phase is slower when in contact with a PFD-coated surface as opposed to a dry or water-coated surface, suggesting enhanced uptake of NO\textsubscript{x} by PFD. Finally, PFD does not appear to significantly raise transmission of N\textsubscript{2}O into the gas phase under a PFD-coated porous membrane. Thus, the mechanism of antifungal enhancement is presumably dependent on the PFD keeping RONS in contact with the liquid-material interface. We will report additional studies to further investigate this theory.

References
We will report results of an ongoing work to develop multi-phase simulation capabilities for thermal and non-equilibrium, low-temperature plasmas. Multi-phase processes become increasingly important for a variety of applications involving arc discharges, laser ablation, atmospheric pressure cold plasmas in contact with liquids, plasma inside liquids, etc. Arc interactions with electrodes are associated with electrode erosion, emission of plasma jets, and ejection of liquid metal droplets from craters on electrode surfaces. Interactions of cold plasma with liquids (electrodes, aerosol particles, etc.) are associated with liquid surface deformation, evaporation, cavitation, etc. Simulations of these phenomena require coupling plasma physics with multi-phase flow science.

We extend our Adaptive Mesh and Algorithm Refinement (AMAR) methodology to add multi-phase capabilities. The Volume of Fluid (VOF) method is used to dynamically track free interfaces between gas, liquid and solid states [1].

The left part of Figure 1 shows an example of simulated development of a liquid pool of molten Cu and formation of splashes and droplets induced by arc root on anode surface. We have also traced the solid-liquid interface at the bottom of the crater. Similar effects are observed on the cathode surface during crater formation and droplet ejection from the rim of the crater. In both cases, the dynamically adapted Cartesian grid helps properly resolving the freely moving gas-liquid interface, electric fields around sharp edges of the interface and droplets emitted from the melted pool by pressure forces.

Current work includes simulations of discharge formation on tip of Taylor cones formed on liquid cathodes. Electric fields near the tips of the cones are enhanced to initiate gas breakdown and the formation of corona, glow, spark and arc discharges. Melting, evaporation of the cathode surface in arc discharges result in the formation of plasma jets expanding from the cathode. During jet expansions, a non-ideal plasma turns into an ideal plasma. We use hybrid fluid-kinetic models to analyze effects of Explosive Electron Emission and ambient gas pressure on the dynamics of plasma processes on liquid cathodes [2]. In our presentation, we will discuss details of the development and implementation of the multi-phase models for simulations of corona, glow and arc discharges with liquid electrodes.

References
Moment Modeling of Nanoparticles in Dusty Plasmas

Steven L. Girshick

Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN (slg@umn.edu)

Previous numerical models developed under Center support have enabled self-consistent simulations of nanoparticle nucleation, growth, charging, transport and heating in nonthermal, chemically reacting plasmas. These studies have modeled systems that evolve in time in a 1-D parallel-plate configuration [1], as well as plasmas that flow through a tube in 2-D (axisymmetric) geometry [2]. This work utilized a sectional approach, in which the particle size distribution is divided into sections of finite width in particle size space, and a separate population balance equation is solved for each section [3]. The sectional approach has a number of advantages. However, when self-consistently coupled to a model for a spatially nonuniform plasma, such models are computationally expensive, sometimes prohibitively so [1, 2], because of the large number of sections that must be considered to minimize errors due to numerical diffusion. It is thus desirable to develop less expensive computational models that still provide acceptably accurate predictions for the properties of most interest. To that end we have recently developed a new model, based on the method of moments for the particle size distribution. While highly developed for neutral aerosols, to our knowledge an aerosol moment model has not previously been developed for nonthermal plasmas, nor indeed for any population of particles that undergo charging.

As seen for example in Fig. 1, our sectional model predicts that under conditions where fresh nucleation occurs a bimodal particle size distribution develops in a nanodusty plasma. Fresh nucleation feeds the small particle “nucleation mode,” while negatively charged particles, confined to the bulk plasma by the electric field, are able to grow, and thus constitute the “accumulation mode,” which can be approximated as having a lognormal size distribution. As in ref. [4] for a neutral aerosol, our new bimodal moment model treats the nucleation mode as monodisperse and the accumulation mode as lognormally distributed. However, several key features are quite different between the treatment of a neutral aerosol and a plasma aerosol. These differences derive primarily from the role of particle charging on the evolution of the particle size distribution, because particle charge strongly affects both coagulation and particle transport. Our new model modifies moment-based models developed for neutral aerosols to account for these effects.

References

Different kinds of Langmuir, magnetic and microwave probes are widely used for plasma diagnostics. Any probe diagnostics implies that the plasma local parameters inferred from the probe measurements are not distorted by the presence of a probe. However, inserting a probe into plasma can lead to local and even global perturbations of the plasma parameters. This can produce erroneous diagnostics results. The criteria for neglecting of such perturbation are well understood for the electron collection by classical Langmuir probes [1]. However, in all other types of probes, neglecting plasma perturbation by probes may lead to essential errors.

We here present an analysis of plasma perturbations by a cylindrical probe, commonly found in practice, for arbitrary collisionality parameter $\beta = \rho / \lambda_i$, where $\rho = a + s$ is the probe-sheath radius, $a$ is the probe radius, $s$ is the sheath width, and $\lambda_i$ is the ion mean free path. Our results were first obtained for infinitely long probes and then for finite lengths probes by solving numerically a set of fluid equations for neutral plasma with cold ions, taking into account ion inertia and a nonlinear ion friction force, similarly to [2] for a spherical probe. An analytical solution for the infinitely long probe in the collisionless case, $\beta = 0$, was also found. Plasma perturbation profiles and the plasma density at the plasma-sheath boundary near the probe are shown in Fig. 1. The comparison of the plasma perturbation profiles with those obtained for a spherical probe [2] shows that, except for $\beta << 1$, the plasma depletion area and drop in density at the plasma boundary for a cylindrical probe are significantly larger than those for a spherical probe. This fact has an important implication for plasma diagnostics when the ion part of the probe I/V characteristic is used according to the commonly accepted formula: $I_p = 0.6 \cdot (2\pi \rho l) \cdot e n_0 (kT_e/M)^{1/2}$ which, as seen in the table in Fig. 1, is valid only for $\beta << 1$. For relatively low argon pressures of tens mTorr with $\lambda_i$ of the order of 1 mm, for high negative probe potentials, the value of $\rho$ may exceed the $\lambda_i$ value, typical for measuring the ion “saturation” current. This results in underestimation of the plasma density inferred from the ion part of the probe characteristic. Thus, the here presented plasma depletion around a cylindrical probe is an additional effect which contributes to high inaccuracy of plasma diagnostics that use the ion part of the probe characteristics.

References
Nonlinearity, Hysteresis, and Symmetry-Breaking in High Frequency CCP’s

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Large area, high frequency capacitively coupled plasmas (CCP’s) [1-6], widely used for thin film fabrication, require extreme processing uniformity. At higher frequency and/or larger area, the radial wavelengths of the surface waves in the plasma can become comparable to the reactor radius, leading to standing wave effects and center-high plasma non-uniformities.

In asymmetric cylindrical reactors, we have observed center-high non-uniformities in CCP particle-in-cell and fluid simulations even when the driving frequency wavelength is much larger than the system size, because the nonlinear sheath motions excite driving frequency harmonics that can be radially near-resonant, enhancing the on-axis power deposition (Fig. 1). We compared the fluid simulations with a transmission line (TL) theory incorporating the full nonlinear sheath dynamics of the symmetric and anti-symmetric surface wave modes [1–4]. Adding a dielectric layer over the substrate electrode improves discharge uniformity by increasing the effective (sheath + dielectric) sheath widths and, thereby, the radial wavelengths of the fundamental and nonlinearly-driven harmonic modes [5].

In asymmetric discharges, nonlinear interaction of the symmetric and anti-symmetric modes leads to discharge hysteresis, as seen in 2D PIC simulations [6]. In symmetric discharges excited symmetrically, nonlinearity near the first anti-symmetric resonance induces symmetry-breaking, giving rise to asymmetric discharge equilibria, as seen in fluid simulations.

References
Advancing Diagnostics to Interrogate Plasma Environments

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Diagnostics play a key role in assessing our understanding of processes that occur in low-temperature plasma discharge environments. Not only do these diagnostics provide quantitative information that can be used to benchmark predictive simulations, but they often provide new insight into otherwise unappreciated phenomenon. In our presentation, we discuss not only the development of advanced diagnostics to provide such new insights but the collaborative application of these diagnostics to study plasma systems of interest to the plasma science community.

In this presentation we discuss continued efforts to develop laser-collision induced fluorescence (LCIF) diagnostic method \cite{1} and its application to interrogate challenging discharge environments. For example, we perform LCIF in a low pressure, highly magnetized environment (Figure 1a) like that found in ion thrusters to study the role cusp bias has on plasma transport and ion extraction \cite{2}. Likewise, near-atmospheric pressure helium jets interacting with co-flow atmospheres containing nitrogen and water vapor are currently being studied to benchmark predictive simulations being developed in the plasma science center (Figure 1b).

Finally, we will present ongoing work to use short-pulse lasers to interrogate electric fields present in rapidly evolving plasma environment and discuss our future plans to extend plasma diagnostics to interrogate the near-surface interface.

