PLASMA DISSOCIATION AND IONIZATION SOURCES ON LIQUID SURFACES

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Motivation

- 'Forever chemicals' (PFAS) are man-made toxic materials that reside on the surface of water.
- PFAS can be effectively degraded by plasma-liquid interaction.[1]
- Understanding interface chemistry is important for optimization of the plasma system.
- In this work, ***nonPDPSIM*** (2D - plasma hydrodynamics model including chemistry) was used to investigate the water interface chemistry.

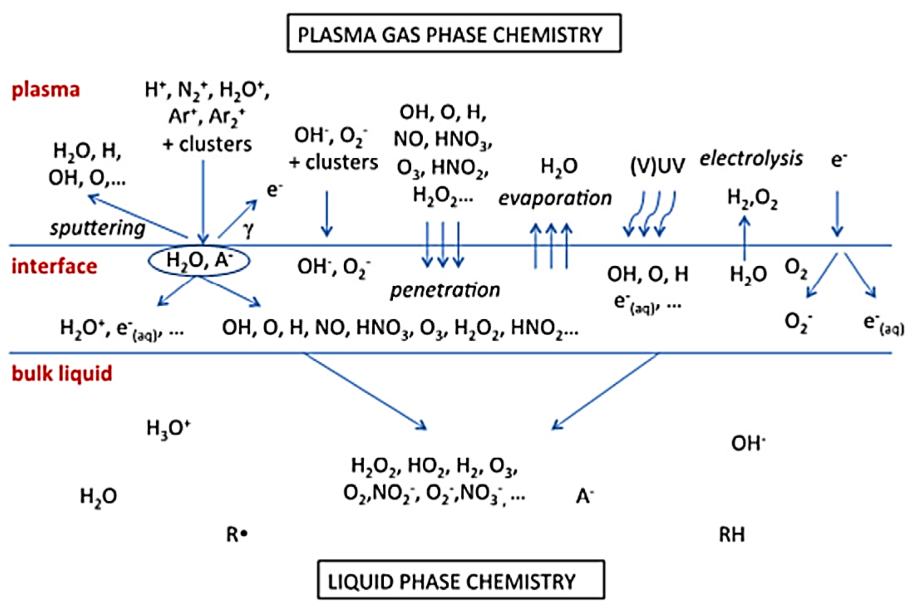


Fig 1. *Plasma-liquid interactions [2]*

Methodology

nonPDPSIM

- **Finite Volume Method (FVM)** enables the use of unstructured meshes.
- **Mass, Momentum, and Energy conservation** for all species
- **Poisson's equation** for charged species
- **Boltzmann equation** for electrons is solved to determine non-Maxwellian energy distribution and update electron-impact rate coefficient.
- **Time-slicing method**, the equations can be integrated with different time step Δt.

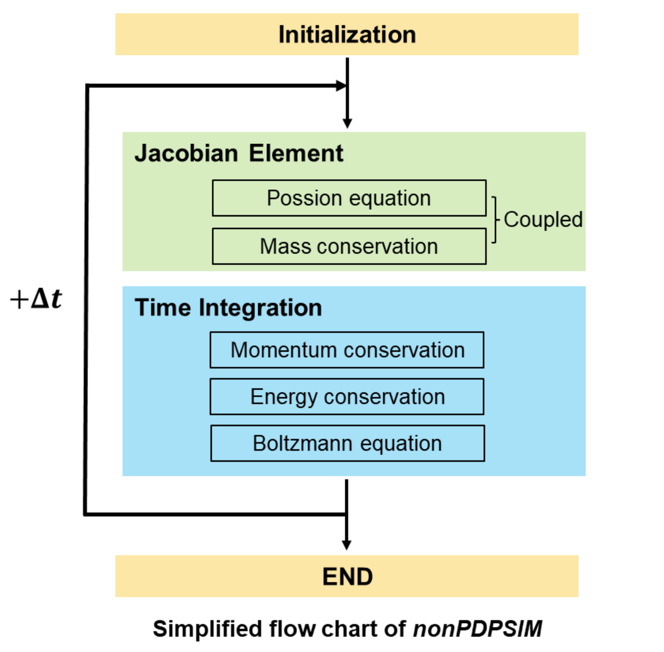
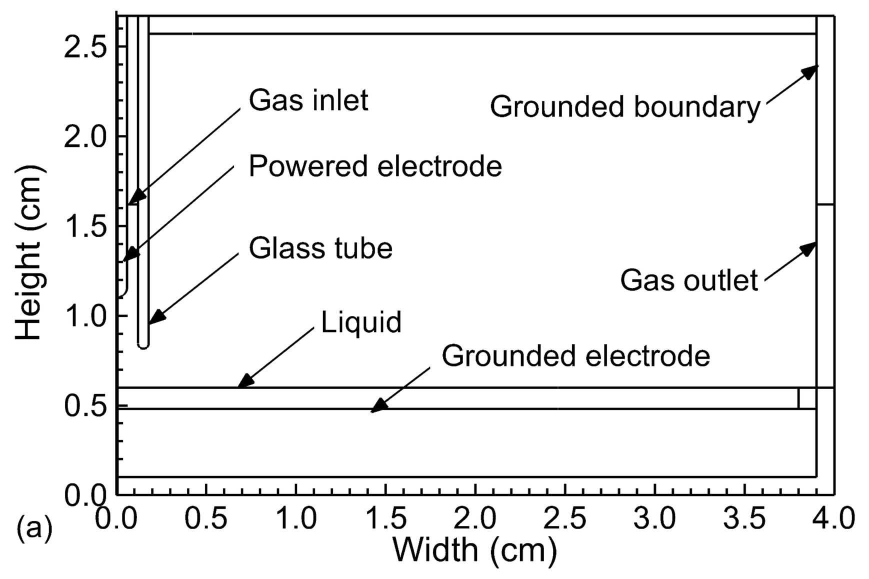


