Use of Sonoluminescence and Sono-Electrochemistry Based Techniques for Fundamental Investigations of Acoustic Cavitation for Megasonic Cleaning Applications

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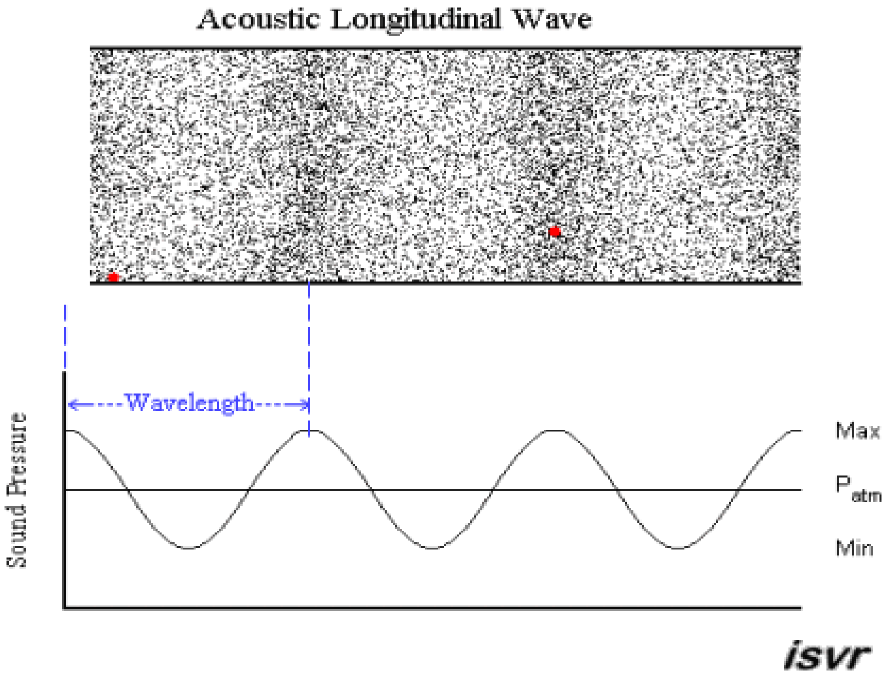
Background on Megasonic Cleaning

Megasonic Cleaning Process

- **Sound waves with frequency of ~ 1 MHz or greater used in combination with different cleaning chemistries for particle removal**

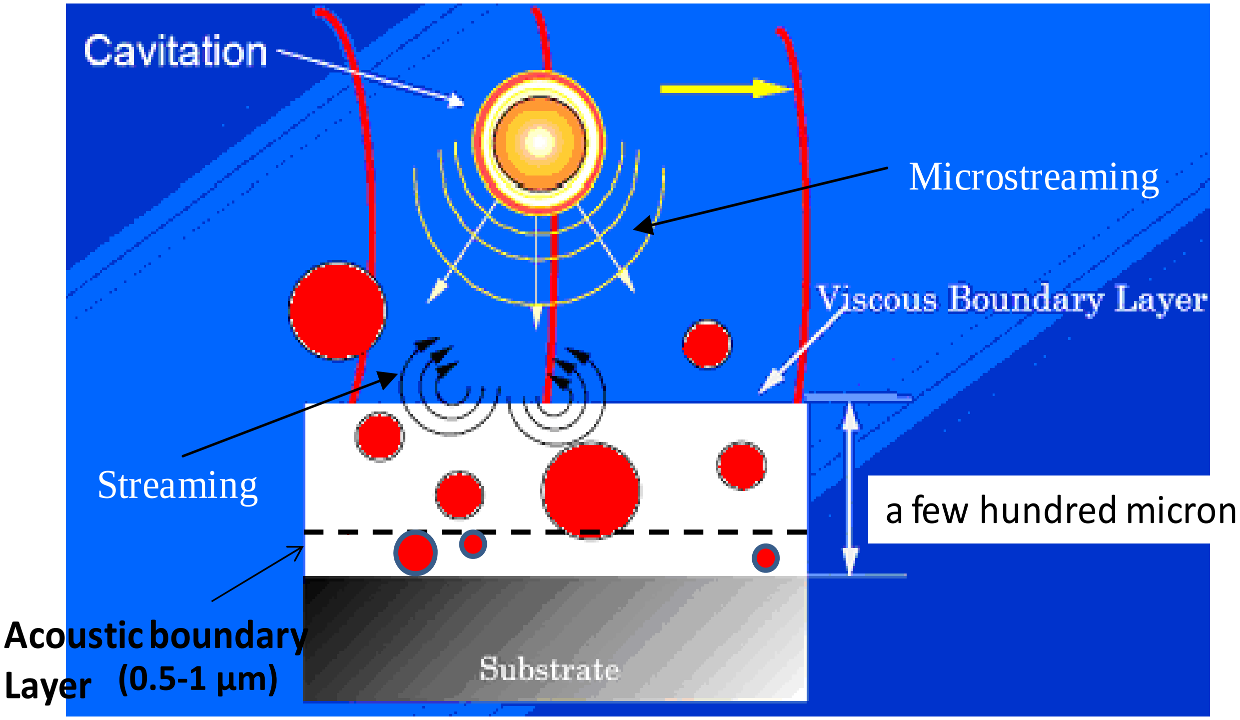


Courtesy of
'Institute of Sound
and Vibration Research'

- Advantage: High particle removal efficiency (PRE)
- Disadvantage: Damage to fragile features

Effects of Acoustic Wave Propagation Through a Liquid

- ➢ **Reduction in Liquid Boundary Layer Thickness on a Surface**
- ➢ **Acoustic Streaming: Eckart, Schlichting and Microstreaming**
- ➢ **Acoustic Cavitation: Stable and Transient**



Adopted from bransoncleaning.com

Variables in Megasonic Cleaning

- Most commonly used control knobs in Megasonic Cleaning are Applied Power and Chemistry of Cleaning Solutions; frequency of sound field is attracting some attention recently
- Power density in single wafer cleaning tools is typically in the range of 0.5 - 3 W/cm^2
- Generally, optimization of **power density** for cleaning based **on the *threshold power for onset of cavitation* is not done**
- **Type and concentration of dissolved gases, temperature and additives such as surfactants to cleaning solution would affect the cavitation threshold**

Common Techniques Used for Megasonic Research

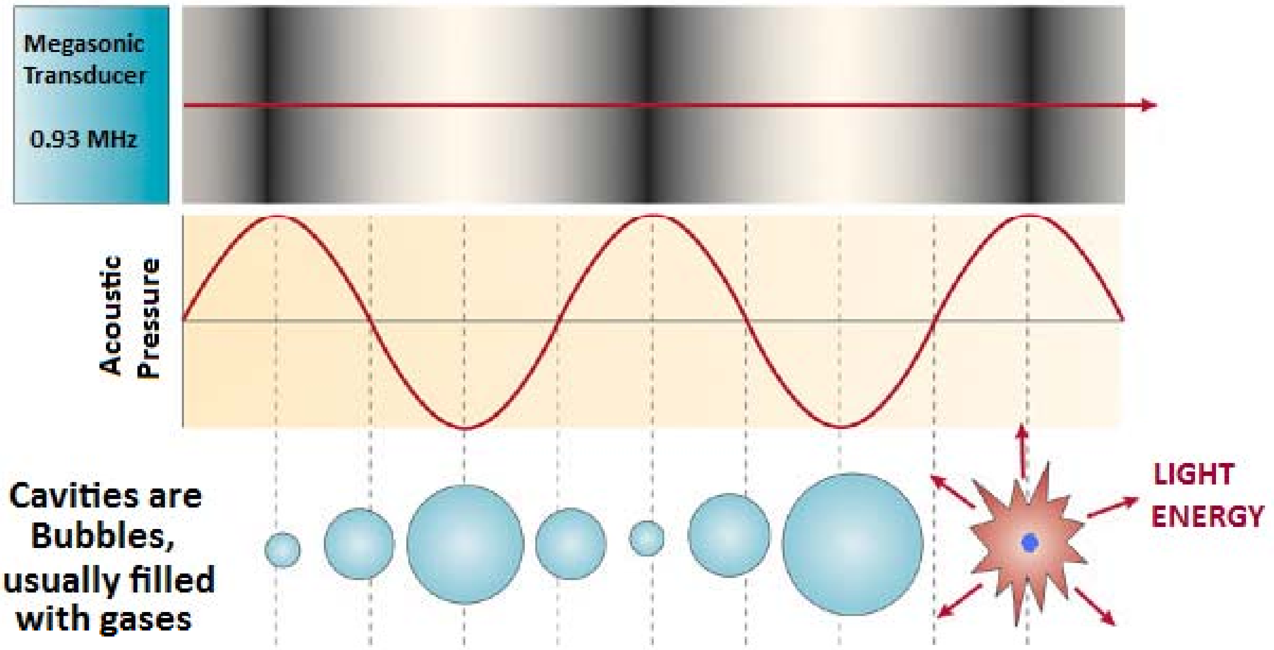
Sonoluminescence Based
(light emission from cavitating bubbles)

