

NANOSECOND PULSE SURFACE IONIZATION WAVE DISCHARGES OVER SOLID AND LIQUID DIELECTRIC SURFACES

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ABSTRACT

Surface ionization wave discharges generated by high-voltage nanosecond pulses, propagating over a plane quartz surface and over liquid surfaces (distilled water and 1-butanol) have been studied at pressures of P=5-30 Torr. At all operating conditions, surface plasma “sheet” is diffuse and fairly uniform, both for positive and negative pulse polarities. No perturbation of the liquid surface by the discharge is detected. Both wave speed and travel distance decrease with pressure. Products of plasma chemical reaction accumulated in the ionization wave discharge over liquid butanol / saturated butanol vapor interface are detected *ex situ*, using FTIR absorption spectroscopy. Reaction products identified include CO, alkanes, alkynes, aldehydes, and lighter alcohols.

1. INTRODUCTION

Kinetics of nonequilibrium electric discharges in liquids and at liquid-vapor interfaces is of great interest from the fundamental point of view [1], for reactive nitrogen / oxygen species generation [2], and for plasma chemical reforming of liquid hydrocarbons and oxygenates for portable fuel cells [3]. Kinetics of plasma chemical reactions at these conditions remains poorly understood.

In the present work, a novel way of sustaining diffuse, highly reproducible plasmas at liquid-vapor interfaces is demonstrated, using surface ionization waves generated by high-voltage, nanosecond pulse duration discharges. The basic concept of this approach is qualitatively similar to volumetric and surface Fast Ionization Wave (FIW) ns pulse discharges, which are known to generate diffuse plasmas

over large volumes or large surface areas [4,5]. Short time scales involved in surface ionization wave discharges launched over a surface of a dielectric, or weakly conductive, liquid (~10-100 ns) preclude bulk motion of the liquid that may be caused by charge accumulation on the liquid surface. At these conditions, high energy electrons generated in the thin near-surface plasma layer initiate electron impact dissociation and ionization of evaporating reactants, with potentially high yield of radical species, such as O, H, and OH in surface plasmas sustained over liquid water and aqueous solutions, and CH in surface plasmas over liquid hydrocarbons and oxygenates. Chemical reactions in repetitively pulsed plasma at a liquid-vapor interface would occur at nearly constant temperature conditions, due to high specific heat of the liquid and high latent heat of vaporization (~0.4 eV/molecule for water and alcohols). This suggests that surface ionization wave discharge plasma sustained at a liquid-vapor interface can be used as an experimental platform for quantitative studies of near-surface plasmachemical reaction kinetics.

The objective of the present work is to determine the range of conditions where nanosecond pulse, diffuse surface ionization wave discharges propagate along liquid-vapor interfaces, and to demonstrate significant potential of this approach for studies of near-surface plasma chemical reactions, in particular electron impact processes generating radical species from evaporating reactants, and their conversion into stable product species.

2. EXPERIMENTAL

The schematic of the discharge cell used for studies of surface ionization wave discharges is shown in Fig. 1. The discharge is sustained in a rectangular cross section quartz channel 25 mm x

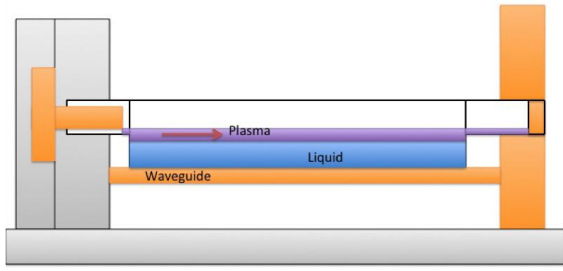


Fig. 1. Schematic of the discharge cell

40 mm, 220 mm long, with a trough in the bottom which can be filled with liquid approximately 5 mm deep. In the present experiments, the liquids used were distilled water and 1-butanol. A nitrogen buffer gas is flowing through the test cell, although some of the measurements were done in an isolated cell, without the flow.