References


Electric field in a nanosecond pulse, surface dielectric barrier discharge are measured using newly developed picosecond Second Harmonic Generation (SHG) diagnostics. During the voltage rise, the positive polarity discharge develops as a sequence of two surface ionization waves, which evolve into filamentary plasma during the voltage reduction, when the current reverses direction. The negative polarity discharge propagates as a single ionization wave, which becomes strongly filamentary during the voltage reduction. In the positive polarity discharge, the first ionization wave results in nearly complete shielding of the vertical field component, until the arrival of the second ionization wave. The peak of the horizontal field component in the second wave, as well as its reversal during the voltage reduction, are well pronounced. In the negative polarity wave, both electric field components are reduced to near zero, before reversing direction when the voltage is reduced. Peak electric field measured, ≈ 24 kV/cm, is somewhat lower than breakdown field in air, due to pre-ionization by the previous discharge pulse. Since the present diagnostics is species-independent, it can also be used for measurements of electric field distributions in plasmas sustained in gas mixtures other than air, such as Ar and He, with high spatio-temporal resolution. These measurements are underway.

Number densities of HO2 radical, water vapor, and metastable excited electronic state of nitrogen, N2 (A3Σu+), in ns pulse discharge plasmas have been measured by newly developed Cavity Ring-Down Spectroscopy (CRDS) diagnostics. HO2 number density is measured in a repetitive ns pulse discharge in a H2-O2-Ar mixture. The results demonstrate that HO2 number density on the order of 1·1010 cm-3 and H2O number density of 1·1016 cm-3 can be measured, using single laser-shot cavity ring-down traces. Time-resolved absolute number density of N2(A3Σu+, v=2) molecules generated in a repetitive ns pulse discharge in nitrogen. Peak number density measured at these conditions is \[ N_2(A^3Σ_u^+, v=2) \approx 0.9 \cdot 10^{10} \text{ cm}^{-3} \]. Time-resolved measurements of N2(A3Σu+, v=0-2) molecules in different gas mixtures excited by a ns pulse discharge are underway.
Effect of Water Vapor Concentration on Plasma Morphology and Kinetics in DBDs and Molecular Beam Mass Spectrometry

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Gas phase non-equilibrium plasmas containing water vapor are of growing interest for many applications. While many studies focus on the applications of these plasmas, the complex plasma physics and kinetics remain poorly understood [1]. In spite dielectric barrier discharges (DBDs) have been extensively studied, the effect of humidity on the morphology and kinetics of DBDs remain largely unknown. In general, the effect of discharge morphology of atmospheric pressure plasmas on discharge kinetics is poorly understood. In addition, several models have been developed for DBDs that are volume averaged or 1 dimensional. These models do not fully consider the potential important effect of the detailed discharge morphology in DBDs and ignore spatial gradients. In this context, we performed detailed measurements of the effect of water vapor on the discharge morphology, OH and H$_2$O$_2$ production in He and Ar DBDs [2].

The He DBD is diffuse at low powers and water concentrations but for higher power and water concentration, a structured pattern appears suggesting a filamentary discharge although with a significantly larger filament radius than in Ar. Figure 1 shows the increasing number of filaments in the Ar DBD with increasing water concentration at a fixed discharge power. The pronounced surface discharge component at low water concentrations also reduces with increasing water concentration. This most likely relates to a change in surface conductivity of the dielectric with changing water concentration. In contrast to the root square dependence of the OH density on the water concentration in He, typical for diffuse discharges, the OH density in Ar increases for small water concentrations and after a saturation of the OH density it reduces for the higher water concentrations. This finding correlates with a change in the discharge morphology: a change in the number of micro-discharge filaments with increasing water concentration and a change in the surface discharge intensity. We have also shown that the ratio of the OH and H$_2$O$_2$ density can be easily estimated from bulk plasma considerations. These estimates show that the H$_2$O$_2$ production is limited by reactions of H$_2$O$_2$ with short-lived species. The H$_2$O$_2$ production is thus strongly dependent on the gas residence time.

In addition, we will provide an overview of the molecular beam mass spectrometer being built with support of the Plasma Science Center as part of a virtual facility of plasma diagnostics located at the University of Minnesota and University of Maryland. We plan to show the first preliminary results together with a description of the new system’s capabilities and summarize future measurement plans.

References
Kinetic Modeling of Non-Equilibrium Plasmas for Modern Applications

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We have studied several non-equilibrium plasma devices where kinetic effects determine plasma self-organization.

We have performed 1D particle-in-cell simulations of capacitively-coupled discharge in a weak (< 50G) applied magnetic field directed parallel to the electrodes. We show that even such weak magnetic field can significantly change properties of the discharge and allow for effective control of plasma fluxes [1,2].

We have also developed a Global Model Code for Negative Hydrogen Ion Sources, GMNIS [3]. The codes ultimate goal is to aid developing optimized negative ion beams for ITER. The code solves volume-averaged equations: continuity for plasma species and electron energy equation for the electron temperature, and include more than 1000 volumetric and surface reactions for interactions of electrons, ground-state atomic and molecular hydrogen, molecular ions and atomic ions, negative ions, 14 vibrationally-excited states of molecular hydrogen, and excited atoms. Results of the code are benchmarked against another code and benchmarking is underway.

Using fluid/electron Monte Carlo (MC) hybrid model, we simulated the chemical composition of CF₄ and Ar/SiH₄ plasmas in capacitively coupled (CCP) plasma discharge. Focus of this study is the electron energy distribution function (EEDF), and its effects on the etching or deposition precursor properties [4].

An analytical model has been developed to map out the low-pressure (left-hand) branch of the Paschen curve at very high voltage when electrons are in the runaway regime and charge exchange/ionization avalanche by ions and fast neutral atoms becomes important. The model has been applied to helium gas between parallel-plate electrodes, at potentials ranging in magnitude between 10 and 1000 kilovolt. [5]

References

Development of a GPU-Accelerated Poisson Solver for Hybrid Fluid/Kinetic Plasma Simulations

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Multi-scale phenomena can occur in atmospheric plasma flows containing small particulates, such as aerosols, that have diameters of tenths to hundreds of micrometers. For aerosol diameters in the range of 0.1 to 10 µm, the small length scale of the particle gives rise to a relatively large local Knudsen number (0.01 to 1.0 for atmospheric plasma), indicating that kinetic phenomena are dominant in the localized region around the particles, while the rest of the flow is a continuum that can be modeled with fluid approaches. This Project has two objectives: (1) development of a robust hybrid fluid/kinetic approach for plasma flow with particulates; and (2) implementation for execution on graphics processing units (GPUs).

To model the multi-scale plasma flows, we are employing the Unified Flow Solver (UFS), a hybrid fluid/kinetic model for simulating gas and plasma flows. [1, 2] UFS takes advantage of heterogenous computing architectures, utilizing traditional multi-core CPUs as well as high-performance graphics processing units (GPUs) to accelerate its calculations. [3] We are extended the GPU capabilities of UFS by implementing a GPU-accelerated Poisson solver. The Poisson solver utilizes the conjugate gradient method with an incomplete LU preconditioner. The performance and convergence of the GPU-accelerated Poisson solver are compared to those of the parallel, open-source linear algebra library HYPRE. The first test case is the solution of the 2D Poisson equation in a square domain with Dirichlet boundary conditions and a prescribed source term [4]. The second test case is identical to the first, with the addition of a circular inner boundary and adaptive mesh refinement. Finally, the solver is applied to simulate a 2D atmospheric-pressure plasma flow over a cylinder of diameter 100 µm. The plasma potential at the left-hand boundary is fixed at 4000 V, and the potential profile along the cylinder surface varies with angle.

Figure 1 – Plasma potential contours from a UFS solution of a 2D atmospheric-pressure plasma flow over a cylinder of diameter 100 µm. The plasma potential at the left-hand boundary is fixed at 4000 V, and the potential profile along the cylinder surface varies with angle.

References
Measurements of Electron Densities and Gas Temperatures in 13.56 MHz Ar Atmospheric Pressure Plasma Jet

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Electron number densities and gas temperatures were measured in an atmospheric pressure Ar plasma operating in open air. The plasma source consisted of a 2 mm ID, 3 mm OD quartz tube with an external, grounded copper ring electrode, and a 1 mm-diam. tungsten needle internal electrode, powered by a 13.56 MHz, ~2 kVp-p sinewave voltage through a matching network. Ar (99.999%) with 0.02% H₂ was flowed through the tube at a flow rate of 1.5 slm. As has widely been reported, these types of sources produce a “plasma jet”, consisting of a propagating ionization wave or “bullet”, extending roughly 1 cm into the ambient air. The jet was allowed to dissipate in air, or was “terminated” with a quartz flat that in some cases was backed by a grounded plate. The plasma was probed by optical emission spectroscopy (OES) collected perpendicular to the jet axis, using an optic fiber with a lens attached, as a function of peak-to-peak discharge current and distance from the exit of the discharge tube. Both time-averaged and time-resolved spectra were recorded with 2 different spectrometers. H Balmer-β emission at 486.1 nm was used to determine electron number density by determining the extent of Stark broadening of the emission line. N₂ from the ambient air gives rise to strong emission from the C⁵Πₜ → B³Π₉ system in the UV region. Gas temperature was extracted from a fit to the rotational spectrum.

Figure 1 shows measurements recorded across the jet at a distance of 5 mm from the tube nozzle. Gas temperature, $T_g$, rises slightly from 850 K at 3.4 A to 910 K at 4.0 A. This gas temperature was used to compute the pressure broadening component of the H Balmer-β emission at 486.1 nm. This was used along with the Doppler width computed from $T_g$ (a negligible broadening effect) to extract the Stark broadening component and obtain the values for electron density, $n_e$, shown in Fig. 1. Electron density increased with discharge current and reached $3 \times 10^{13}$ cm$^{-3}$ at the highest current investigated. Time-averaged Ar 416 nm and H Balmer-β emission intensities were also recorded and were also found to increase with increasing discharge current, though not as much as the measured electron density.