Measured using a Photomultplier Tube (PMT) and/or a spectrometer

Acoustic Emission Based
(pressure field in the liquid)

Measured using a Hydrophone

Sonoluminescence (SL) from Cavitating Bubbles



Cavities are Bubbles, usually filled with gases

Figure adapted from:
Nature Reviews
Cancer **5**, 321-327 (2005)

STABLE CAVITIES

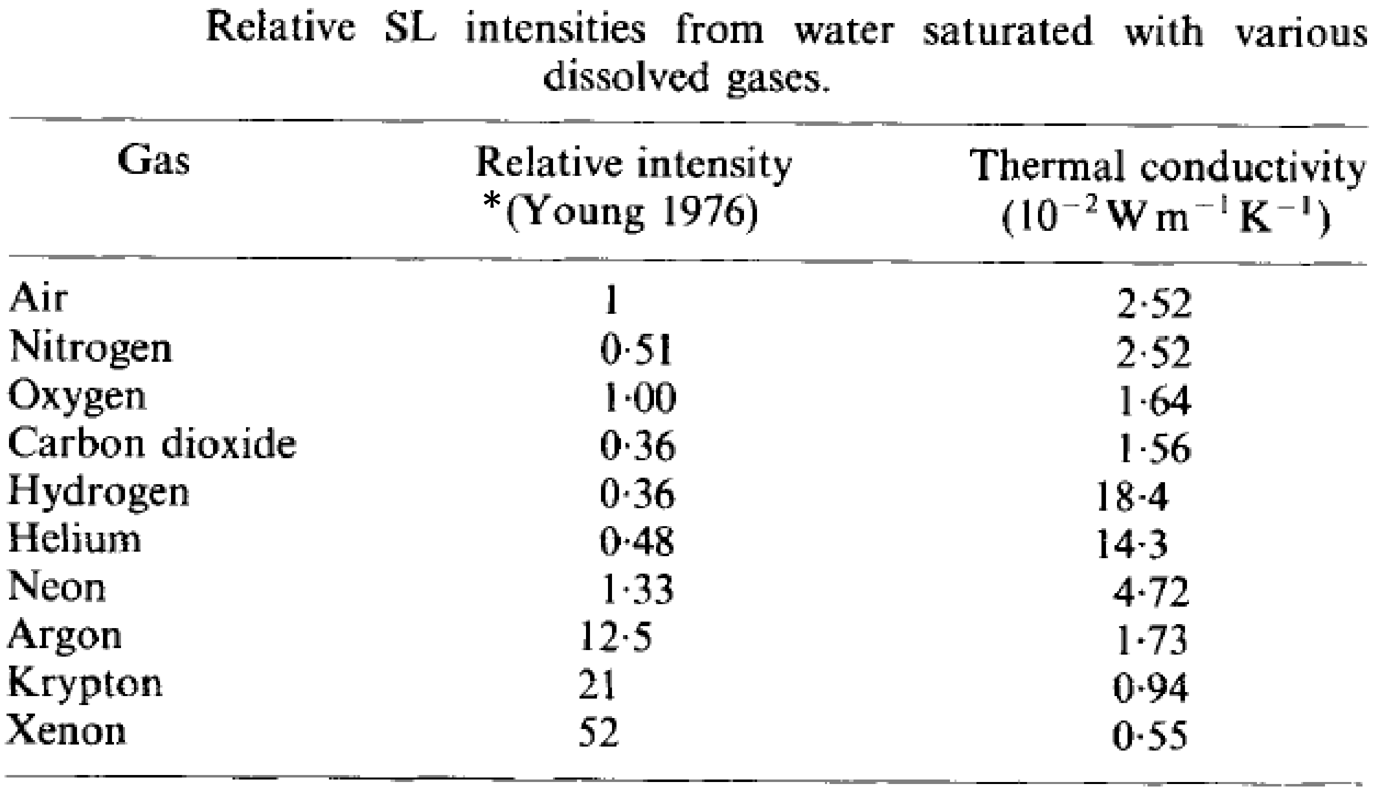
During the wave cycle cavities oscillate in size. If they do not implode, they are called STABLE Cavities

TRANSIENT CAVITIES

If they implode, they are called TRANSIENT Cavities. When they implode they release LIGHT, giving SONOLUMINESCENCE

- ***At collapse, the gas inside the cavity reaches extremely high temperatures (a few thousand degrees) and pressures (a few hundred bars).***
- ***Results in production of free radical species***
- ***Recombination of free radicals gives rise to photon emission.***

SL from Water Saturated with different Dissolved Gases



Relative SL intensities from water saturated with various dissolved gases.

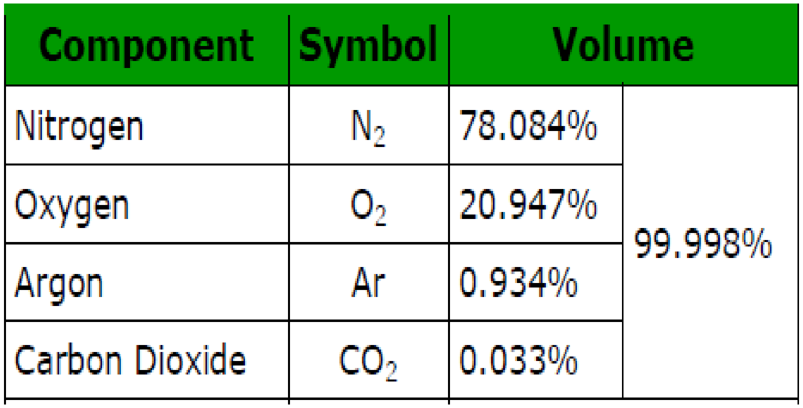
Gas	Relative intensity *(Young 1976)	Thermal conductivity (10^{-2} W m^{-1} K^{-1})
Air	1	2·52
Nitrogen	0·51	2·52
Oxygen	1·00	1·64
Carbon dioxide	0·36	1·56
Hydrogen	0·36	18·4
Helium	0·48	14·3
Neon	1·33	4·72
Argon	12·5	1·73
Krypton	21	0·94
Xenon	52	0·55

* F. Young, J. Acoust. Soc. Am., vol 60, pp. 100-104 (1976)

- **Aqueous solution containing saturated level of gas was subjected to 20 KHz sound frequency at 10 W/cm^2 and SL was measured by a photomultiplier tube (165 to 650 nm)**
- **In general , gases with Higher thermal conductivity showed lower SL**

Recent Work at the University of Arizona

- **Investigated the SL-behavior of major dissolved gases (N_2, O_2, Ar and CO_2) in a controlled manner in Aqueous Solutions**

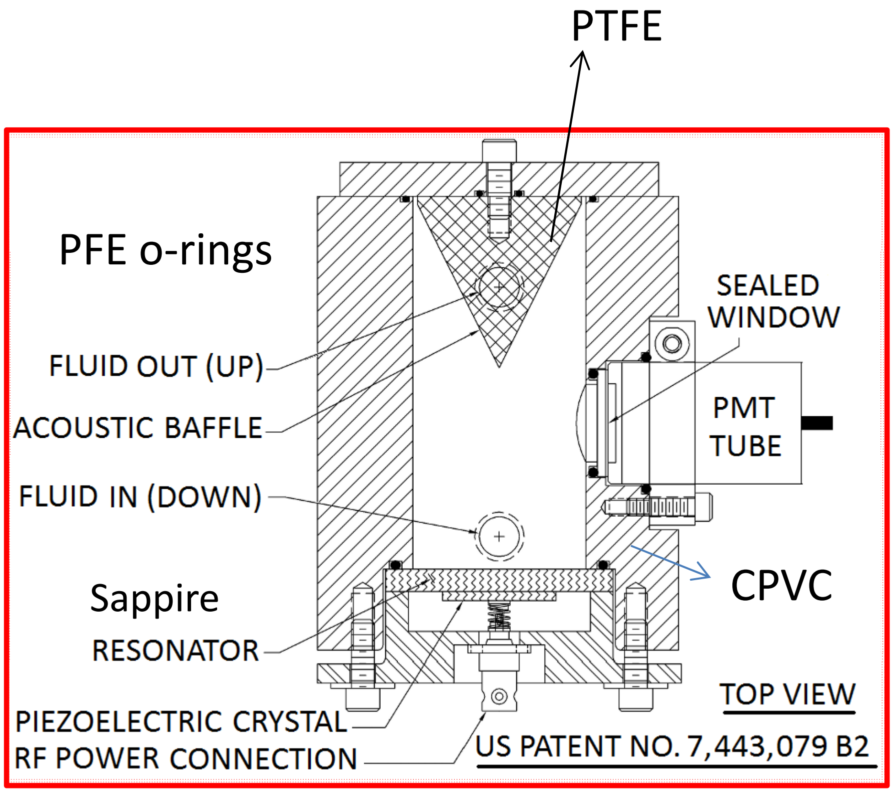


Component	Symbol	Volume	
Nitrogen	N_2	78.084%	99.998%
Oxygen	O_2	20.947%	
Argon	Ar	0.934%	
Carbon Dioxide	CO_2	0.033%	

- **Controlled SL by consumption/release of some of these gases using chemical means**