Fig 3. *Simplified flow chart of* ***nonPDPSIM***

Description

- 1000 sccm
- Ar/H_2O = 98/2 (1 atm)
- -15kV pulse for 70ns, 0.5 cm gap
- Cartesian symmetry
- Surfactant layer: 50 μM C_3F_8
- Parametric study for voltage, conductivity, water temperature



Plasma Properties

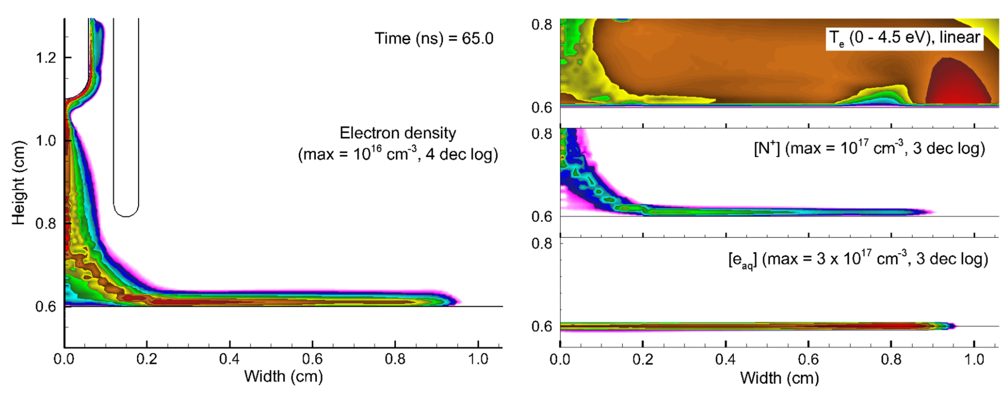


Fig 4. *Plasma properties for base case*

- Bulk ionization wave strikes water surface and launches a surface-ionization-wave (SIW), charging the surface negatively and partially flowing current ($\vec{j} = q\vec{\Phi}_{flux}$), through the water due to conductivity.
- SIW sustained by T_e = 4.0 – 4.5 eV in electric field enhanced head.
- As the ionization head move along the surface, the electrons are solvated into the water and positive ions are left behind, creating a sheath near the liquid.