Measurements as a function of time and position will be presented, as well as comparisons with previous results from a difference plasma source, operating at much lower frequency (200 kHz).
Moderate Pressure Plasma Source of Nonthermal Electrons

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Plasma sources of electrons offer control of gas and surface chemistry without the need for complex vacuum systems [1]. The plasma electron source presented here is based on a cold cathode glow discharge (GD) with a cylindrical anode operating in a dc steady-state mode in a moderate pressure range of 2 – 10 torr. Ion-induced secondary electron emission (SEE) is the source of electrons accelerated to high energies in the cathode sheath potential. The source geometry is a key to the availability and the extraction of the nonthermal portion of the electron population. The source consists of a flat cathode and a cylindrical anode, 1 mm apart (Fig. 1). Our estimates show that the length of the cathode sheath in the plasma source is commensurate (~0.5 – 1 mm) with the inter-electrode distance so the GD operates in an obstructed regime without a positive column. Estimations of the electron energy relaxation confirm the non-local nature of this GD hence the nonthermal portion of the electron population is available for extraction outside of the source. The use of a cylindrical anode presents a simple and promising method of extracting the high energy portion of the electron population (Fig. 1). Lower energy electrons generated as a result of ionization process within the source, are scattered by collisions with the working gas and collected by the anode thereby conducting the dc current to the anode.

Langmuir probe measurements and optical emission spectroscopy confirm the presence of nonthermal electrons with energies ~15 eV outside of the source [2]. These electrons become available for surface modification and radical production outside of the source. The extraction of the electrons of specific energies by varying the anode geometry opens exciting opportunities for future exploration. For example, the decomposition of CH₄-CO₂ gas mixture using the developed plasma source of electrons (Fig. 1a) is shown in Fig. 1b. We will discuss results of most recent studies of the effect of ion induced secondary electron emission on electron energy distribution function in the source plasma.

References

Cold atmospheric plasma (CAP) sources produce chemically reactive species that effectively modify materials which enables numerous applications. To understand the plasma-surface interaction (PSI) mechanism and build correlation between gas phase species and material surface responses, comprehensive characterization of both plasma/gas phase and surface/subsurface are desired. With the support from the Department of Energy Plasma Science Center (DOE-PSC), we established a virtual facility based on shared apparatus located at Universities of Maryland and Minnesota that joins resources and expertise [1].

Recently, we added a Fourier transform infrared spectrometer (FTIR)-based characterization platform to the virtual facility. Equipped with a liquid N$_2$ cooled HgCdTe (MCT) detector, 1-16 m variable path length gas detection cell, specular reflectance, diffuse reflectance (DRIFTS) and attenuated total reflection (ATR) accessories, this new FTIR system is capable of quantitatively measuring the type and density of reactive gas molecules (sub-ppm to a few percent) and the chemical composition of thin films (a few monolayers to μm), powders, etc.. For example, as shown in Fig. 1 (a) the IR absorption of N$_2$O and N$_2$O$_5$ generated by a surface micro-discharge (SMD) were measured with 0.5 cm$^{-1}$ resolution. The density of these species depends on working gas composition and reaches maximum values of 3.41 $\times$ 10$^{15}$ cm$^{-3}$ and 2.35$\times$10$^{15}$ cm$^{-3}$, respectively. In Fig. 1 (b) we show the IR spectrum of 10 nm polystyrene (PS) films when exposed to the same SMD source. It can be seen that CAP treatment damages the benzene ring of PS and converts it into ether (C-O) and carbonyl (C=O) moieties.

Along with other characterization tools such as ellipsometry, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), the virtual facility will contribute significantly to the understanding of PSI for plasma catalysis, bacterial sanitation, etc..

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References
Interest continues to increase in low-temperature atmospheric-pressure plasmas, fueled mainly by realized and potential biomedical applications. For selected area exposure, the so-called atmospheric pressure plasma jets (APPJs) are most popular. APPJs are ideal for treating specimens, including bacteria-covered surfaces, or living tissue.

By far the most common configuration of APPJ entails flow of a working gas (normally He or Ar) through a dielectric capillary tube. The gas exiting at the end of the tube (nozzle) entrains ambient gas (normally open air) which mixes with the working gas. The composition of the ambient gas directly affects the plasma chemistry and plasma-surface interactions. One method to control the ambient gas is to enclose the system in a chamber. Such action, however, limits the inherent portability of the APPJ. A more compact design uses a co-axial tube forming an annular space where a gas of selected composition flows, shielding the working gas from the ambient, thus resulting in a well-defined system. [1]

In this work, a computational investigation of an APPJ with a co-axial shielding gas was performed. The neutral gas flow patterns and species concentration distributions were predicted with a convective mass transport model. These were then used in a fluid plasma model to predict the behavior of the system. The test case used He, N₂ and open air as the working, shielding and ambient gas, respectively. O₂ in open air was considered as “contaminant”.

For laminar flow, the “contaminant” concentration on the substrate was reduced monotonically (and could reach sub-ppm levels) as the shielding gas flow rate was increased. Fig. 1 shows the nitrogen ion density for an 80 ns trapezoidal excitation pulse with peak voltage of +4 kV. The flow rate of both working and shielding gases was 1 slm. The N₂⁺ density peaks at the separating zone between He and N₂ shielding gas. Although the ionization potential of N₂ is much lower than that of He, the majority ion was He⁺ (~10¹⁵/cm³). The spatiotemporal variation of species concentration profiles, as well as the electron temperature and electric field as a function of the shielding gas flow rate will be discussed with an eye on how flow can influence the discharge physics.

Reference
For similar discharges, the physical parameters of the plasma in one gap are proportional to those in the others [1]. The similarity of gas discharges enables extrapolation of features of plasmas with length scales for which experimental studies may not be feasible. The validity of the similarity law is confirmed under limited discharge conditions, and needs further investigation.

Recent studies of the similarities of low-temperature plasma discharges are presented based on both experiments and computational methods. The classical Paschen law was extended to discharge gaps with different aspect ratios, and the breakdown voltage $U_b$ was identified as a function of the reduced gap length $pd$ and the aspect ratio $d/r$, i.e., $U_b=f(pd, d/r)$ [2]. Here, $p$ is the pressure, $d$ the gap length, and $r$ is the discharge radius. Current studies include gas breakdown characteristics in microscale plasmas up to atmospheric pressure. The voltage-current characteristics are used to identify similar glow discharges. The similarity relation holds in a certain pressure range and for limited scaling factors. Moreover, the similarity relation for the cathode fall thickness in glow discharges is confirmed based on the light emission distributions in geometrically similar gaps. By using the newly developed Kinetic Global Model framework (KGMf), the effect of nonlinear processes on the similarity law is studied in high-pressure microdischarges with different scaling factors [3].

The scaling law illuminates the physics of discharge configurations difficult to diagnose experimentally, provides a pathway to improved designs, and a simulation basis for validation of properties in scaled models. Several applications of the similarity law are introduced, including large glow discharges, e.g. for cleaning ITER; ultra-small discharges, e.g. microdischarges in analytical chemistry, and discharges of ultra-large scale in the atmosphere.

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References
All low temperature plasmas are bounded in some sense – there is a point in space where the gas transitions from being ionized to being non-ionized. These transition zones can take the form of solid or liquid boundaries, as with dielectric barrier discharges (DBDs) or confinement resulting from a significant change in electric field or transport coefficients. The latter is the case for atmospheric pressure plasma jets (APPJs) sustained in a rare gas flowing into humid air. The E/N (electric field/gas number density) required to sustain the plasma in the air bounding the rare gas plume is larger than in the plume. Boundaries can also be electrical. Due to geometry or other factors, such a dielectric constant or charging of a surface, the E/N available to the plasma can vary in space from above self-sustaining to below self-sustaining. The end result is a transition zone which electrical boundaries or gradients confine the plasma.

In this talk, results from computational investigations of bounded atmospheric pressure plasmas will be discussed with the goal of providing insights to methods boundary-based control of DBDs and APPJs. Using the modeling platform nonPDPSIM [1], examples for bounded APPJs will be discussed for the following scenarios.

1) The use of APPJs in treating liquids in well-plates produce several layers of boundaries – the physical boundary produced by the well, the change in gas flow patterns that mixes ambient air into the well and electrical boundaries produced by the dielectric well plate.

2) Electrode configuration in APPJs and location of ground determine electrical boundaries which influence the penetration of ionization waves into the ambient and power deposition for a given voltage. (See Fig. 1.)

3) The orientation of APPJs (i.e., perpendicular to the surface or a non-normal angle) determines gas flow patterns as well as electrical boundary conditions.

4) Perhaps the most boundary-limited of atmospheric pressure plasmas is the plasma-enhanced packed bed reactor. The propagation of ionization waves through the lattice critically depends on the orientation of dielectric surfaces to the applied electric field and electrical properties of the solids.

References

Catalytic Enhancement by a Cold Atmospheric Pressure Plasma Jet: CH$_4$/O$_2$/Ar with Supported Ni Catalyst

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Cold atmospheric plasma (CAP) sources are important sources of reactive chemical species which have been shown to be useful to numerous new applications. One particular area of interest is the enhancement of catalytic material behavior using plasma sources as a source of reactive species and energy. It is believed that this enhancement may be due to complex interactions of the plasma based species with the catalyst surface [1]. In this study we examine the effect of an atmospheric pressure plasma jet (APPJ) on a nickel catalyst supported on Al$_2$O$_3$ and SiO$_2$ particles used for the conversion of methane system in the presence of oxygen for methane removal from the atmosphere or the production of syngas. This APPJ has been well studied and the density of various reactive species, including atomic oxygen, has been characterized.