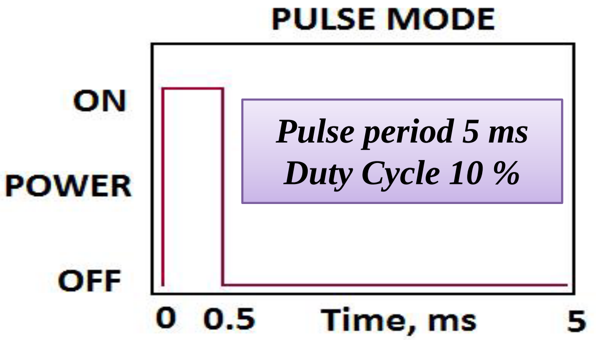
CAVITATION THRESHOLD (CT) CELL

ProSys CT Cell

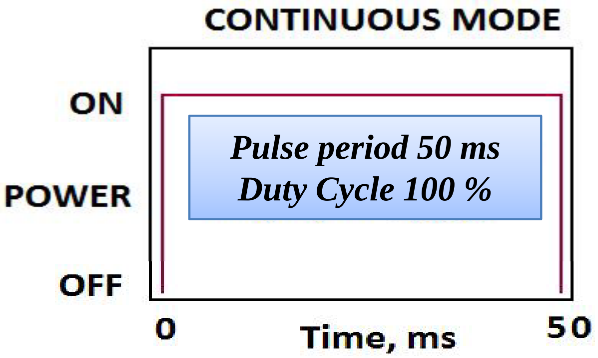


CT Cell Details

- *Volume = 163 cc, Length = 10.4 cm*
- *Internal Diameter = 4.8 cm*
- ***Frequency = 0.93 MHz***
- ***Wavelength Range = 270 to 650 nm***

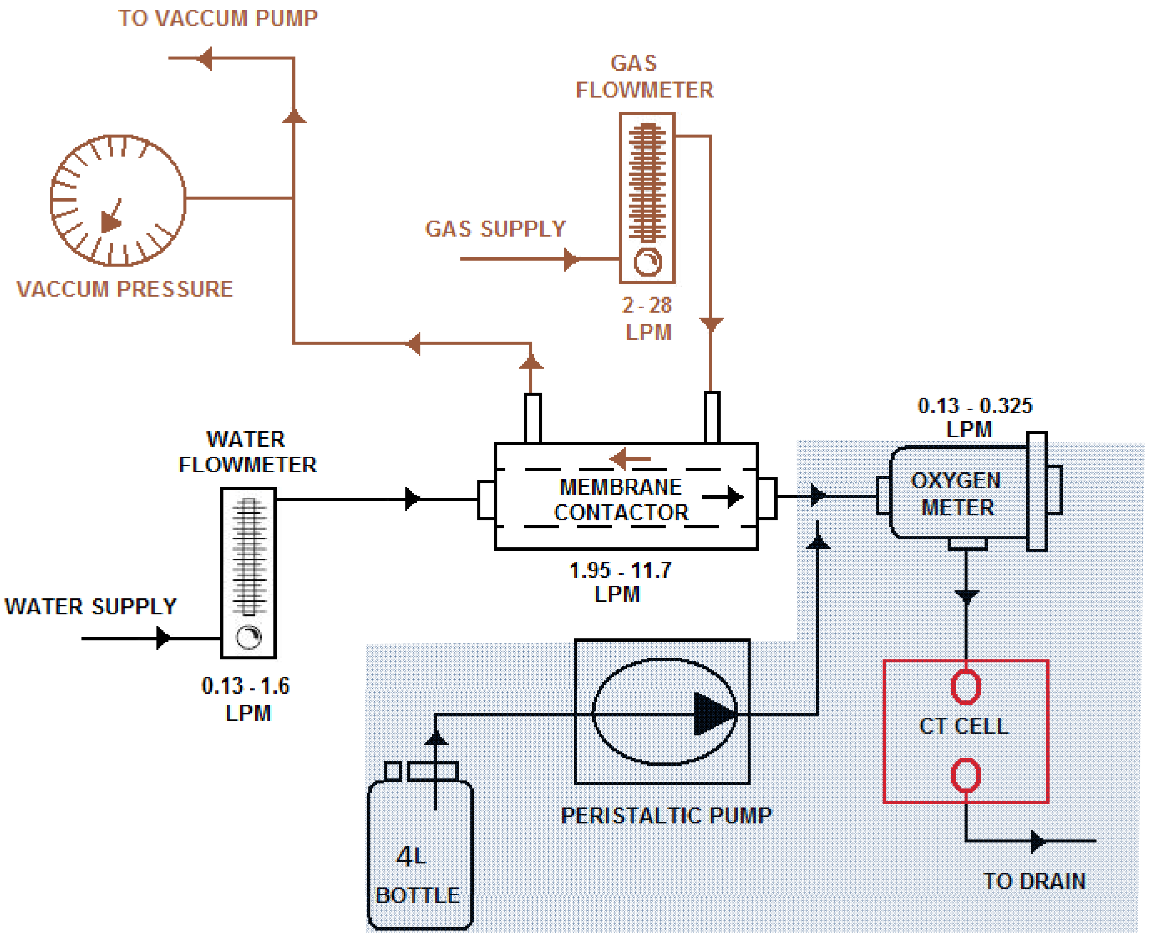


Pulse period 5 ms
Duty Cycle 10 %



Pulse period 50 ms
Duty Cycle 100 %

Experimental Setup



Gas Solubilities in DI Water

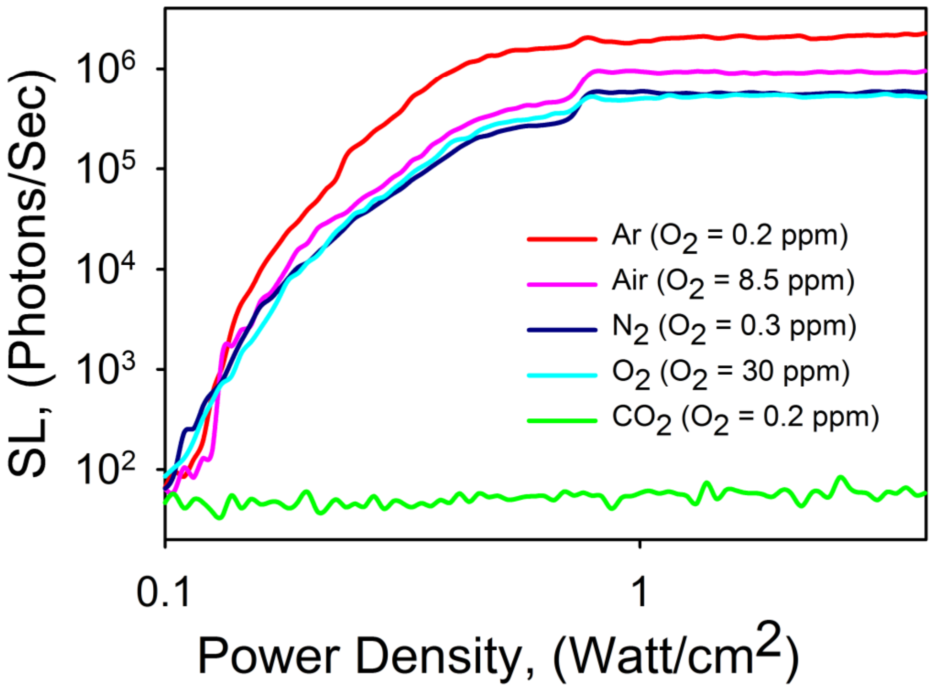
Saturating Gas Levels at 25 °C, 1 atm pressure

[Gas]	DIW Saturated With				
PPM	Air	N_2	O_2	CO_2	Ar
N_2	13.6	17.5	-	-	-
O_2	8.4	-	44	-	-
CO_2	0.5	-	-	1500	-
Ar	0.5	-	-	-	55

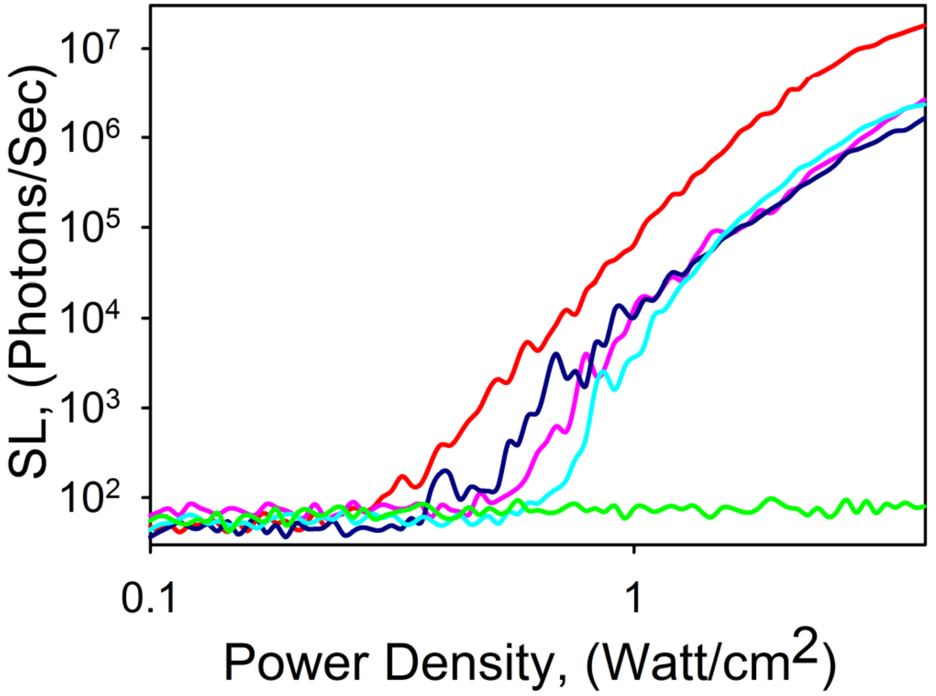
- **Ar, N_2, CO_2** were bubbled in DI Water until **$[O_2] < 0.3$ ppm**
- **Air Saturated Water** obtained by overnight exposure of DI water to clean room air and confirmed by ensuring **$[O_2] > 8.2$ ppm**