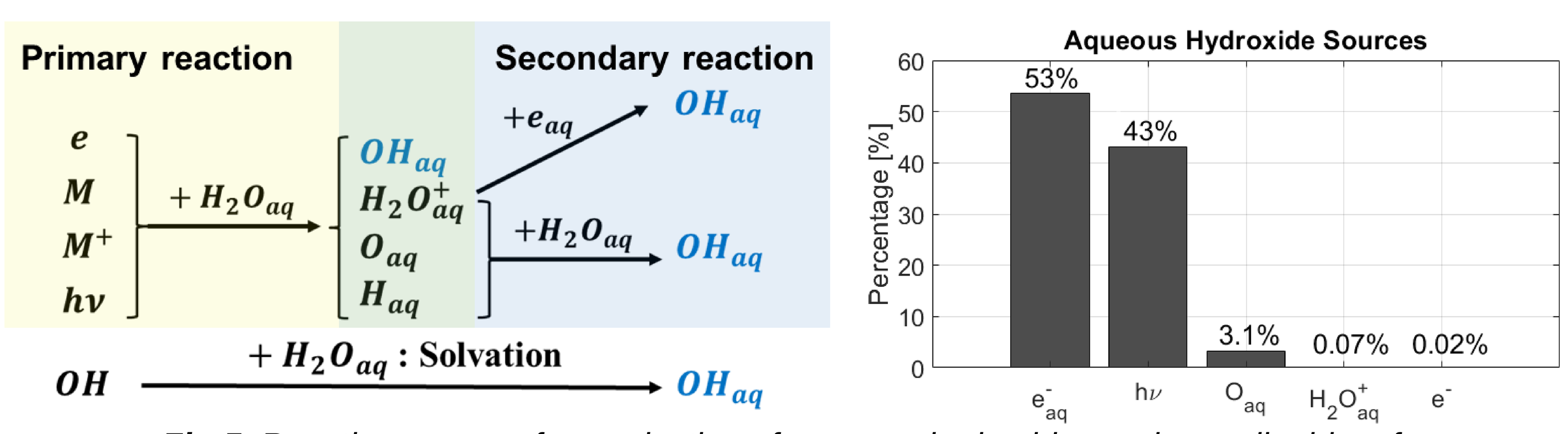
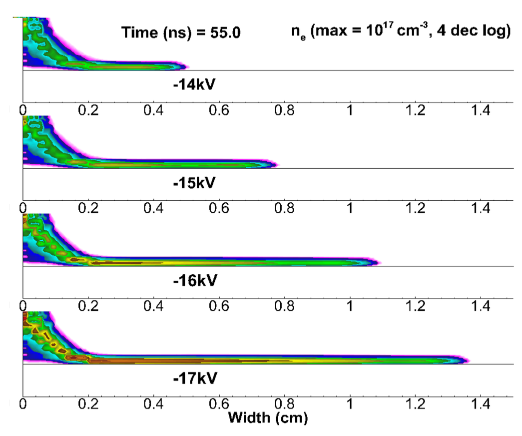


Fig 5. *Reaction sources for production of aqueous hydroxide on plasma-liquid surface*

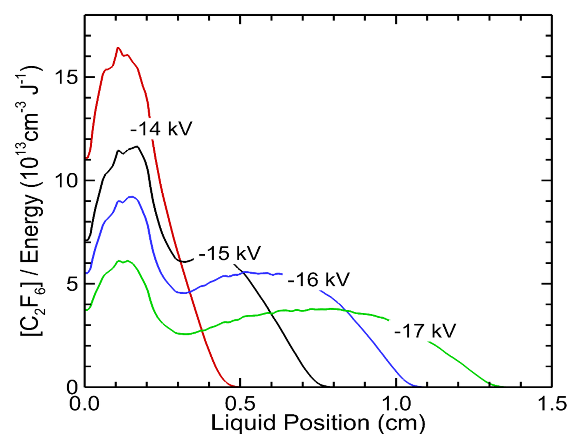
- In the primary reaction, photolysis accounted for 43%, of production, much greater than direct electron impact.
- In the secondary reaction, the dissociative recombination of solvated electron with water ion led to 53% of total OH_{aq} production.
- Solvation, heavy particle impact and other secondary reactions were small in comparison.

Parametric Study

Voltage



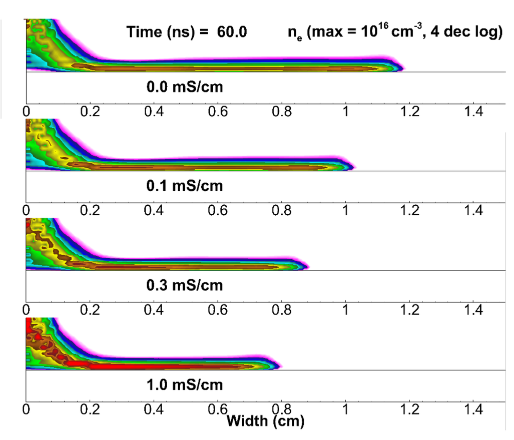
- Propagation of surface ionization wave (SIW) is determined by rate of charging of underlying capacitance of water.
- At low voltage, less current flows through the conductive plasma channel, resulting in slower charging of the capacitance.
- For -15 kV, SIW propagates at 3 x 10^7 – 5 x 10^7 cm/s.