We find that the plasma enhancement of catalytic behavior for a commercial supported nickel catalyst is evident for a range of plasma to catalyst interactions. A Fourier transform infrared spectrometer (FTIR) system in conjunction with a catalyst cell were used to monitor the methane conversion and the production of reactant products. Figure 1 shows the extracted data from a FTIR spectrum for CH$_4$, CO$_2$, CO, and H$_2$O peaks for a plasma treatment of catalyst at room temperature over a range of plasma current levels which scales nearly linearly with plasma power. We find that the plasma catalyst interactions lead to the selective production of carbon monoxide products. However the catalyst alone at high temperature tends to produce increased carbon dioxide and water vapor. Plasma treatment of the catalyst also enhances the thermal catalysis behavior of the catalyst after the plasma treatment showing an increase in the amount of methane converted.

The catalyst surface will be investigated using samples made of thin nickel layers deposited onto silicon dioxide samples by in situ ellipsometry which can monitor thickness and index changes of the surface during plasma treatment. This technique is particularly useful for monitoring carbon deposition on the catalyst surface and changes to surface morphology. X-ray photoelectron spectroscopy is used to investigate the oxidative changes of the nickel surface due to plasma treatment and carbon absorption from the catalytic breaking of the methane.

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References
Gas breakdown in microplasmas and microdischarges with characteristic lengths less than 1mm is key in many applications, including micro-electro-mechanical systems (MEMS), micro-switches, and microchip devices [1, 2]. With sharply reduced dimensions, discharge characteristics are strongly influenced by geometric features, such as electrode surface protrusions [3].

Using a two-dimensional fluid model, the Townsend breakdown voltages in microgaps are quantified. The microdischarge model includes the dark discharge region, the Townsend discharge region, and the subnormal glow region, identifies the breakdown voltage when the discharge current enters the subnormal region. Fig. 1 shows the breakdown voltage as a function of gas pressure for a cathode hemiellipsoidal protrusion (450μm by 200μm), compared to parallel plate gap distances of 50μm to 500μm spanning the max and min for the protrusion case. The cathode surface protrusion results in a Paschen curve, which transitions from wide gap behavior at low pressure to narrow gap behavior at high pressure, resulting in relatively low breakdown voltage in a wider range. This can be observed in Fig. 2, the discharge automatically optimizes its discharge path to obtain the lowest breakdown voltage. The effects of the discharge polarity and the microgap aspect ratio on the breakdown voltages are also investigated.

Protrusions in microdischarges have a profound impact on breakdown voltage, whether resulting from surface roughness, damage, or by design. This work allows both uncertainty quantification of breakdown variability, and design of microgaps with controlled breakdown voltage across many orders in pressure via shaped protrusions.

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References
Correlation between Remote Plasma Oxidation (RPO) of Polymers and Long-lived Reactive Neutrals

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Cold atmospheric plasma (CAP) is known for generating many chemically reactive species including energetic charged species, UV photons, short-lived strongly oxidative neutrals and long-lived weakly oxidative neutrals. Previously we have studied the effect of UV photons and short-lived neutrals such as O and OH on polymers [1, 2]. In this work we investigate the effect of remote plasma oxidation (RPO) of polymers by long-lived neutrals [3] using a surface micro-discharge (SMD) operated in various N₂/O₂ mixture environments.

We chose SMD as a model CAP source for long-lived neutrals because the active plasma region of SMD is confined in a thin discharge layer on the dielectric surface which reduces the transport of short-lived neutrals and ions to target surfaces. In order to correlate the response of polymers under the exposure of SMD, we characterized both the density of gas phase reactive species and the chemical modification of polymer surfaces and subsurfaces. Using IR and UV absorption techniques, various long-lived reactive oxygen and nitrogen species (RONS), such as O₃, N₂O₅, HNO₃ and NO₃, were detected. The density of these RONS varies with working gas composition, and is shown in Figs. 1 (b) and (c). Using real-time ellipsometry, X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), the evolution of polymer film thickness, refractive index, surface and bulk chemical composition were evaluated for each working gas composition in Fig. 1. These measurements revealed three consecutive stages of polymer transformation during RPO by long-lived neutral species: (1) surface adsorption and oxidation; (2) bulk film permeation and thickness expansion; (3) etching from material surface. We further correlated these transformation stages with the SMD generated RONS species measured by IR and UV absorption. The key RONS were identified for each polymer transformation stage.

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References
Interaction between Plasma and Water Micro-Droplets as a Model for Plasma-Induced Reactivity Transfer into Liquids

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The interaction of non-equilibrium plasmas operating at atmospheric pressure and close to room temperature with a liquid phase is a complex multiphase phenomenon, which has led to the development of many plasma-based applications including, water treatment, material processing, decontamination, health care and agriculture. These applications are enabled by the transfer of highly reactive chemistry produced in the gas-phase plasma to the bulk liquid phase, through an interfacial region. This multiphase reactivity transfer is transport limited due to reactions of many plasma-produced short-lived reactive species (such as OH) in the gas phase or near the interfacial region while their bulk liquid concentrations remain very small.[1]

The focus of this study is to assess the interactions of a controlled and well-defined diffuse and homogeneous plasma (with an ionization degree ~ $10^{-7}$–$10^{-8}$) with individual liquid micro-droplets having fixed size to understand this complex interaction, particularly the transport of OH radicals from the gas to the liquid phase. This is investigated by quantifying the conversion of a model hydrocarbon compound (formate) in water, with known chemical kinetics with OH. Formate does not react with the abundant H$_2$O$_2$ produced by the plasma. The RF driven plasma is generated in He-H$_2$O. The absolute gas-phase OH densities, measured using broadband absorption spectroscopy without liquid droplets, range from $0.6$ to $4\times10^{20}$ m$^{-3}$ at a constant discharge power of 15 W. The discharge geometry and the droplet ejection parameters allowed a small droplet (containing formate) residence time of the order of 10 milliseconds leading to the decomposition of 40% of the initial formate concentration. This decomposition rate in droplet treatment is almost 2 orders of magnitude faster than that achieved in the bulk liquid treatments.[2]

A 1-dimensional diffusive reactive transport model has been developed assuming that only the dominant neutral plasma species, OH and H$_2$O$_2$ enter the droplet from the gas-phase plasma.[3] Figure 1 shows the calculated formate concentrations in good agreement with the experimentally measured decomposition. The obtained results in this study show the importance of OH radical reactions near the plasma-liquid interface.

References
Poster Presentations

Evaluating the EEDF for the Global Modeling of Low-temperature Plasmas

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Low-temperature plasma simulations involving multiple species with many chemical reactions are computationally expensive. Reducing the number of reactions by identifying the significant pathways in plasma chemistry is imperative to meet simulation needs with high-efficiency. The resulting set of the most influential reactions is defined by comparing reaction rate coefficients instead of reaction cross sections, and then used in fluid or PIC simulations. A global (volume-averaged) model was proposed to find a reduced set of reactions in many-species systems. The newly developed Kinetic Global Model framework (KGMf) was designed to explore plasma kinetics in atmospheric pressure microdischarges as well as pulsed powered nanosecond discharges.

In high-pressure discharge regimes, the electron energy distribution function (EEDF) becomes non-Maxwellian and evolves dramatically in both space and time. Evaluating the EEDF in BOLOS (open-source implementation of Boltzmann equation solver in Python) inside KGMf is of great importance to calculate the collisional source term. Currently, the implementation of the EEDF solver enables EEDF evaluation based on predefined time step, absolute value or relative change of discharge parameters, such as electron temperature, reduced electric field or species density.

In a case study of low-temperature argon plasmas, we present the effect of EEDF evaluation frequency on reaction rate coefficient, as well as electron density and breakdown transition.

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References

An Investigation of Micro-Discharges in Dynamic Porous Media

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Plasma enhanced packed bed reactors (PBRs) are being investigated for applications in pollution remediation, chemical synthesis (including catalysis), and plasma-aided combustion. PBRs operate as dielectric barrier discharges with intense plasma interactions with the aggregate media and gas within interstitial spaces. The plasma formation and propagation through these systems are a function of many parameters, including applied voltage waveforms, dielectric media composition and surface morphology, packing fraction, and pressure. Optical analysis of traditional 3-dimensional PBRs is difficult due to overlapping layers of the dielectric beads. Therefore, a 2-dimensional PBR composed of dielectric disks was developed to enable optical emission imaging of plasma formation and propagation. The discharge modes of the plasma and their sensitivity to the packing material and pressure were experimentally and computationally investigated. It was found that filamentary micro-discharges (FMs) and surface ionization waves (SIWs) were the dominate modes of plasma propagation. Each FM led to the formation of a surface hugging SIW until an additional transition to a FM was observed.