SL in DI Water Saturated With Different Gases

Pulse Mode



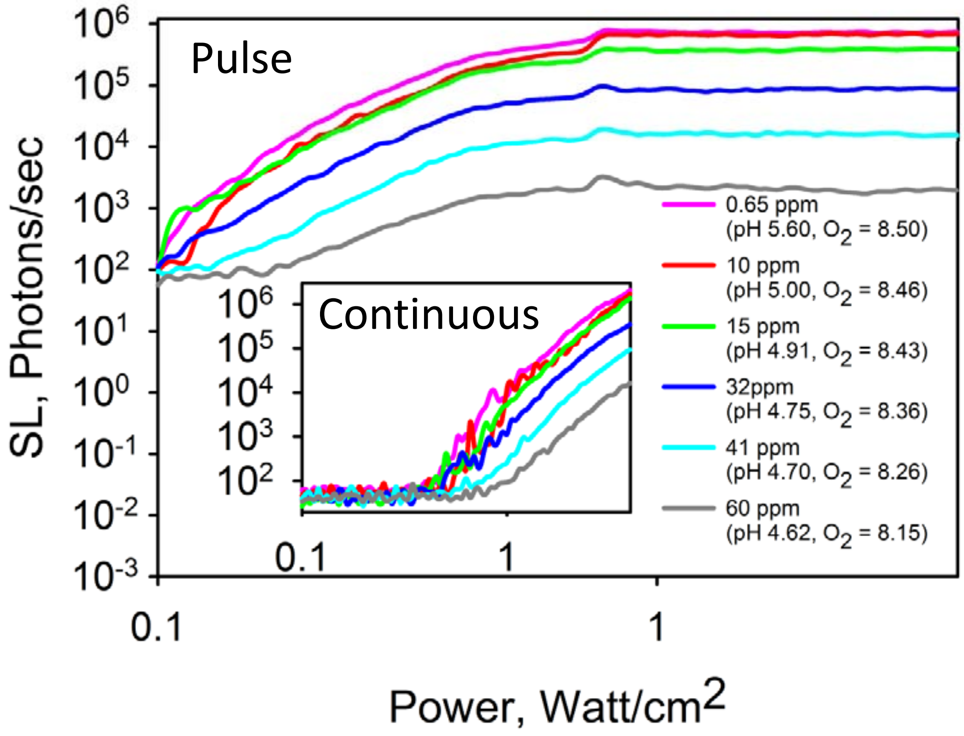
Continuous Mode



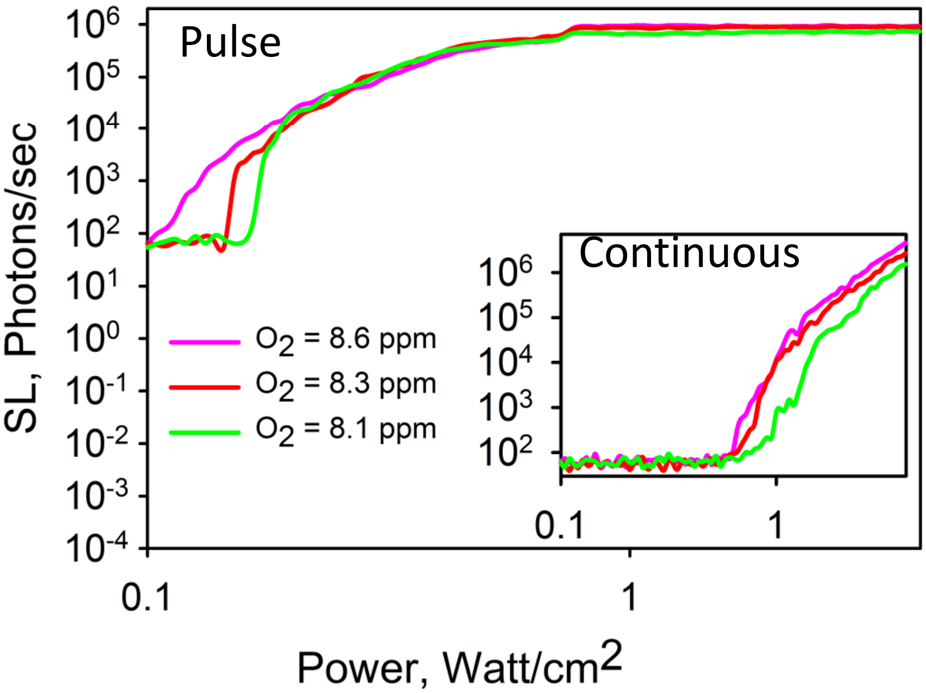
- **All gases except CO_2 (pH ~ 4, dissolved CO_2 ~ 1500 ppm) are capable of generating SL. CO_2 is completely incapable**
- **N_2 and O_2 saturated DI Water generates SL efficiently even though Ar, a gas believed to be essential for SL, is presumably absent**

SL Suppression by **Bubbling of CO_2**

CO_2 Effect



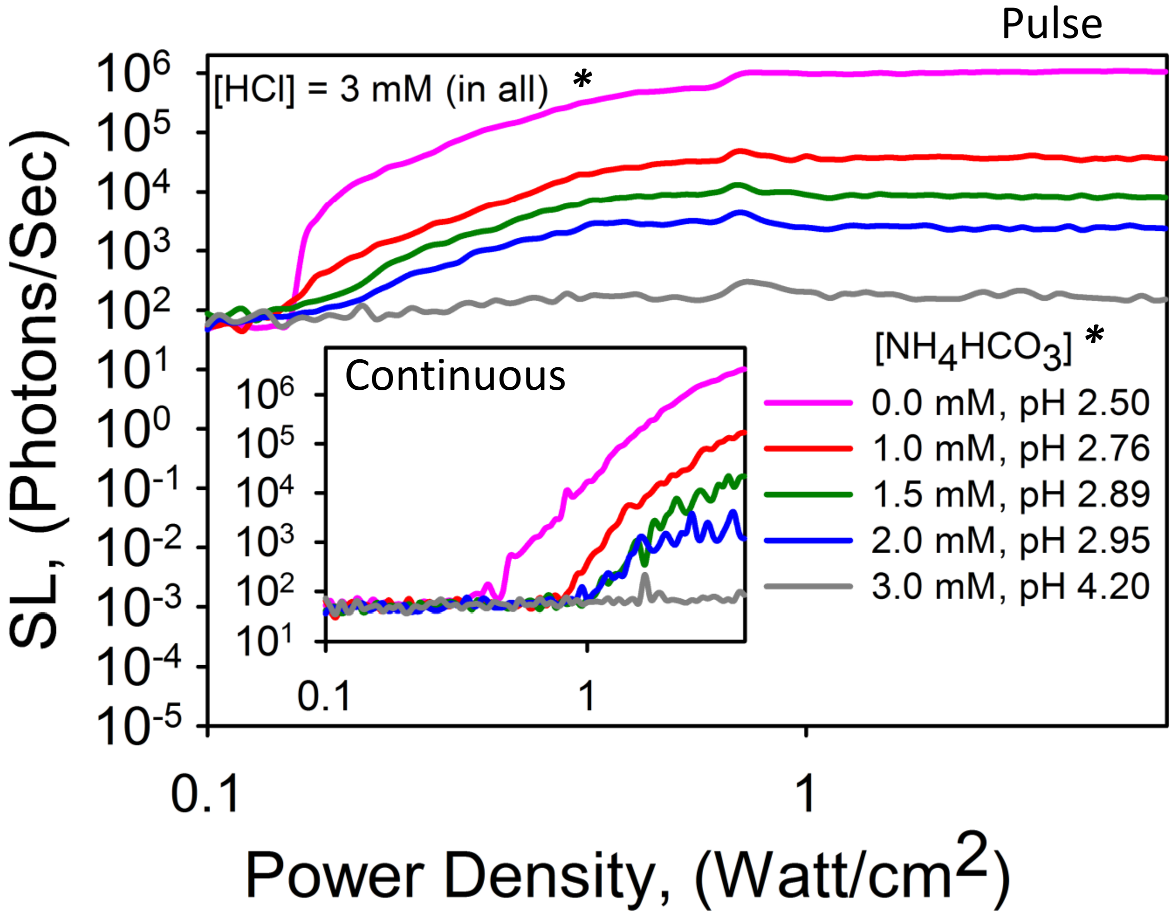
Vaccum Degassing Effect



CO_2 > 60 ppm suppresses SL almost completely. Addition of CO_2 decreases levels of other dissolved gases slightly.

