Gas-Liquid Chemical Reactions with Nanosecond Pulses: Role of Pulse Delivery in Bursts on Hydrogen Peroxide Production

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Abstract: Delivering nanosecond pulses in a gas-liquid plasma reactor using sets of bursts of pulses can affect the formation rate and energy yield of hydrogen peroxide. Increasing the number of pulses within a burst can lead to higher production rates while maintaining relatively high energy yields. Increasing the burst period lowers both production rate and energy yield. Adjusting the internal frequency (frequency of pulses in a burst) can also lead to optimal energy efficiencies and production rates although the optimal values of frequency for energy yield is shifted to higher frequency from that of the production rate.

Keywords: nonthermal plasma, gas-liquid, nanosecond pulse, pulse delivery in bursts

1. Introduction

Electrical discharge plasma formed in contact with liquid water is of interest for applications in chemical, biomedical, agricultural, electrical, and materials engineering [1-3]. To focus on an element of a filamentary plasma channel propagating along a gas-liquid water interface, we developed a small, tubular reactor [4, 5] that allows for control of the gas and liquid flows, measurement of the interfacial area and gas and liquid volumes, and determination of transport and plasma properties (**Figure 1**). The chemical reactions analyzed in this reactor include hydrogen peroxide formation [6, 7], hydrocarbons [8] and organic dyes [9] oxidation, degradation of organic contaminants combined with bioreactors [10], nitrogen oxide formation [11, 12], hydroxyl radical generation [13], degradation of fluorinated compounds [14,15], and formation of hydrogen [16]. Time averaged optical emission spectroscopy provided average electron density and plasma gas temperature [6, 7]. Time resolved electron density during a single pulse by optical emissions spectroscopy demonstrated the roles of pulse frequency and pulse width on the plasma electrons, which were correlated to the formation of hydrogen peroxide and degradation of fluorinated surfactants [15].

In previous work we have shown that augmentation of single pulse "shape" (rise-time, pulse width, input voltage) and frequency can influence the energy yield/efficiency of various chemical reactions occurring in the reactor by manipulation of the plasma properties (plasma gas temperature, electron density, electron energy)[1-5]. However, optimization of a chemical reactive system with these parameters alone is limited due to the significantly different time scales of the plasma interactions as compared to the time scales of the reactive chemistry and mass transfer between the gas a liquid phase.

The formation of useful chemical species such as H_2 and H_2O_2 by plasma chemical reactions depends upon the tradeoff between reactions that form these species and reactions that degrade these species. Ideally, one seeks to promote the formation reactions while suppressing the degradation reactions. This is complicated by the extensive set of highly reactive species generated in the plasma. In the case of plasma contacting liquid water, the plasma, which contains energetic free electrons, causes water to be dissociated into two key species, namely the atomic hydrogen radical, H·, and the hydroxyl radical, ·OH. The hydrogen radical can recombine to make H_2, and the hydroxyl radicals can recombine to make H_2O_2. These are examples of the forward product-generating reactions. However, both H_2 and H_2O_2 can be degraded by reactive plasma species (including the ·OH). Therefore, it is of interest to find ways to promote the formation reactions while minimizing the degradation reactions. One way to reduce degradation reactions is to have very fast plasma pulses so that the forward reaction is favored and the time for reverse reactions suppressed. Another way is to have a second phase, here water, that can take up the product, for example H_2O_2, into the liquid where the degradation reactions are slower. In addition, the residence times of the gas and liquid, i.e., the average contact time in the reactor, along with the times for the plasma pulse, diffusion times, and reaction times, affect the relative rates of formation and degradation and the time scales among these different processes span many orders of magnitude.

The general goal of this work is optimization of the plasma generation towards more efficient removal of contaminants (e.g., organic compounds such as PFAS) and generation of reactive species (e.g., ·OH, ·H, e_{aq}^-) and stable products (e.g., H_2, H_2O_2, NO_3^-). In the current work, the mode of the pulse delivery is investigated with specific consideration on the delivery of bursts of nanosecond pulses separated by various inter-pulse time periods. **Figure 2** shows a schematic of the delivery of pulses within the framework of a burst. A set of pulses is delivered with an "inner burst" frequency followed by a relaxation time before additional similar sets are delivered within the context of an overall "outer burst frequency".

2. Methods

The present work focuses on the measurements of hydrogen peroxide (H_2O2) and the effects of the burst mode on the generation and energy yield. Experimental setup, methods for H_2O_2 measurement, power supply, and

pulse power determination are reported in previous work [15]. For this presentation we will also include mathematical models to describe the chemical reactions occurring in the gas-liquid (argon-water) system based upon previous work [6].

3. Results

Preliminary work is shown in figures 3 to 5. **Figure 3** shows H_2O_2 production rate (mol/s) with the number of N-cycles (pulses in a burst) and constant burst period and internal frequency. Production rate increases linearly with the number of cycles while the energy yield is relative unaffected. This result shows that increasing the number of pulses in a burst can lead to higher H_2O_2 production while not dropping efficiency. In contrast, for fixed internal frequency and N-cycles, the production rate and energy yield decrease with increasing burst period as shown in **Figure 4** suggesting that more time between pulses in the burst does not enhance performance. Variation of the internal frequency with fixed burst period and 5 N-cycles (**Figure 5**) leads to maximal values of production rate (at 200 kHz) and energy yield (at 300 kHz) at different frequencies suggesting that control of the production rate and energy yield can be made through changing these process parameters.