The dominating discharge mode was found to be dependent on the pressure of the system as well as the dielectric constant of the packing media. In general, plasma propagation through the 2d PBR at 1 atm is initiated by localized micro-discharges between adjacent dielectric disks, which in turn give rise to the propagating SIWs. As the pressure was reduced below 1 atm, the discharge was more diffuse regardless of the dielectric media and therefore became a more volume-filling plasma. A mode transition from dominating FMs to SIWs occurred at approximately 200 Torr as the pressure was reduced. Careful choice of the properties of the packing aggregate and pressure enables manipulation of plasma parameters and therefore some control over the reaction selectivity of the system.
Studies focusing on the influence of dust particles on a discharge afterglow are scarce. In general, after the power source is removed, the electron temperature decreases rapidly on a time scale of the energy relaxation time, typically on the scale of microseconds. After this plummeting of the electron temperature, the inequality $T_e > T_i$ no longer applies. After the power source is removed, the electron density is also expected to decrease rapidly via recombination and/or diffusion losses to the boundaries. However, if electron detachment from the particles is a significant process, it can contribute to electron generation in the afterglow. Indeed, a previous study reported that the electron density started to increase when the discharge RF power was switched off in a low-pressure plasma [1]. We hypothesize that electron detachment from the particles occurs in atmospheric pressure discharges as well and that electron detachment may help stabilize the plasma by providing a level of remnant electron density (pre-ionization, Figure 1) in the plasma that facilitates a uniform breakdown in the next discharge pulse.

In this study, the evolution of the electron desorption and electron-ion recombination on particle surfaces during the afterglow was investigated through modeling. A previous study proposed that electrons are bound to the surface by self-induced short-range polarization potential [2]. The electron binding energy to the charged particle surface and the electron desorption rate were evaluated using quantum mechanical calculations [2]. Based on this theory [2], we calculated the electron desorption time, which is shown in Figure 2 as a function of the dielectric constant, $\varepsilon$, and the temperature, $T_p$, of the nanoparticles. For high surface temperatures or low dielectric constants, the electrons quickly gain energy due to interaction with particle phonon modes, leading to short electron desorption times. Based on these results, we are using a numerical code for particle charging to investigate the evolution of the particle charge in plasma afterglows. We investigate whether electron desorption from particles may provide sufficient preionization to stabilize an atmospheric pressure discharge.

**References**

Investigations of EEDFs and Plasma Compositions in SiH$_4$/Ar and CF$_4$ Plasmas

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Using fluid/electron Monte Carlo (MC) hybrid model, we simulated the chemical composition of CF$_4$ and Ar/SiH$_4$ plasmas in capacitively coupled (CCP) plasma discharge. Focus of this study is the electron energy distribution function (EEDF), and its effects on the etching or deposition precursor properties.

In the hybrid model, the electron MC module is used to calculate EEDFs as well as electron impact reaction rate coefficients, in order to provide effective reaction coefficients for fluid model.[1] Figure 1 shows EEDFs variation over a radio frequency (RF) cycle in the plasma center and periphery region (0.5 cm away from the lower electrode) during sheath expansion phase 0.2, 0.3 $T_{RF}$, and during sheath collapse phase 0.8, 0.9 $T_{RF}$ in CCP discharge in Ar/SiH$_4$ gas mixture for $f_{RF}=13.56$ MHz, voltage amplitude $V_{RF}=200$ V, gas pressure $P=500$ mTorr and electrode distance 2 cm. It is evident from the figure that the amount of energetic electrons is higher for the dilute 10% mixture of SiH$_4$ in Ar. At higher SiH$_4$ concentrations in Ar high energy electrons disappear due to increased inelastic collisions. Because the EEDF affects chemical reaction, the gas composition can be controlled in complex electronegative gas discharge by changing EEDF. Using the hybrid model, we also studied gas composition in CF$_4$ etching plasmas.

References
Heterogeneous Loss Coefficients for Cl on Plasma-Conditioned Yttrium Oxide Chamber Wall Surfaces

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In plasma processes, especially low pressures, heterogeneous reactions on the chamber walls are important and can often dominate neutral radical densities in plasma reactor.\textsuperscript{1, 2} Studies of heterogeneous loss coefficient, $\gamma_{\text{Cl}}$, in power-modulated chlorine inductively-coupled plasmas will be presented. Power at 13.56 MHz applied to the plasma was modulated between a high power and low or no power state. Optical emission and actinometry with trace rare gas were recorded over the 200 to 900 nm region where emissions from Cl, Cl\textsubscript{2} and Xe occur. Langmuir probe measurements were also measured to provide time-resolved $T_e$ and $n_e$ during a power modulation cycle, either from high-to-low or high-to-no power.

A reduced global model was used to extract the single variable, $\gamma_{\text{Cl}}$. $\gamma_{\text{Cl}}$ was determined from fitting Cl number density between optical actinometry\textsuperscript{3} and global model calculations in power-modulated plasmas. There are two methods for data fitting. 1) from the best fit of the predicted absolute Cl number densities to the measured values. 2) from a match between the computed and measured relative change in $n_{\text{Cl}}$ as a function of time. Due to the uncertainty in both the measured and computed absolute $n_{\text{Cl}}$, the latter approach was used and a factor $U$ is applied to adjust model agrees on absolute $n_{\text{Cl}}$. In Fig. 1, $\gamma_{\text{Cl}}$, along with $U$ are shown for three different conditions, under which $\gamma_{\text{Cl}}$ varies from 0.11 to 0.22.

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References
A Study of Plasma Induced Nanostructure Formation and Surface Morphology Changes on Tungsten at Atmospheric Pressure

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The formation of nanostructures such as “fuzz”, holes, and flakes were observed on stainless steel and tungsten anodes that in a 1 atm glow discharge with helium as the feed gas. The structures exhibited morphology similar to the tungsten fuzz growth observed in experiments that simulate wall conditions in fusion reactors [1-3], suggesting similar physics might be present in both scenarios. The anode surface temperature ranged between 1000 and 1300 K with an ion fluence rate of order of $10^{24}$ s$^{-1}$m$^{-2}$. In this work, scanning electron microscope (SEM) and transmission electron microscopy (TEM) were used to characterize the evolution of nanostructure formation as a function of time. Observed nanostructures were found to vary with the morphology of the discharge plasma attachment. As an example, figure 1 shows a SEM image that illustrated heavily textured; intricately nanostructure surface features were observed beyond the center region after 16 minutes of exposure. Significant nanohole coverage is observed in regions outside the main plasma attachment, in presumably the cooler, lower plasma density region of the attachment. There the morphology at closer inspection appears almost weblike, nanoflake and fiber shaped structures were found at the edge of the plasma ring with rod-like structures appearing in between. The composition of the structure was found to be predominantly the native metal by using Energy Dispersive X-ray (EDX) Spectroscopy. This work gives some insight into the formation of nanostructures at atmospheric pressure which has not only applications of material processing but also provides potentially another avenue to study fuzz formation processes relevant to fusion plasma-wall interactions.

References
Synthesis of Nanoparticles in Carbon Arc: Measurements and Modeling

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This work studies the region of nanoparticle growth in atmospheric pressure carbon arc. Detection of the nanoparticles is realized via the planar laser induced incandescence (PLII) approach. Measurements revealed large clouds of nanoparticles in the arc periphery, bordering the region with high density of diatomic carbon molecules. Two-dimensional computational fluid dynamic simulations of the arc combined with thermodynamic modeling explain these results due to interplay of the condensation of carbon molecular species and the convection flow pattern. The results have shown that the nanoparticles are formed in the colder, outside regions of the arc and described the parameters necessary for coagulation. Growth of the nanoparticles was described using a simplified model of agglomeration of carbon clusters, similar to one used in Ref. [1], the results being favorably comparable to measurements of the nanoparticle size distribution, done by time-resolved (TiRe) LII approach [2].

![Figure 1 – Results of measurements and simulations of spatial distributions of diatomic carbon (measured using filtered fast imaging) and carbon nanoparticles (measured using LII diagnostics): The C₂ bubble and the nanoparticles growth region; results of the simulations are shown by white lines over the experimental photo. Locations where nanoparticles have certain average size are shown with white lines over the experimental photo. Locations where nanoparticles have certain average size are shown with white dashed lines. Yellow dashed lines indicate locations of the signal line integration in measurements of the nanoparticles average diameter performed using TiRe LII technique. Areas from which a TiRe LII signal was collected are highlighted and the mean particle diameter for each area is shown.](image)

References

The interaction of cold plasma with liquid is important in many applications including plasma medicine. Plasma activated media (PAM) is usually a liquid medium in a single or multi-well plate container that is exposed to a plasma jet for different exposure times.[1] Parameters such as the distance between the liquid and the plasma nozzle of the jet or the volume/geometry of the liquid container can affect the chemistry of the PAM and, therefore, the biological outcomes. For example, the liquid containers in experiments have different sizes and shapes; from a large surface to volume ratios as in Petri dishes to smaller ratios as in centrifuge tubes or 96-well plates. Geometrical parameters of a liquid container such as the width and depth of a plate can alter the dynamics of the gas, effluent of plasma, or chemical composition of the gas – liquid interface. Water vapor pressure can be higher in a deep-well plate compared to above a Petri dish. Such geometrical parameters can affect the residence time of gas species and transport of plasma produced species to the surface of the liquid and so, the chemistry of the PAM.

In this research, we modeled an atmospheric pressure helium plasma jet, as shown in Figure 1, having two ring electrodes embedded in a dielectric material operating in ambient air – a configuration often called the plasma pencil.[1] The top electrode is powered by a 30 kV and approximately 200 ns pulses and the bottom electrode is grounded. The nonPDPSIM 2D plasma hydrodynamics model was used in this research. This platform solves Navier-Stokes equations for neutral gas flow, Poisson’s equation for electric potential, transport equations for neutral, charged species, and electron energy, and radiation transport for photoionization.[2] The helium and air reaction mechanism includes 78 gas and liquid phase species and more than 1000 reactions.

The consequence of the geometrical parameters including shape and diameter of a plate and jet-to-liquid distance on short and long-lived reactive oxygen and nitrogen species (RONS) will be discussed. These geometrical properties can change gas flow field, species residence time in plasma – liquid interface, propagation of the plasma ionization wave, and eventually activation of the liquid in the well-plate.