When Air-saturated DI Water is vaccum degassed to a comparable level, SL remains unaffected. Thus, SL suppression is due to added CO_2 and not due to removal of other gases upon addition of CO_2.

SL Suppression by CO_2 Released From NH_4HCO_3

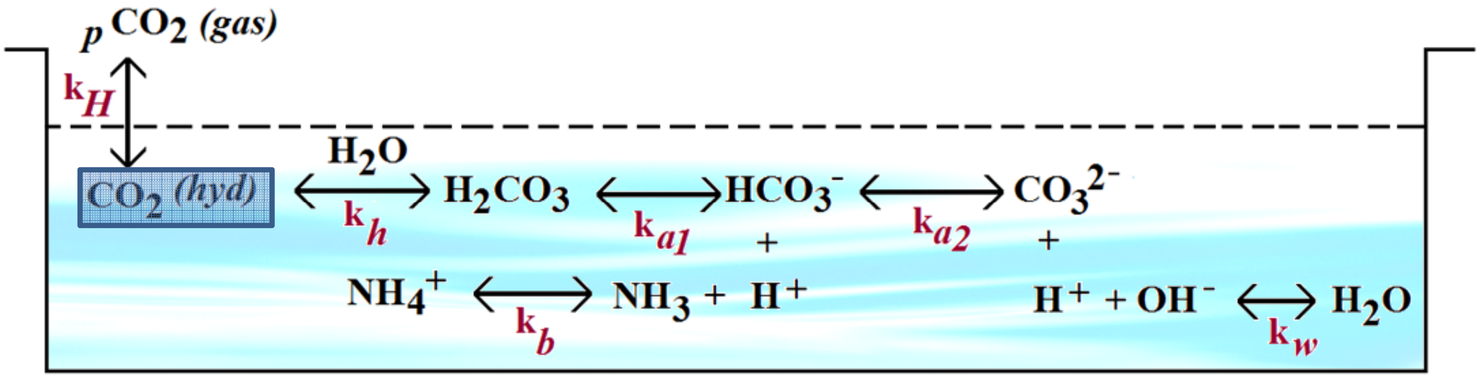


**** Neither HCl alone nor NH_4HCO_3 alone had any effect on SL, ruling out any role of HCO_3^- or H^+ (pH)***

- **3 mM HCl is added to induce release of CO_2 from NH_4HCO_3**
- **NH_4HCO_3 = 3 mM suppresses SL almost completely**
- **Initial dissolved gases is unchanged in this experiment as indicated by $[O_2]$ = 8.5 ppm, thus SL suppression is due to CO_2 release**

These results show CO_2 to be not only incapable but also a strong inhibitor of SL generation.

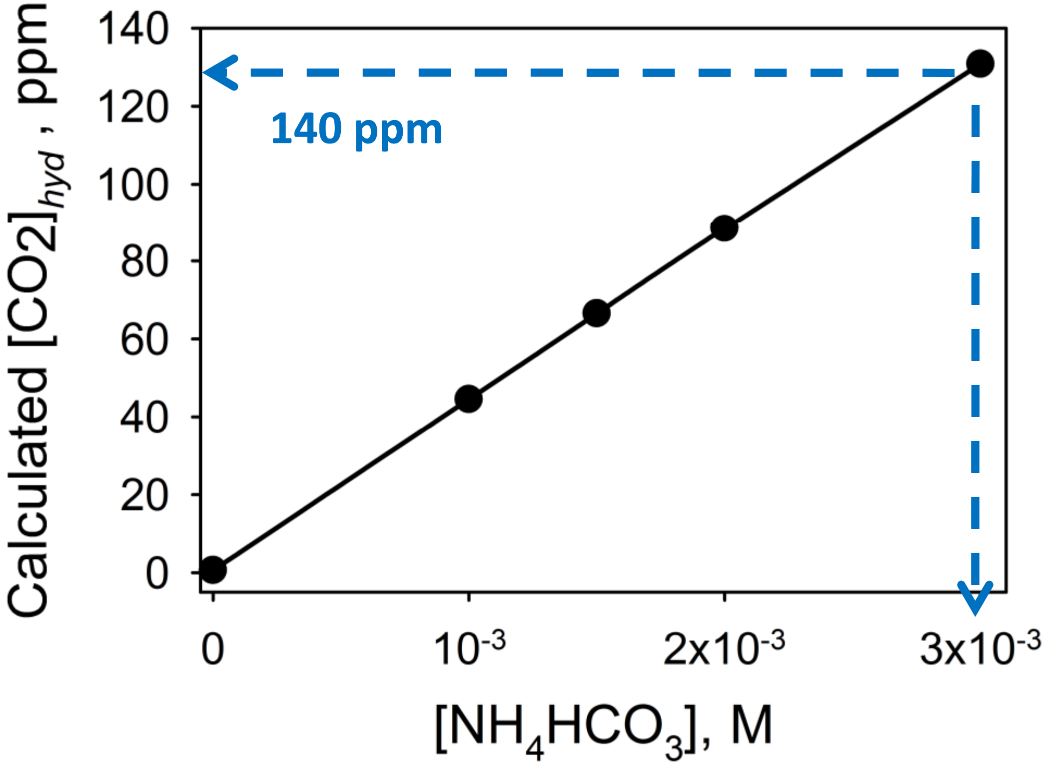
Calculation of CO_2 Evolved From NH_4HCO_3



- **Upon acidification of NH_4HCO_3, the linked equilibria in water is shifted towards formation of hydrated CO_2 i.e. CO_2 (*hyd*).**

- **Equations for equilibrium, mass and charge conservation can be solved numerically and [CO_2(*hyd*)] and [H^+] concentrations determined as a function of added [NH_4HCO_3].**

- **Minimum [CO_2 (*hyd*)] concentration necessary for Complete SL suppression using CO_2 release compounds is 140 ppm, which compares well with >60 ppm value obtained with direct CO_2 bubbling experiments**



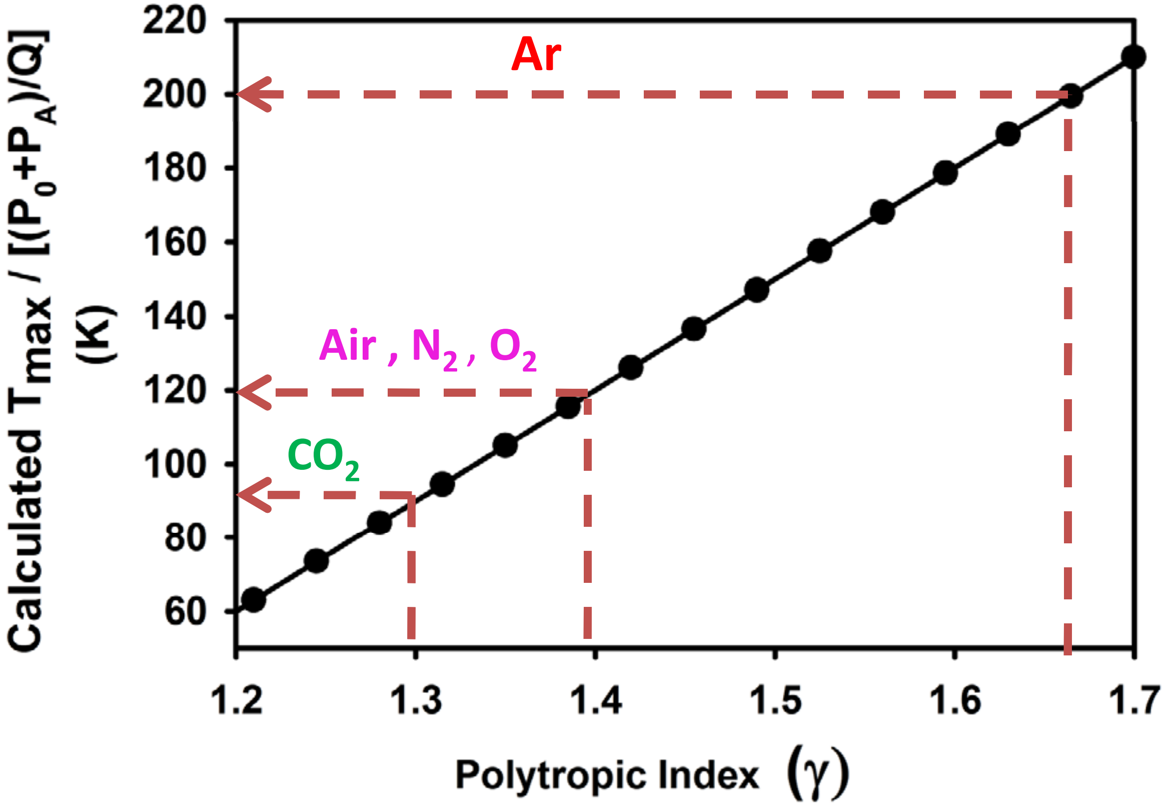
SL Generation Correlates With γ = Cp/Cv

- ***SL*** is generated when the maximum temperature inside a bubble reaches a certain threshold value

- ***T_{max}*** , the Maximum temperature reached in an acoustic cavity depends on γ and is given by

$$T_{\max} = T_0\left[\frac{(P_0 + P_A)(\gamma - 1)}{Q}\right]$$

$$\frac{T_{\max}}{(P_0 + P_A)/Q} = T_0(\gamma - 1)$$



$T_{\max}$ = Max Temperature, Q = Initial Pressure in the Bubble,

T_0 = Initial Temperature, γ = Polytropic Index

P_A = Acoustic Pressure Amplitude,

P_0 = Pressure in Bulk Solution in Absence of Sound Waves

Suslick and Co-workers (*J. Phys. Chem. A 1999*) have reported T_{max} = 4000 deg C for Argon saturated water-benzene mixtures, which can be reproduced from the plot above using $(P_0+P_A)/Q$ = 21.4 and γ = 1.67 for Argon.