The high voltage electrode on the left and the grounded electrode on the right are made of copper. An adhesive copper foil electrode is attached to the bottom wall of the channel and connected to the grounded electrode, to operate as a waveguide for the surface ionization wave discharge. The electrodes are powered by a high-voltage nanosecond pulse generator which produced alternating (positive/negative) or single polarity pulses with peak voltage of ~10-20 kV and pulse duration of ~50-100 ns [6]. The pulse generator was operated at pulse repetition rates of 100 Hz - 500 Hz. Pulse voltage and current are measured by Tektronix P6012A high voltage probe and by Pearson 2877 current probe. A capacitive probe [6], placed above the quartz channel and moved along the test section, was used to detect the ionization wave arrival and measure the wave speed. Plasma emission images are taken by Andor iStar ICCD camera with a UV lens, using a 13 ns gate. To obtain "side view" and "top view" emission images, the capacitive probe was removed and replaced with a mirror placed at 45° degrees angle, such that both images were taken at the same time.

To detect plasma chemical reaction products generated in a surface ionization wave discharge over a liquid / vapor interface, it was operated in an isolated cell without the buffer gas flow, i.e. in a saturated vapor above the liquid surface. After operating the discharge for 5-10 minutes, the mixture of reactants and products was sampled into a cell placed into an absorption port of a Varian 6600-IR FTIR spectrometer, and absorption spectra were taken with spectral resolution of 0.25 cm⁻¹, over a spectral range of 700-6000 cm⁻¹.

3. RESULTS AND DISCUSSION

Figure 2 shows positive polarity pulse voltage, current, and coupled energy waveforms for surface ionization wave discharge propagating over distilled water surface in the cell filled with nitrogen at P=20 Torr and a flow rate of 0.2 SLM, at pulse repetition rate of 500 Hz. At these conditions, peak voltage and current are approximately 11 kV and 13 A, voltage pulse FWHM is about 100 ns, and coupled energy is about 5 mJ/pulse. Figure 3 shows the wave *x-t* trajectory. Wave arrival time at a given axial location is defined as a moment when the capacitive probe signal peaks. From Fig. 3, it can be seen that the wave speed, defined as the trajectory slope, decreases from 0.2 cm/ns in the region closer to the high voltage electrode to approximately 0.05 cm/ns, as the applied voltage decreases and as the wave moves closer to the grounded electrode. Comparing the pulse voltage waveform and the capacitive probe data, it was determined that ionization wave starts when the pulse voltage is rising and continues to propagate

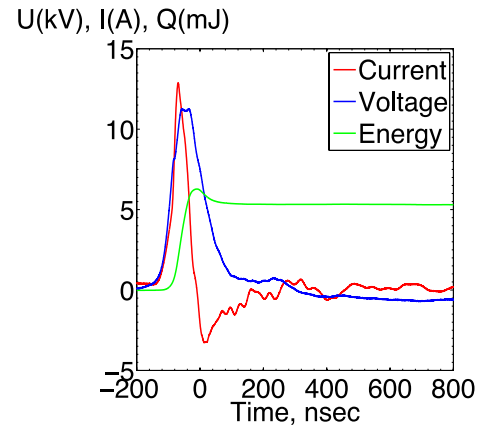


Fig. 2. Pulse voltage, current, and energy waveforms in surface ionization wave discharge over distilled water in N₂ buffer.

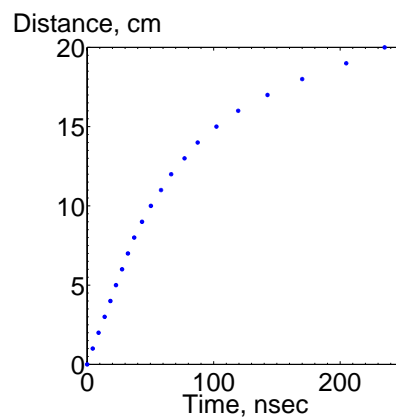


Fig. 3. Trajectory of positive polarity surface ionization wave over a distilled water surface at the conditions of Fig. 2.