References

Figure 1 – (a) Schematic of plasma jet treating water in plate. (b) O$_2$ and OH gas density in (top) a high-wall and (bottom) a flush-wall plate 200 ns after the voltage pulse.
Molecular Beam Mass Spectrometry of Atmospheric Pressure RF Discharges

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Mass spectrometry (MS) is widely used as a diagnostic method in plasma processing [1]. However, the measurement of short-lived reactive species in atmospheric pressure plasmas by MS remains challenging as collisions of sampled species between the sampling orifice at atmospheric pressure and the mass spectrometer operating at $10^{-8}$ bar needs to be avoided in order to measure the actual plasma species instead of the reaction products of these species induced by the sampling process. Optical laser diagnostic methods are often used to measure short-lived species in situ although MS has the advantage to be able to detect various species simultaneously including ions and to measure species fluxes or densities at the plasma-sampling orifice/electrode interface. The latter enables linking the obtained results directly with plasma-surface interactions while densities from laser diagnostics require assumptions for the transport of the measured reactive species density at the measurement position to the interface [1].

In this work, a molecular beam mass spectrometer (MBMS) is designed and developed to measure both neutral and ionic species from atmospheric pressure plasma jets. The schematic diagram of the experimental system is shown in Figure 1. Three pumping stages are used to reduce the pressure from the atmospheric environment ($10^5$ Pa) to the pressure at which the MS operates ($10^{-7}$ Pa). This reduction by 12 orders of magnitude in pressure is achieved through 3 different pressure stages separated by aligned skimmers and pumped down by 3 turbo-molecular pumps. The diameter of the sampling orifice is chosen to be 50 μm, smaller than the typical sheath thickness at atmospheric pressure, to avoid penetration of the plasma into the first low pressure stage [2].

A supersonic expansion of the sampled species occurs in the first stage and the subsequent skimmers create the molecular beam in which neutrals and ions from a plasma can be sampled by the MS. When sampling neutral species, a resonant chopper is used between the two conical skimmers modulating the molecular beam to improve the signal to background ratio of the MS signal.

To enable ion sampling, the resonant chopper is removed and the distance between the 2nd and 3rd skimmer is reduced. These two floating skimmers are biased generating an electrostatic field that guides the ions into the ion optics of the MS. The experimental setup is currently being built and we plan to present the first preliminary MS data of an RF plasma jet in open air at the meeting.

References
Measurements of Excited Species and Radicals in Ns Pulse Discharges

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Cavity Ring-Down Spectroscopy (CRDS) diagnostics is used to measure number densities of HO$_2$ radical, water vapor, and metastable excited electronic state of nitrogen, N$_2$(A$^3\Sigma_u^+$), in ns pulse discharge plasmas. In the first experiment, an injection-seeded Optical Parametric Oscillator (OPO) is used to generate a narrowband laser output used in the CRDS spectrometer (spectral linewidth of 0.03 cm$^{-1}$). Water vapor number density is measured in the effluent of a microwave discharge sustained in an H$_2$-O$_2$-Ar mixture. Hydroperoxyl radical number density is measured in two environments, a chemically reacting Cl$_2$-O$_2$-CH$_3$OH-Ar mixture initiated by laser-induced photolysis, and a repetitive ns pulse discharge in a H$_2$-O$_2$-Ar mixture. The results demonstrate that HO$_2$ number density of 1·10$^{10}$ cm$^{-3}$ and H$_2$O number density of 1·10$^{16}$ cm$^{-3}$ can be measured, using single laser-shot cavity ring-down traces. The injection-seeded OPO pumped CRDS spectrometer has been shown to have sufficient bandwidth for simultaneous measurements of water vapor and hydroperoxyl radical in reacting flows.

In the second experiment, time-resolved absolute number density of N$_2$(A$^3\Sigma_u^+$, v=2) molecules generated in a repetitive ns pulse discharge in nitrogen has been measured by a CRDS spectrometer using a Nd:YAG pumped narrowband dye laser and a high-pressure Raman cell. This spectrometer has a much broader tuning range (up to 50 nm), but a slightly larger spectral linewidth, $\approx$ 0.07 cm$^{-1}$. Peak number density measured at the present conditions is $[N_2(A^3\Sigma_u^+, v=2)] \approx 0.9\cdot10^{10}$ cm$^{-3}$. Measurements of other vibrational states of N$_2$(A$^3\Sigma_u^+$, v=0-2) molecules in different gas mixtures excited by a ns pulse discharge are underway.

Figure 1 – CRDS spectra of HO$_2$ generated in CRDS experiment #1: (a) laser-induced photolysis in a Cl$_2$-O$_2$-CH$_3$OH-Ar mixture at P=65 Torr and (b) ns pulse discharge in a H$_2$-O$_2$-Ar mixture at P=50 Torr. Absorption path is 2 cm (a) and 10 cm (b). In both cases, HO$_2$ number density is 1·10$^{10}$ cm$^{-3}$.

Figure 2 – N$_2$(B$^3\Pi_g$, v=4 $\leftarrow$ A$^3\Sigma_u^+$, v=2) band absorption spectrum measured in CRDS experiment #2, in a ns pulse discharge in nitrogen at P=20 Torr.
Perfluorodecalin as Solvent for Enhanced Plasma-Liquid Interactions

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Interactions of atmospheric pressure plasmas with adjacent liquid phases challenges current plasma science, requiring knowledge of the physical properties of the plasma state as well as chemical interactions between plasma and liquid. Most research on plasma-liquid interactions has involved aqueous phases, but little work has been done on non-aqueous liquids. Reactive oxygen and nitrogen species (RONS) are key for many important applications, but the way they interact with non-aqueous phases is poorly understood. For example, perfluorodecalin (PFD) has been shown to increase the through-nail antifungal effect of plasma treatment on toenail fungus [1]. The enhanced solubility of gas-phase species by PFD [2] is a likely cause, but the mechanism of plasma treatment enhancement by PFD has not been studied. Here, we demonstrate the ability of PFD to dissolve high concentrations of plasma-produced RONS and explore the mechanism by which PFD can enhance treatment of porous membranes.

To compare plasma treatment of PFD to water, multiple series of experiments have been undertaken. In one set, O₃ produced by a commercial plasma-based ozone generator has been dissolved in both PFD and water. UV-vis spectrometry shows that approximately an order of magnitude more O₃ is dissolved in PFD than in water. Another set of experiments focuses on the effect of PFD with respect to NOₓ. These were performed using a surface microdischarge (SMD) operating in air within an enclosed chamber, with the voltage high enough (12kVpp) to put the SMD into NOₓ mode. In these experiments, it is shown that PFD causes a decrease in the steady-state gas-phase N₂O concentration above a porous membrane. In comparison, the presence of water on the porous membrane simply acts as a barrier, raising the gas-phase PFD concentration until the water evaporates and the membrane becomes transmissive to NOₓ (cf. Fig. 1). This suggests that the PFD acts as a sink for NOₓ, dissolving plasma-produced species at higher concentrations than water and holding them in contact with the membrane. Accordingly, PFD could be used to enhance RONS solvation from plasmas operating in either O₃ or NOₓ mode, allowing the operator to tune the power density to select the optimal plasma mode for individual applications.

Finally, it is shown that PFD does not enhance transmission of N₂O through a porous membrane and back into the gas phase on the other side. Additionally, evaporation of plasma-activated PFD is shown to release both N₂O and NO₂, while neither species was measurable above the noise level upon evaporation of plasma-activated water. This strengthens the hypothesis that, in treatment of porous membranes by plasmas, PFD can enhance biological effects by concentrating RONS and holding them in contact with the membrane.

References
Optical Diagnostics in a RF Atmospheric Pressure Plasma Jet  
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The atmospheric pressure plasma jet (APPJ) has many potential applications, especially in plasma medicine, due to its ability to generate reactive oxygen and nitrogen species. The plasma electron density is of particular interest, since it directly affects the flux of reactive species delivered to the substrate. The gas temperature is also of interest especially in cases where the APPJ interacts with temperature sensitive substrates, such as living tissue. In this work, Stark broadening was used to determine the electron density and $N_2 (C^3\Pi_u \rightarrow B^3\Pi_g)$ emission was used to estimate the gas temperature in an APPJ emerging into open air. The source involves a quartz tube with 2 mm inner diameter and 3 mm outer diameter. A 1 mm-thick grounded copper ring electrode was wrapped around the quartz tube near the gas exit (nozzle). A 1 mm-diameter tungsten needle, placed coaxially inside the tube, was powered by a 13 MHz, ~2 kV$_{p-p}$ sine-wave voltage. Argon (99.999%) with 0.02% $H_2$ flowed through the tube at 1.5 slm. An inductor was used for impedance matching to maximize power input to the plasma.

Time averaged spectra were recorded on the jet axis, 5 mm away from the nozzle, using an optical fiber with an attached lens. The hydrogen Balmer-β line (486.1 nm) was used to derive the total broadening (Fig. 1), and the $N_2 (C^3\Pi_u \rightarrow B^3\Pi_g)$ line was used to estimate the gas temperature, and thus the Van der Waals broadening. Preliminary measurements indicated that as the discharge current increased from 3.4 A$_{p-p}$ to 4 A$_{p-p}$, the gas temperature increased from 847 to 911 K, and the electron density increased from 0.9 to 1.3 x 10$^{14}$ cm$^{-3}$ (Fig. 2). Further data and comparison with published works will be presented.
Plasma/liquid interactions are of interest for pollution control, water purification, disinfection, and medical treatment. The means of transfer of reactive species from the plasma into the bulk liquid, however, are poorly understood. One method to optimize the transfer is by maximizing the surface-to-volume ratio of the liquid. Higher surface area allows for greater solvation rates, while smaller volume leads to enhanced mixing and faster saturation. This can be accomplished by plasma activation of liquid aerosols.