Plausible Mechanisms For Reduction Of SL Signal By Carbon Dioxide

1. The maximum temperature reached in a carbon dioxide bubble is lowest because of its low γ value.

2. *S*cavenging of free radicals by CO_2 may contribute to the reduction of SL signal (It is a common practice to bubble CO_2 in ozonated DI water to kill free radicals and extend ozone half life)

3. Cushioning effect from dissolved CO_2 due to its higher solubility compared to other gases

Cavitation Studies Using Electrochemical Measurements

Cavitation Studies Using Electrochemical Measurements

- Increased interest over the past two decades in ultrasonic cavitation studies using microelectrode based electrochemical measurements

- Microelectrode allows monitoring of single bubble activity through cavitation effects of the bubble

- Much of the available literature correlating cleaning additives (surfactants, dissolved gases etc) and bubble behavior is in the ultrasonic frequency range

- Since, the semiconductor industry, uses megasonic range frequencies for cleaning applications (due to lower damage to structures at these frequencies), current work was focused on investigating bubble behavior at ~ 1 MHz

Concept

Electrochemistry in Sound Field to Characterize Bubble Behavior

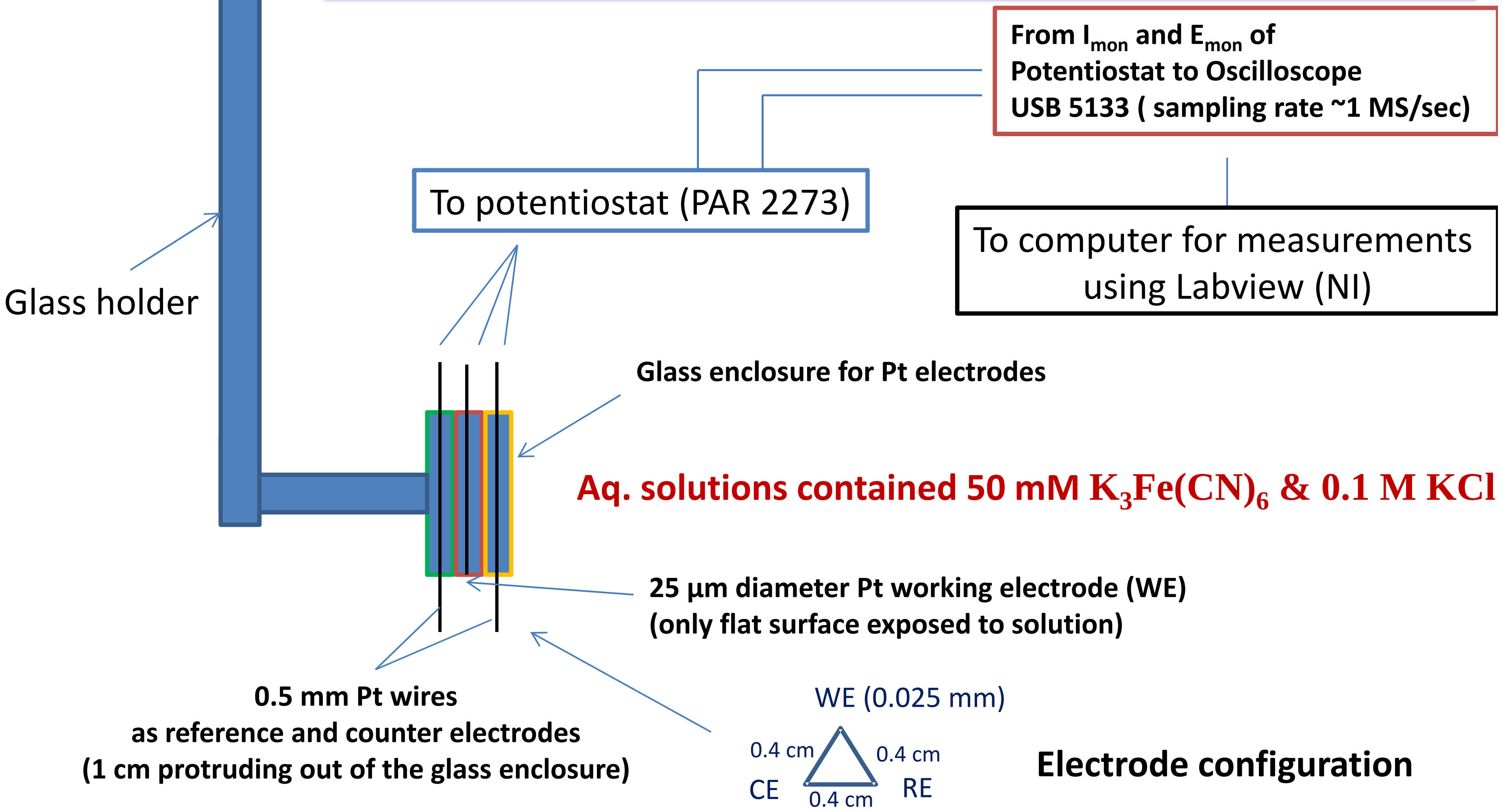
- When an electroactive species such as ferricyanide gets reduced at an electrode surface (such as platinum), current is generated

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

- Different bubble behaviors such as oscillation and collapse can lead to mass transport of the ferricyanide species towards the electrode surface
- By measuring current at high sampling rates (in MHz range), bubble behavior can be monitored using a microelectrode

Experimental Set-up

High Resolution Electrochemical Measurement (Cyclic Voltammetry and Chronoamperometry) set up



From I_{mon} and E_{mon} of Potentiostat to Oscilloscope USB 5133 (sampling rate ~1 MS/sec)

To potentiostat (PAR 2273)

To computer for measurements using Labview (NI)

Glass holder

Glass enclosure for Pt electrodes

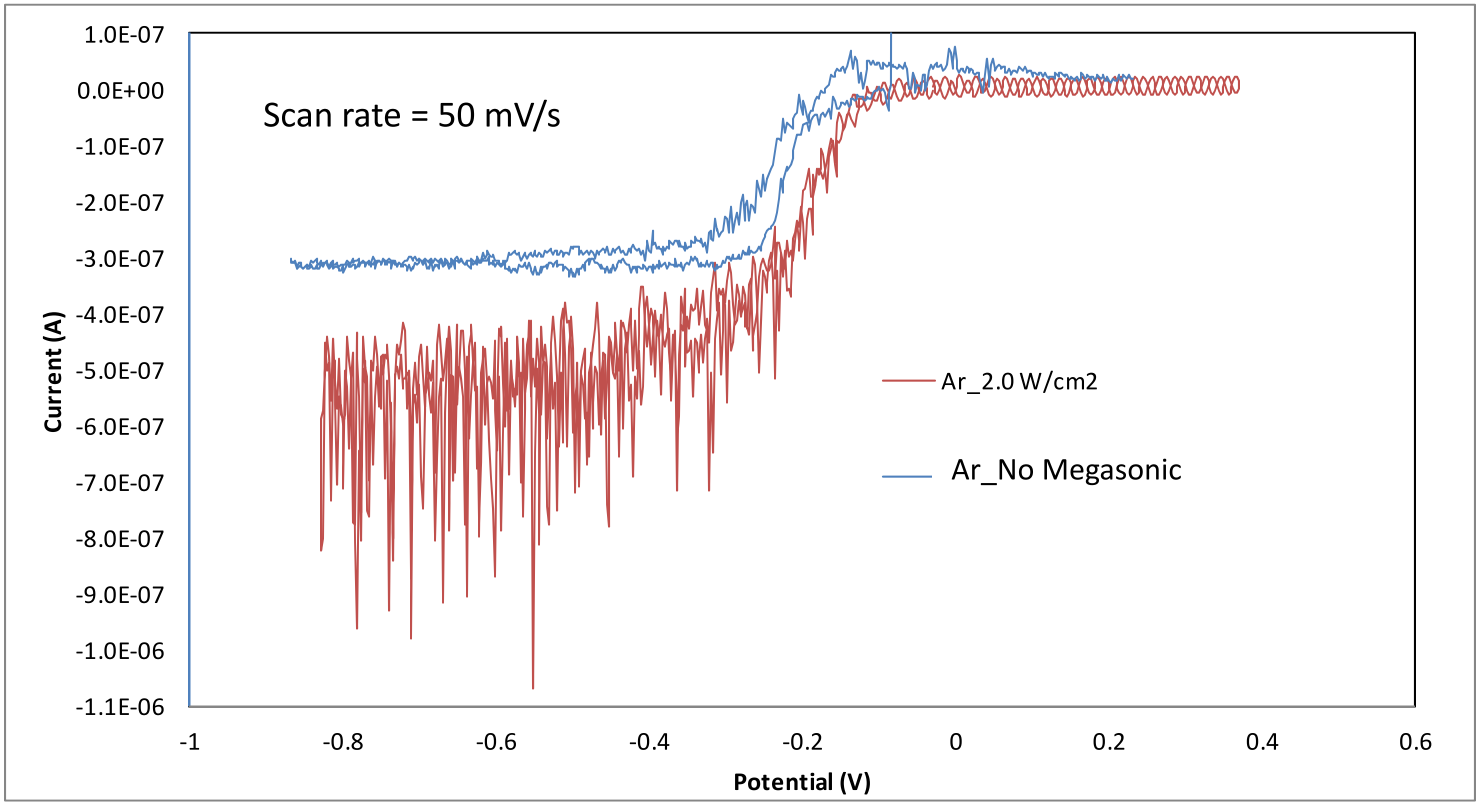
Aq. solutions contained 50 mM $K_3Fe(CN)_6$ & 0.1 M KCl