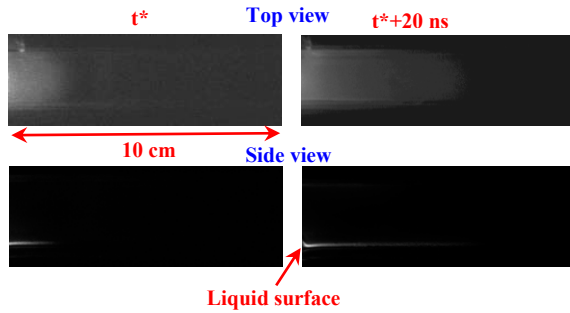


Fig. 4. ICCD images of positive polarity surface ionization wave discharge over a distilled water surface, taken 20 ns apart

when the voltage decays, at a gradually decreasing speed. ICCD images of the positive polarity surface ionization wave discharge (side view and top view) at the conditions of Figs. 2, 3 are shown in Fig. 4, for two moments of time separated by 20 ns. It can be seen that the wave propagates along the liquid surface near the bottom of the test section, the wave front appears nearly straight, and the plasma emission behind the wave front is diffuse and nearly uniform. The experimental results demonstrated close similarity between surface ionization waves propagating over distilled water surface and over a quartz wall (i.e. without water in the test section). Specifically, pulse peak voltage, current, coupled energy, as well as wave $x-t$ trajectories (wave speeds) over the quartz wall and over distilled water are very close to each other, although plasma emission intensity distributions over the water surface are somewhat less uniform compared to the surface discharge over the quartz wall. The results obtained using negative polarity pulses are similar to the ones for the positive polarity, although coupled pulse energy, peak wave speed, and the distance over which the wave propagates for the negative polarity pulses are lower.

No significant difference was detected between ionization waves generated when operating the pulser using alternating polarity or only single-polarity pulses. This suggests that surface charge is removed from the liquid surface between the discharge pulses, either due to relatively high conductivity of the surface plasma layer or due to finite conductivity of the liquid, $\sim 10^{-4}$ - 10^{-3} S/m for distilled water.

The discharge parameters over liquid butanol surface are fairly close to the ones measured to those measured over distilled water. In this case, somewhat weaker ionization wave also propagates over the top surface of the test cell (see Fig. 5), likely due to a lower dielectric constant of 1-butanol compared to that of water,

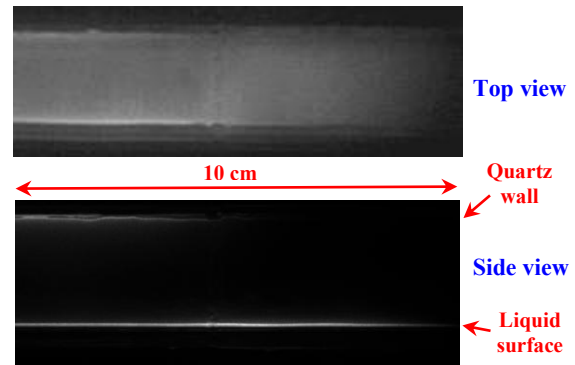


Fig. 5. ICCD images of positive polarity surface ionization wave discharge over 1-butanol surface. $P=20$ Torr.

$\epsilon=17.8$ vs. $\epsilon=78.5$. The ionization wave speed over butanol surface is higher compared to that measured over the quartz wall and over distilled water surface, both for positive polarity and negative pulse polarities. The wave over butanol surface was observed to propagate over a longer distance from the high-voltage electrode, all the way to the grounded electrode, producing readily detectable visible emission near the grounded electrode which was not detected in surface discharges over quartz wall or distilled water surface. This suggests that a direct current path was established between the high-voltage electrode and the grounded electrode during the discharge pulse. For all three sets of conditions (discharge over quartz wall, distilled water surface, and butanol surface), ionization wave speed and the distance over which the wave propagated were observed to decrease when buffer gas pressure was increased from $P=20$ Torr to 40 Torr.