Dielectric barrier discharges interacting with single water droplets having radii of 5 μm to 20 μm at different frequencies (10 kHz to 1 MHz) were computationally investigated using the plasma hydrodynamics model nonPDPSIM [1]. The reaction mechanism includes 58 gas-phase and 37 liquid-phase species, and over 1,500 reactions [2]. We found that the droplets, acting as a dielectric at short time-scales, provide electric field enhancement increasing the probability of discharge formation in their proximity (Fig. 1). This is similar to the plasma response to dielectric beads in packed bed reactors.

The densities of reactive species in the aerosol having high Henry’s Law constants, $h_0$, had a strong dependence on the radius of the droplets. This is because the liquid bulk can support high densities of these species, and their densities typically do not saturate regardless of droplet diameter. The opposite is true of species with low $h_0$. The densities of these species may rapidly saturate in the liquid and so do not have a dependence on either radius or frequency of the DBD. Higher frequency operation aided in decreasing the time required for saturation by increasing the local gas-phase density, elevating rates of solvation during the pulsing phase. Most of the reactive species were found to be processed at the thin surface layer of the liquid, leading to high rates of production of $\text{H}_3\text{O}^+$, $\text{NO}_3^-$, $\text{H}_2\text{O}_2$, and $\text{O}_3$ within the bulk. The high molarities of hydronium ion also led to a drop in pH from 7 to below 2 for the smaller droplets.

References
Ignition Time and Transport Properties of Inductively Coupled Plasmas Using Low-High Pulsed Power

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Pulsed-power inductively coupled plasmas (ICPs) with power-on and power-off pulse repetition frequencies of 10s kHz are becoming more commonly used in etching processes during semiconductor device fabrication. Due to the use of highly attaching halogen gases, electrons are nearly fully converted to negative ions during the power-off period in such processes. With a low electron density at the start of the next pulse, instabilities can occur resulting from the ensuing E-H transitions. Plasma ignition delays may also occur. To address these issues, a low-level power could be maintained during the “power-off” period to ensure a minimum plasma density at the beginning of the next “power on” cycle. The remaining post-“power-off” electrons can then seed the next plasma ignition, thereby improving plasma stability and reducing ignition delays.

The behavior of an ICP sustained 1-5 kHz pulsed power using Ar/Cl\textsubscript{2} mixtures at tens of mTorr will be discussed based on computational and experimental results. The computations were performed with the 2-D Hybrid Plasma Equipment Model (HPEM). The experiments include measurements of electron density ($n_e$), temperature ($T_e$) and electron energy distributions using a Langmuir probe. The power is modulated with a high power during the power-on period and a low power during the power-off period. Instabilities during the power-on and power-off transition were specifically studied.

For long modulation periods the model predicts that $T_e$ stays in a quasi-steady state for both the high- and low-power period. With nominal changes in impedance matching conditions, two different results are observed in the experiments: one agrees well with predictions and one with a reproducible delay in plasma ignition, reflected in low $T_e$ and $n_e$. The model also predicts that $T_e$ in the skin-depth of the antenna (10-11 cm above the substrate) spikes to values above the steady state on the ramp from low-to-high power; and below the steady state on the ramp from high-to-low power. However, a few cm above the substrate, measurements and model results show little modulation in $T_e$ or in optical emission. The influence of the power, pressure, PRF and bias on the substrate on the bulk plasma properties will be discussed.

References
Instabilities in Power Modulated Chlorine Plasmas

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As need for low variance processes increases in semiconductor device manufacturing, the use of pulsed plasmas has increased as an extra tunable parameter. Power-modulated pulsed plasmas (i.e. rapid switching from high to low power), have been shown to have advantage over traditional pulsed plasmas (rapid switching from high to no power) [1-4]. Studies of ignition in power-modulated chlorine inductively-coupled plasmas are presented. Power at 13.56 MHz applied to the plasma was modulated between a high power and low power state. Photomultiplier tube, power delivery, and Langmuir probe measurements revealed at least two periodic steady-state conditions upon switching from high to low power: a “normal” mode in which electron temperature ($T_e$) remains constant, while electron and ion number densities ($n_e$ and $n_i^+$) and optical emission spectroscopic (OES) intensities smoothly drop to a level roughly equal to the fractional drop in power. The second is an “anomalous” mode, shown in Figure 1, in which $n_e$, $n_i^+$ and optical emission intensities plummet before rising to values more commensurate with the drop in power. Whether the plasma operates in the normal or anomalous mode is sensitive to settings on the matching network and is also a function of pressure and pulsing parameters.

**References**


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**Figure 1** – Power-modulated chlorine plasma at 10mTorr, 400Hz pulse frequency, and 40% duty cycle. Forward and reflected power, photomultiplier tube intensity, and phase angle between forward and reflected power with time are shown. The average power was 200 W, and the “called for” power ratio was 1.67:1.
Benchmarking of Global Model Code for Negative Hydrogen Ion Sources

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Benchmarking and validation of codes is important part of achieving the goal of making codes to become predictive tools [1]. We have developed a Global Model for Negative Hydrogen Ion Sources, GMNIS, and performed benchmarking of the GMNIS with another code, Global Enhanced Vibrational Kinetic Model, GEVKM [2]. The codes ultimate goal is to aid developing optimized negative ion beams for ITER [3]. The both codes solve volume-averaged equations: continuity for plasma species and electron energy equation for the electron temperature, and include more than 1000 volumetric and surface reactions for interactions of electrons, ground-state atomic and molecular hydrogen, molecular ions \( \text{H}_2^+ \) and \( \text{H}_2^+ \), atomic ions \( \text{H}^+ \), negative ions \( \text{H}^- \), 14 vibrationally-excited states of molecular hydrogen \( \text{H}_2 \) (\( v=1\text{-}14 \)), and excited atoms \( \text{H} \) (\( n=2, 3 \)). Dissociative attachment of low-energy electrons to vibrationally-excited hydrogen molecules plays a key role in the formation of \( \text{H}^- \). The vibrationally-excited hydrogen molecules are generated in collisions with fast electrons [3].

Figures 1 and 2 show the vibrational population of molecular hydrogen at two pressures and the negative ion density as a function of pressure calculated by both codes, respectively. Small differences in magnitude of the vibrational population and the \( \text{H}^- \) density appear because the set of reactions considered in two models is not exactly the same. Further validation of codes with experimental data is still required and is underway.

References
Ionization Wave Dynamics of a Plasma Jet in Contact with a Dielectric Surface

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Atmospheric pressure plasma jets (APPJs) are used as a source of reactive oxygen and nitrogen species (RONS) for emerging biomedical applications of plasmas. These APPJs generally consist of a dielectric tube with a rare gas flowing through the tube. These plasmas operate with a pulsed voltage, and during each pulse an ionization wave (IW) propagates through the tube and exits into the ambient air to contact a surface. This IW propagation can be sensitive to the ambient conditions of the jet. In this investigation, ultrafast laser collisional induced fluorescence (LCIF) was used to measure the electron density as the ionization propagates from the end of the jet and impinges upon the surface.[1]

The electron density 30 ns after the IW contacts the surface is shown in Fig. 1 for a jet operating at 200 Torr. The lower pressure was selected to optimize conditions for the diagnostics.

Though normally operated in ambient air, placing this jet in a controlled environment ensures that the surrounding electrical grounds are well defined and the gas composition is controlled. First the behavior of the plasma in a pure helium environment was investigated. The IW exits the tube and propagates toward the surface. Upon contacting the surface, a restrike occurs which increases the electron density. Then the plasma spreads out across the surface as a surface ionization wave, charging the dielectric, as shown in Fig. 1a.

A gas shroud was included in this jet design to enable a surrounding gas flow which has a different composition than that of the main gas flow, while maintaining a controlled environment. When a molecular gas (in this case N\textsubscript{2}) surrounds the primary gas flow, the IW preferentially propagates in the rare gas, where there are fewer electron energy losses to vibrational and rotational excitation.

Adding a molecular gas shroud confines the plasma to regions of higher helium concentration. It also results in faster IW propagation and a higher electron density due to increased Penning ionization and photoionization in the presence of molecular gases. The effects of gas pressure and the flow rate of the rare gas will also be discussed.

References
The Excitation of Bernstein Waves in Magnetized Capacitive Discharge

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We have performed 1D particle-in-cell simulations of capacitively-coupled discharge in applied magnetic field for the 10 mTorr helium gas pressure, the applied 27.12 MHz RF frequency and the 1000 V applied voltage and 10 cm gap. The external magnetic field, B, parallel to the electrodes, was varied from 0G to 50G. We observed excitation of the Bernstein waves \cite{1}, which are electrostatic waves in the magnetized plasma. Many theoretical and experimental studies of the Bernstein waves were performed in fusion plasmas for plasma heating and current drive \cite{2,3}. However, few studies have been conducted for the low temperature plasmas, see Ref. \cite{4} and references within.