25 µm diameter Pt working electrode (WE)
(only flat surface exposed to solution)

0.5 mm Pt wires
as reference and counter electrodes
(1 cm protruding out of the glass enclosure)

Electrode configuration

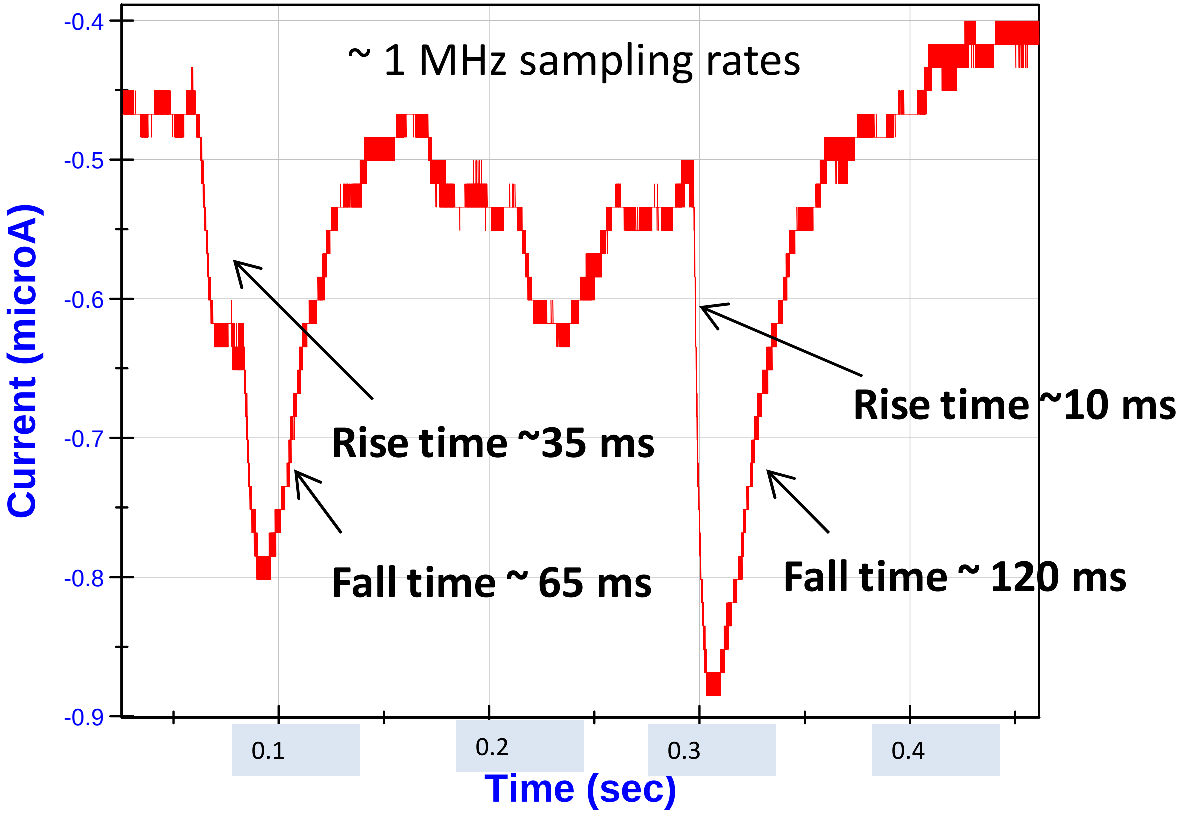
Cyclic Voltammetry in Ar saturated DI water containing 50 mM $K_3Fe(CN)_6$ and 0.1 M KCl solution



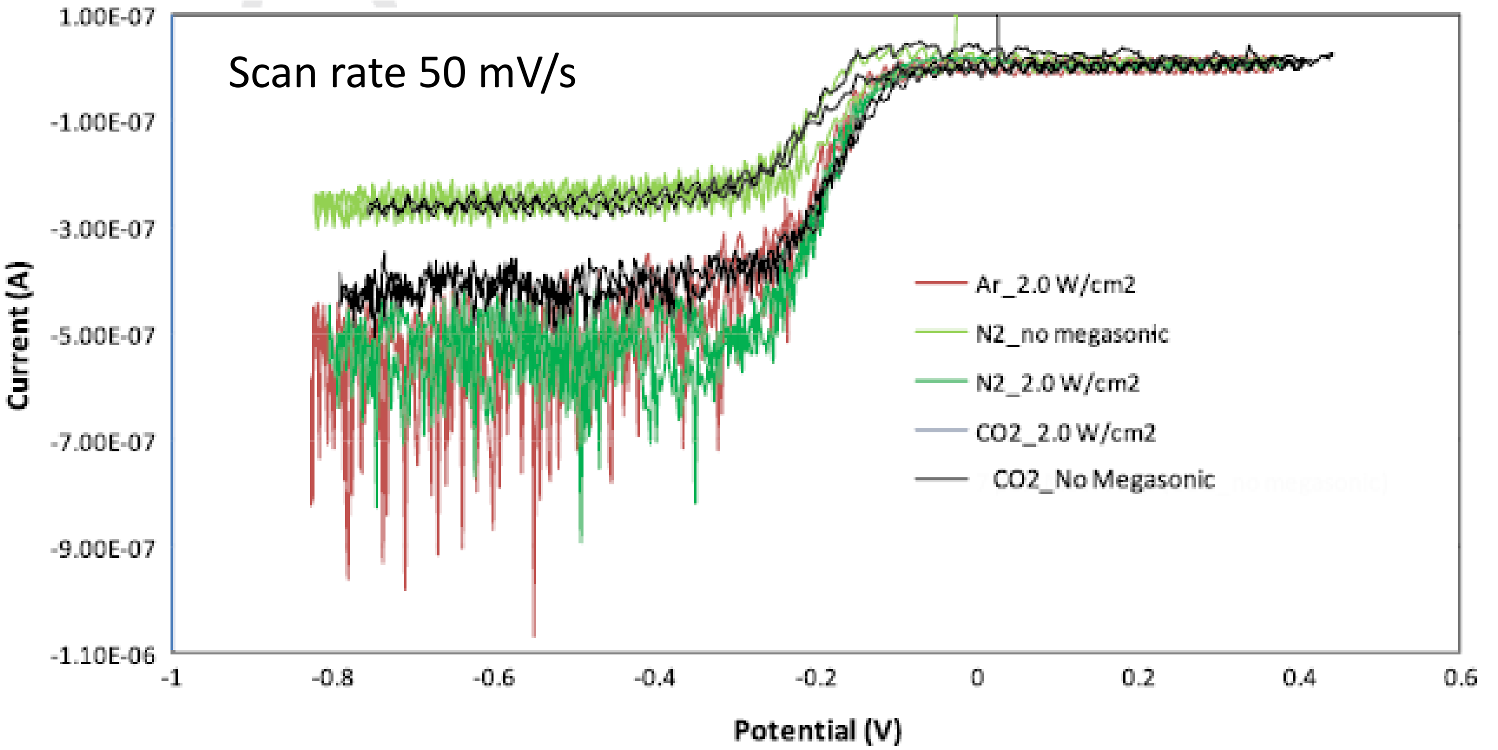
- **Limiting current increases with application of megasonic field**
- **Appearance of current transients on limiting current in the presence of meg field**