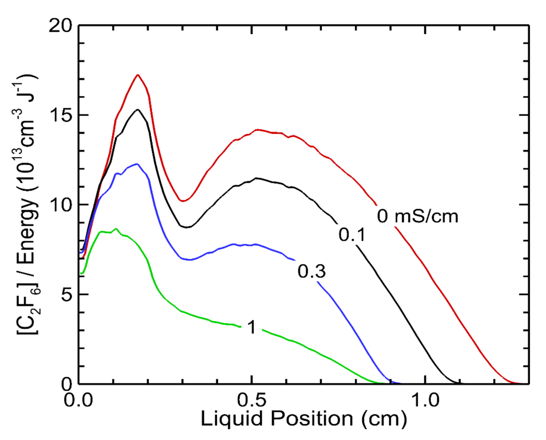
- With higher voltage, higher rate of surfactant dissociation
- However, dissociation efficiency optimizes at lower voltage due to power deposition in bulk plasma.
- The efficiency was the highest at -16kV in this configuration.

Min Max

Conductivity

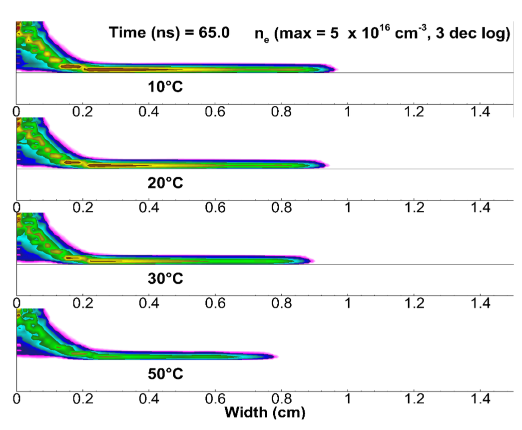


- SIW propagates by charging the capacitance and partially flowing conductive current through the water.
- With higher water conductivity, more charge flows through the water rather than accumulating on the surface.
- Consequently, rate of charging the capacitance decreases and the propagation slows down.

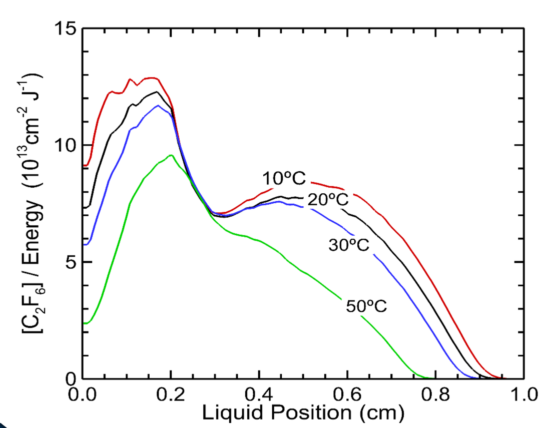


- As more conduction current flows, higher electron flux is required to charge the capacitance of water.
- The higher electron flux did not lead to an increase in degradation, because photolysis is the primary source of dissociation.
- The higher current with lower dissociation resulted in a decreased degradation efficiency.

Water temperature



- Vapor pressure exponentially increases with water temperature, and vapor density ($\propto P/T$) correspondingly increases.
- Higher water vapor density produces a more resistive discharge.
- At 50°C, propagation of surface ionization wave (SIW) is significantly slowed down.



- With high temperature, photons tend to be absorbed by water vapor, rather than C_3F_{8aq}, leading to a net decrease of degradation rate.
- The increase of heavy particle impact due to high temperature near the water surface was negligible.
- Increased efficiency at 10°C might not be meaningful, as additional energy is needed to cool the water.

Conclusion

- Reaction mechanism at the water surface contaminated by surfactant molecules C_3F_8 was investigated.
- The propagation of the surface ionization wave is determined by the rate at which the water capacitance charges while conductive current partially flows through the water.
- On the gas-liquid interface, water (H2Oaq) was dissociated into aqueous hydroxide (OH_{aq}) primarily by **photolysis** (43%) and **recombination** (53%) between solvated electron and water ion.
- Higher voltages led to greater dissociation of surfactant molecules and faster SIW propagation (at the cost of lower energy efficiency).
- Lower conductivity and temperature resulted in greater dissociation of surfactant molecules (with improved energy efficiency).
- For future work, a set of PFAS reactions can be incorporated to investigate the degradation sources of long-chain surfactants.

References

[1] Stratton G, Dai F, Bellona C et al. Plasma-Based Water Treatment: Efficient Transformation of Perfluoroalkyl Substances in Prepared Solutions and Contaminated Groundwater (2017)

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