Shutting off the nitrogen buffer gas flow resulted in test cell pressure reaching near saturated vapor pressure ($P_{\text{sat}}=4.8$ Torr for 1-butanol and $P_{\text{sat}}=17.5$ Torr for water at $T=20^{\circ}\text{C}$). At these conditions, surface ionization discharge was still observed to propagate over the liquid / vapor interface, both in butanol and water, in spite of strong electron affinity of water vapor. In butanol, shutting off the buffer flow and operating in saturated vapor resulted in a significant increase of peak pulse current and coupled pulse energy, both for positive and negative polarity discharge pulses, from 4 to 8 mJ/pulse for positive polarity. Ionization wave speed also increased, reaching peak values of 0.4 cm/ns and 0.5 cm/ns for positive and negative polarity waves, respectively, and remained nearly constant along the discharge channel, ≈ 0.27 cm/ns, for both polarities.

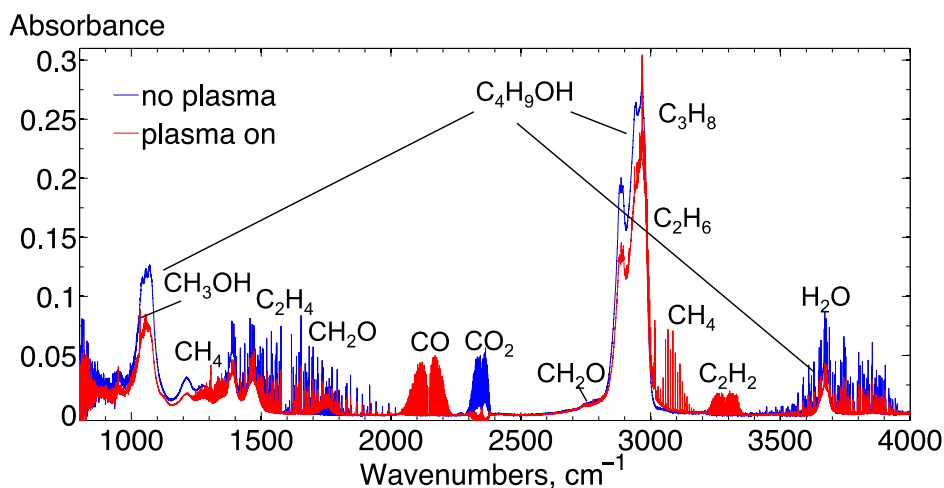


Fig. 6. FTIR absorption spectra of samples taken with and without surface ionization wave discharge operated at the liquid butanol / saturated butanol vapor interface at $P=5$ Torr and pulse repetition rate of 500 Hz, without buffer gas flow.

FTIR absorption spectra of plasma chemical reaction products accumulated in the discharge were taken by sampling the products from the cell filled with liquid butanol / saturated butanol vapor at a pressure of $P=5$ Torr, with and without ionization wave discharge operated at the liquid / vapor interface at pulse repetition rate of 500 Hz, over 10 minutes. The results are shown in Fig. 6. It can be seen that both absorption spectra, taken with and without the discharge, exhibits presence of butanol vapor (C_4H_9OH) and water vapor, which is likely present in liquid butanol. However, the spectrum taken after operating the discharge also shows presence of plasmachemical reaction products, including carbon monoxide (CO), methane (CH_4), acetylene (C_2H_2), ethane (C_2H_6), propane (C_3H_8), formaldehyde (CH_2O), and methanol (CH_3OH). Absolute number densities of reaction products and their specific energy cost can be calculated from these spectra using calibration case mixtures as well as synthetic spectra, as has been done in our previous work [7]. Preliminary estimate of CO partial pressure in the absorption cell, based on FTIR calibration spectra taken using known amounts of CO, is $P_{CO}=1.3$ Torr, i.e. CO mole fraction in the mixture at these conditions is approximately 26%.

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