Examples of Current Peaks

Conditions: Ar saturated Aq. Solution of 50 mM $K_3Fe(CN)_6$ & 0.1 M KCl, Megasonic conditions: Continuous mode, 2 W/cm^2



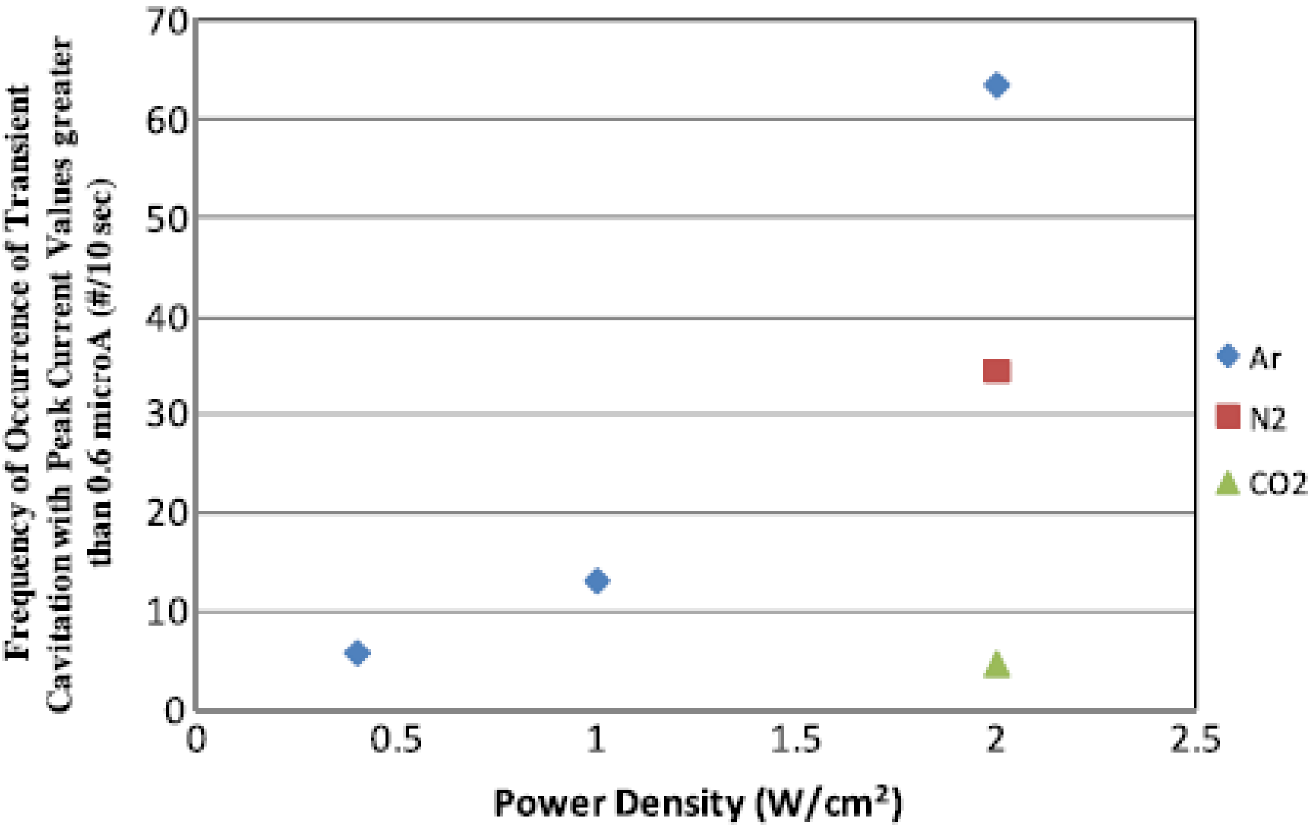
Effect of dissolved gases (CO_2, N_2 and Ar) in 50 mM $K_3Fe(CN)_6$ and 0.1 M KCl solution on current voltage behavior



***Current transients strongly depend on the nature of the dissolved gas**

*** Number and magnitude of current peaks were observed to decrease in the following order for dissolved gases: argon > nitrogen > carbon dioxide**

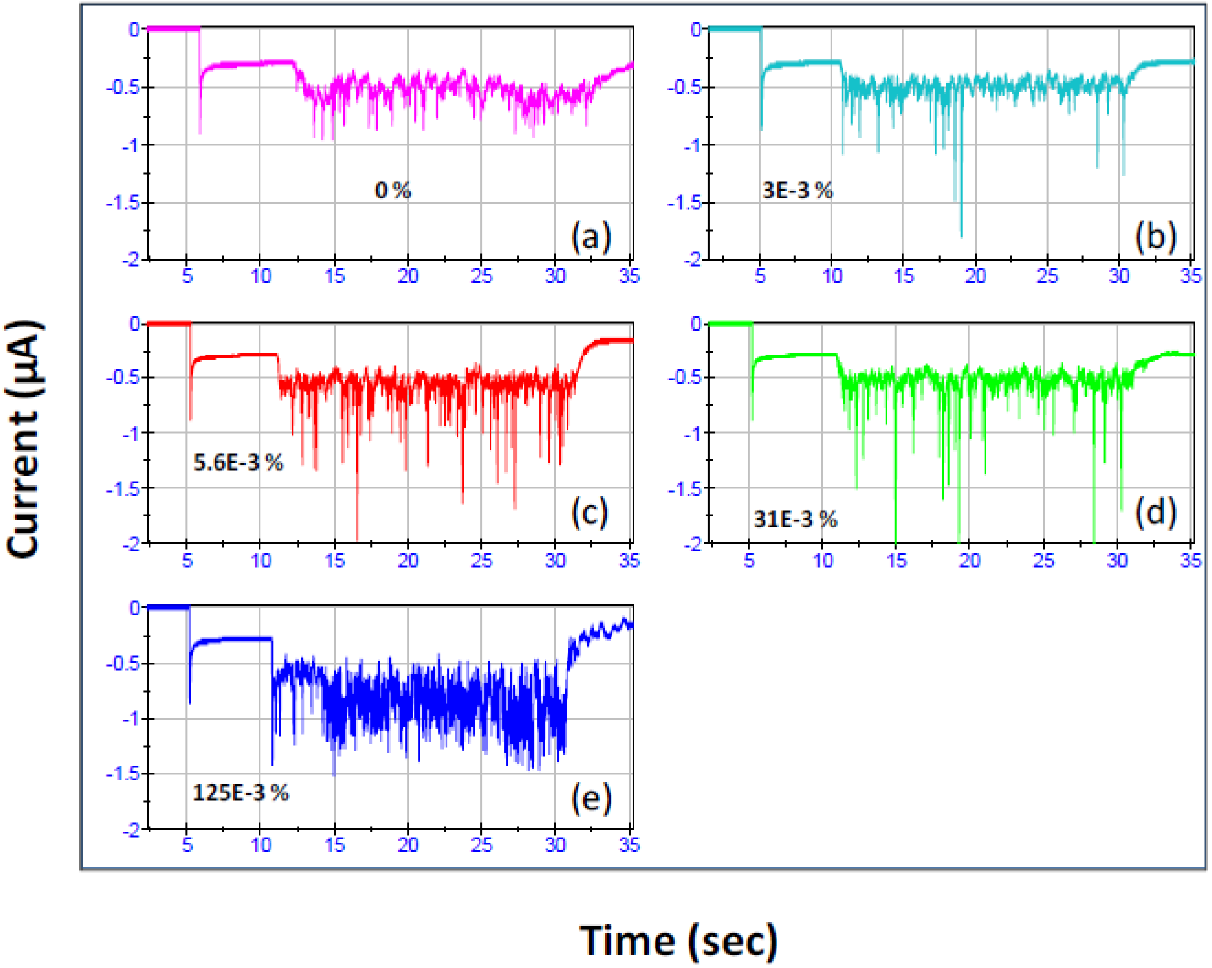
Frequency of occurrence of transient cavitation as a function of power density for various dissolved gases



* In the case of Ar saturated ferricyanide solution, the frequency of occurrence of 'current peaks' increases from 6 to 65 in 10 s with increase in power density from 0.4 to 2W/cm^2

* The number of 'current peaks' at 2W/cm^2 reduces to 35 and 5 (in 10 s) when the experimental solution contained saturated levels of N_2 and CO_2, respectively

Role of Triton® X-100 on current during reduction of ferricyanide ions (50 mM) in Ar saturated aqueous solution



(Continuous mode; 0-6 s = no applied potential and no megasonic irradiation, 6-11 s = applied potential of -0.6 V and no megasonic irradiation, 12-32 s = applied potential of -0.6 V and megasonic irradiation at ~ 1 MHz, ≥33 s = applied potential of -0.6 V and no megasonic irradiation)

Amplitude and frequency of occurrence of transient cavitation peaks depends on the concentration of Triton® X-100 in the solution

Summary

- **Sonoluminescence and Sono-electrochemistry based techniques can be very useful in probing acoustic cavitation**

- **Dissolved gases and additives such as surfactants play an important role in modulating transient cavitation which affects both particle removal and feature damage**

ACKNOWLEDGEMENTS

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