Figure 1 shows the spatio-temporal plot of the electron current density for B=15G. Oscillations can be clearly observed. In fact, the oscillations have been observed for B=10÷25G. The signature of the excitation of Bernstein waves is that they are excited at multiple of the cyclotron frequency, $\omega_c$ by nonlinear resonances with the RF frequency, $\omega$ ($n \omega_c = m \omega$), where $n$ and $m$ are integer numbers. This resonance condition between the RF frequency and cyclotron frequency is satisfied for all cases simulated where oscillations were observed. We also verified that the necessary condition of excitation of the Bernstein waves is that the electron collision frequency is lower than the electron cyclotron frequency.

The time-averaged electron energy distribution function (EEDF) at the center of discharge is shown in Fig. 2 for B=5÷30G. It is found that the amount of high-energy electrons is increased when the Bernstein waves are excited, which indicates that the Bernstein waves heat electrons effectively.

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Catalytic Enhancement by a Cold Atmospheric Pressure Plasma Jet: Species Selectivity

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Cold atmospheric pressure plasmas have numerous applications such as materials processes, biomedical applications, and micro-fabrication due to the produced ‘cocktails’ that contain abundant reactive chemical species, ions, broadband radiations, etc. One of the potential applications of increasing interest is the enhancement of catalysis processes via cold plasma. It is believed that this enhancement of thermal catalysis results from a synergy effect [1] owing to the complex interactions of the plasma produced species with the catalyst surface.

In this study, we firstly investigated the conversion rate of methane to syngas on a silica-alumina supported nickel catalyst enhanced by an atmospheric pressure plasma jet (APPJ). This APPJ has been well characterized with regard to the production of reactive species such as atomic oxygen, ozone, nitric oxide, and other parameters [2]. In this work chemical conversion is characterized by FTIR absorption spectroscopy of methane, CO, CO₂, and H₂O. In figure 1, an FTIR absorption spectrum of the various species seen when an unheated nickel catalyst is exposed to the Ar effluent of the APPJ and the CH₄/O₂ is injected subsequently.

We found that CO is only produced when the nickel catalyst and plasma are jointly used. When a nickel catalyst is heated to a temperature as high as 800 °C, no CO produced without the plasma, and only CO₂ and H₂O were produced. This indicates that the APPJ in combination with the nickel catalyst can selectively produce syngas related components. Using Beer’s law, measured absorbance and the absorption cross section of CO at room temperature, the produced CO density is of the order 10¹⁵ cm⁻³. Moreover, it is found that CO production is proportional to the plasma power and catalyst temperature. The CO production decreases when the plasma jet moves far away from the nickel catalyst.

The distance dependence of CO production suggests that short-lived species, such as atomic oxygen, metastable argon, etc., may play a role in the methane conversion to syngas. We correlate the production of various species from the plasma conversion and compare it with surface effects that occur to further understand the selective production of gas species from methane conversion.

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References
Self-neutralized Nearly Monoenergetic Positive Ion Beam Extracted From a Pulsed Plasma

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Neutralization of the space charge of an ion beam extracted from a plasma is crucial for advanced plasma processes which require precise control of the ion flux and the width of the ion energy distribution (IED). In previous studies, filaments thermionically emitting electrons were used for neutralizing the space charge, which would otherwise cause the ion beam to diverge owing to Coulomb explosion.[1,2] However, the performance of the neutralizing filaments is restricted by their limited lifetime and required extra power supplies. This work reports that a self-neutralized positive ion beam can be extracted from a pulsed plasma. In particular, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias in the afterglow (plasma-off) of the plasma.

To better understand the mechanism of self-neutralization of the ion beam, space-time resolved measurements were carried out using a movable Faraday cup to investigate the ion and electron currents along the beam axis. IED measurements were also performed using a Retarding Field Energy Analyzer (RFEA) to characterize the behavior of the beam under different plasma operating parameters (plasma source pressure and power delivered to the plasma).

Space-time resolved measurements, of the kind shown in Figure 1, revealed that there could be two different periods during which electrons leave the source, serving as ion beam neutralizing agents: one is during the activeglow (plasma-on) fraction of the cycle, and the other is during the early stages of the afterglow (plasma off). Moreover IED measurements indicated that the ion flux and the energy spread of the self-neutralized ion beam can be optimized by tuning the pressure and power used for operating the plasma.

References
Spatiotemporal Measurement of Reactive Oxygen Species (ROS) Production at the Plasma-liquid Interface Using Chemiluminescence

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Understanding plasma-liquid interactions is crucial to environmental and medical applications of low temperature atmospheric plasma such as water purification and wound healing. In plasma-based water purification, plasma-in-contact-with-water drives advanced oxidation processes in the plasma-liquid interface, delivering reactive oxygen nitrogen species (RONS) into the bulk liquid and decomposing various organic contaminants. Previously, chemical probe potassium iodide/starch was used to visualize reactive oxygen species production and chemical front propagation in bulk liquid. [1] However, the contributions of various reactive oxygen species are not quantified. Employing scavengers and probes that exhibit chemiluminescence, the production of species such as hydroxyl radical and superoxide is measured, to better understand the complex chemistry happening at the interface.

In this work, the chemical luminol was used to image the interface region. Luminol undergoes chemiluminescence when oxidized primarily by superoxide and hydrogen peroxide, secondary reaction pathways include interaction with other oxidative species such as peroxyxnitrite. As the chemiluminescence is transient, it represents the production of reactive oxygen species spatiotemporally. This allows for direct visualization of the active interface region. Additionally, combining this with various scavengers, such as superoxide dismutase (SOD) for superoxide, dimethyl sulfoxide (DMSO) for hydrogen peroxide, and uric acid for peroxynitrite, the production rate of various reactive oxygen species can be measured. Emission spectroscopy will be used to verify luminol’s chemiluminescence reaction pathways. Resolving reactive oxygen species’ production and transport in bulk liquid sheds light on how chemistry at the interface impart reactivity in bulk liquid.

References
Role of H\(^+\) Atoms in the Reduction of Silver Ions at the Plasma-Liquid Interface by an RF Driven Atmospheric Pressure Plasma Jet

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Atmospheric pressure plasmas offer a green alternative for the synthesis of nanomaterials [1]. Plasma-liquid interaction results in numerous applications such as the synthesis of silver nanoparticles through the reduction of a metal precursor in the liquid phase. Plasma can efficiently dissociate water generating H\(^+\) and OH radicals at the plasma-liquid interface [2]. While the importance of OH oxidation and electron-induced reduction reactions have been studied in considerable detail [2-3], the potential importance of H radicals has generally not been considered. In this work, we investigate the role of H in the reduction of silver ions leading to the formation of silver nanoparticles [4].

A well-characterized radio-frequency driven atmospheric pressure plasma jet is used to study the role of H\(^+\) in the reduction of silver ions in solution. The absolute gas phase H\(^+\) density was obtained in the free jet by two photon absorption laser induced fluorescence. The jet operates in a humid air environment. These measurements showed that the density of H radicals generated by Ar + 0.64% H\(_2\) plasma is more than an order of magnitude higher than Ar plasma for the same plasma power (Fig. 1). The synthesis of silver nanoparticles was determined using broadband absorption and transmission electron microscopy. The absorption of silver nanoparticles generated by Ar plasma is higher compared to Ar + 0.64% H\(_2\) plasma when the plasma touches the liquid. This is attributed to the larger flux of reactive species generated by the Ar plasma due to the stronger coupling with the liquid compared to the Ar + 0.64% H\(_2\) plasma. It was found that VUV photons generated by the plasma can also reduce the silver ions in the solution. While Ar plasma generated in all cases silver nanoparticles with a broad size distribution, Ar + 0.64% H\(_2\) plasma generates a large amount of silver nanoparticles with a size of 2-3 nm. The important role of H radicals in the reduction of silver nanoparticles was consistent with several other experimental findings including the strong impact of 2-propanol, a selective scavenger of H\(^+\) atoms but not of solvated electrons, on the absorbance and particle size distribution. Furthermore, the generation of silver nanoparticles was observed even at a distance of 6-7 mm from the visible tip of the plasma jet. The presence of O\(_2\) in the jet effluent enhances the conversion of electrons into negative ions and does not favor the injection of electrons as a viable mechanism for Ag\(^+\) reduction in this case.

References

Temporal and spatial distributions of electric field vector components in Dielectric Barrier Discharge (DBD) plasma actuators powered by AC sine wave voltage waveforms are measured by picosecond Second Harmonic Generation (SHG) laser diagnostics. Absolute calibration is provided by measuring a known electrostatic electric field between two parallel plate electrodes. Horizontal and vertical components of the electric field vector are determined by measuring the second harmonic signals with different polarizations. The electric field is averaged over the actuator span (25 mm), with spatial resolution across the laser beam of approximately 100 µm and temporal resolution of 2 µs. The results indicate that the detectable electric field extends over a significant distance along the dielectric surface (up to at least 9 mm), and to a significant height above the actuator (up to at least 4 mm). The horizontal electric field produced during the negative voltage half-period exceeds considerably the field measured during the positive half-period, up to a factor of 2 to 3, and is directed toward the high-voltage electrode, over an extensive spatial domain above the actuator. This indicates clearly the dominant effect of negative ions generated in the plasma on the ion wind, resulting in flow entrainment away from the high-voltage electrode.

Since the present diagnostics is species-independent, it can also be used for measurements of electric field distributions in plasmas sustained in gas mixtures other than air, such as Ar and He, with high spatio-temporal resolution. Figure 2 shows preliminary results of electric field measurements in an AC atmospheric pressure helium plasma jet exhausting into ambient air and impinging on liquid water, 100 µm from the surface. These measurements provide essential insight into the mechanism of plasma-flow and plasma-liquid interaction, and produce extensive sets of data for detailed validation of high-fidelity kinetic models.
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