4. Conclusions

The formation of H_2O_2 by nanosecond pulsed discharges in gas-liquid plasma reactors can be controlled through modification of the means of delivering the pulses. Specifically, delivery of pulses in bursts, or sets, of pulses offers a means to have high production rates at relatively high energy yield. Increasing the burst period lowers both production rate and energy yield. Internal frequency can also lead to optimal energy efficiencies and production rates which are slightly shifted in optimal values.

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6. References

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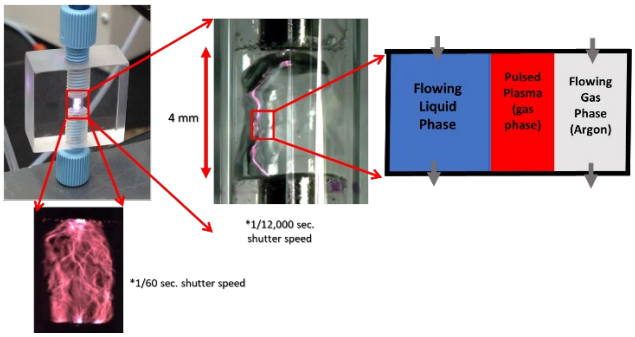

Fig. 1. Gas-liquid plasma reactor. High speed camera images showing plasma channels covering gas-liquid interface.

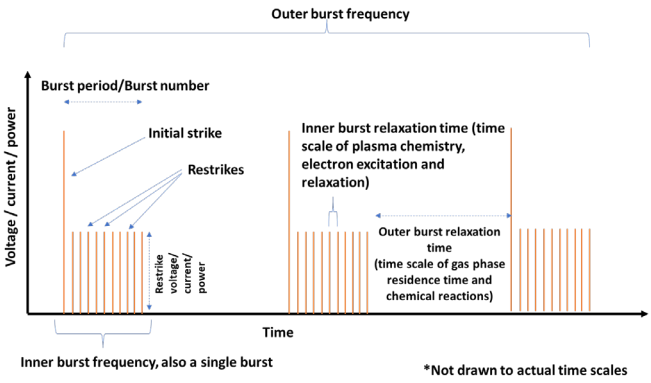

Figure 2. Summary of burst mode operation.

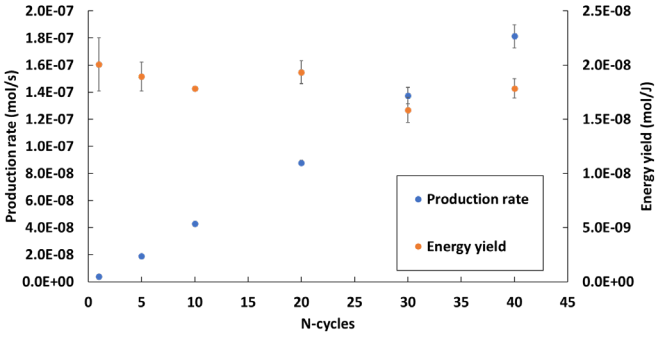

Figure 3. H_2O_2 production rate and energy yields with the number of N-cycles (pulses in a burst) at fixed 1 ms burst period and 100 kHz inner burst frequency.

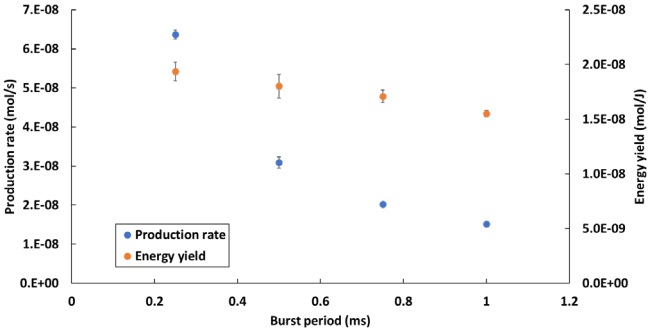

Figure 4. H_2O_2 production rate and energy yield with burst period at fixed 5 N-cycles (pulses in a burst) and 100 kHz internal frequency.

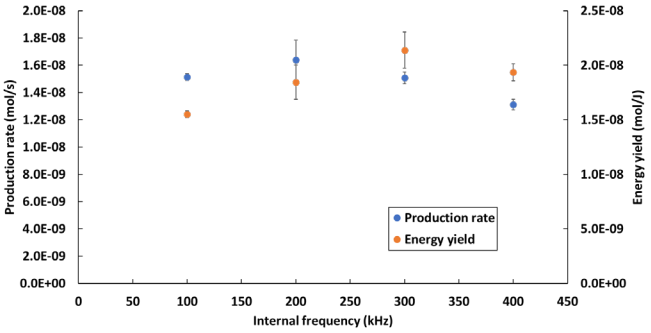

Figure 5. H_2O_2 production rate and energy yield with variation of inner frequency and constant 1 ms burst period and 5 N-cycles (pulses in a burst).