

Plasma-based water purification: Challenges and prospects for the future

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Plasma-based water purification: Challenges and prospects for the future

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Freshwater scarcity derived from seasonal weather variations, climate change, and overdevelopment has led to serious consideration for water reuse. Water reuse involves the direct processing of wastewater for either indirect or directly potable water reuse. In either case, advanced water treatment technologies will be required to process the water to the point that it can be reused in a meaningful way. Additionally, there is growing concern regarding micropollutants, such as pharmaceuticals and personal care products, which have been detected in finished drinking water not removed by conventional means. The health impact of these contaminants in low concentration is not well understood. Pending regulatory action, the removal of these contaminants by water treatment plants will also require advanced technology. One new and emerging technology that could potentially address the removal of micropollutants in both finished drinking water as well as wastewater slated for reuse is plasma-based water purification. Plasma in contact with liquid water generates a host of reactive species that attack and ultimately mineralize contaminants in solution. This interaction takes place in the boundary layer or interaction zone centered at the plasma-liquid water interface. An understanding of the physical processes taking place at the interface, though poorly understood, is key to the optimization of plasma-based water purifiers. High electric field conditions, large density gradients, plasma-driven chemistries, and fluid dynamic effects prevail in this multiphase region. The region is also the source function for longer-lived reactive species that ultimately treat the water. Here, we review the need for advanced water treatment methods and in the process, make the case for plasma-based methods. Additionally, we survey the basic methods of interacting plasma with liquid water (including a discussion of breakdown processes in water), the current state of understanding of the physical processes taking place at the plasma-liquid interface, and the role these processes play in water purification. The development of plasma diagnostics usable in this multiphase environment along with modeling efforts aimed at elucidating physical processes taking place at the interface are also detailed. Key experiments that demonstrate the capability of plasma-based water treatment are also reviewed. The technical challenges to the implementation of plasma-based water reactors are also discussed. We conclude with a discussion of prospects for the future of plasma-based water purification. *Published by AIP Publishing.*
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I. INTRODUCTION

Fresh water is a scarce commodity, making up only 2.5% of the total water present on Earth and less than a fraction of this percentage is actually readily assessable in the form of ground and surface water sources (Fig. 1).¹ This life-sustaining commodity is being stressed presently by population growth and overdevelopment, which has also led to aquifer depletion.²⁻⁴ In many respects humans compete with industrial and agricultural water needs. Indeed, some 70% of all freshwater draws are associated with agriculture.^{5,6} Pollution reduces water quality and thus has the effect of reducing the availability of water that can be used for potable or agricultural applications.⁷ Pollution here refers to the introduction of harmful contaminants such as organic chemicals or microbes derived from human or animal waste into freshwater sources. According to WHO, nearly a billion people lack access to clean drinking water and an estimated

500 million die each year from disease associated with contaminated sources.⁸ In response to fresh water scarcity, the National Academies has listed “access to clean drinking water” as an engineering grand challenge.⁹ Climate change is another driver that affects fresh water availability. Here shifting climate modifies precipitation patterns leading to extreme drought in areas as can be seen in the NOAA’s current projections, depicted in Figure 2.^{10,11} Managing fresh-water scarcity in light of the aforementioned issues has become a high priority.^{12,13} Fresh water stress can be addressed to a degree with advanced water treatment technology. Four problem areas in particular, that could benefit from the introduction of treatment capability beyond conventional water treatment methods include: (1) contaminants of emerging concern (CEC) in drinking water, (2) ballast water contamination of ecosystems, (3) waste water production in the petroleum industry, and (4) drought-induced freshwater supply stress.

Contaminants of emerging concern (CECs) include those micropollutants that are found in trace amounts in drinking water and in recent time have received public

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^{a)}Invited speaker.

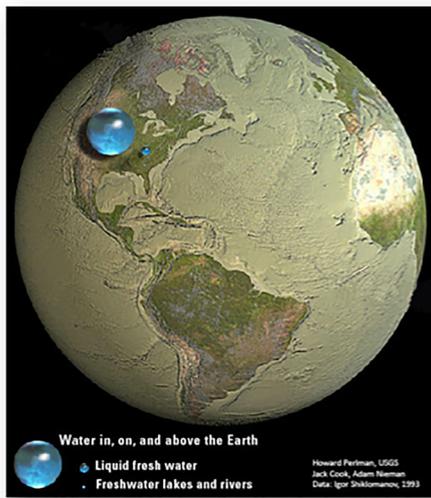


FIG. 1. Schematic depiction of freshwater availability. Courtesy of the USGS.

attention owing to potential human health and environment impacts.^{14,15} These contaminants have the potential to cause illness in humans but are currently unregulated by the EPA.^{16,17} These include a wide range of organic chemicals, such as pharmaceuticals, industrial solvents, volatile organic compounds,¹⁸ and personal care products. There are multiple pathways for these contaminants to reach source water. Perhaps the most direct is direct emission from wastewater plants into rivers.¹⁹ A recent U.S. Geological Survey study showed that conventional drinking water treatment plants, which typically process water via coagulation and filtration followed by disinfection, are not able to remove many of these contaminants.²⁰ Because the release of foreign ballast water into ports can lead to the introduction of invasive species as well as chemical contaminants, the U.S. Coast Guard and the International Maritime Organization are requiring new ships to incorporate advanced technologies to decontaminate the water before releasing.^{21–24} The petroleum industry's oil and gas drilling (e.g., hydraulic fracturing) operations generate some 2.4 billion gallons of contaminated waste water per day in the process of resource extraction.^{25,26} This water, which is heavily contaminated, is usually disposed of in deep injection wells largely due to

the difficulty and cost of treating and reprocessing the water conventionally for reuse.²⁷ Advanced treatment methods could enable the reuse of this water, which has the potential to make the operation sustainable, thereby relieving freshwater stress on neighboring municipalities.²⁸ The final area where advanced technology can make a difference is enhancing municipality water supply resilience to scarcity issues driven by overdevelopment or drought. Figure 2 shows NOAA predicted precipitation patterns into 2100. Based on these projections, many regions, particularly the American southwest, might experience significant reduction in precipitation, which adds to fresh water stress. Water reuse is a potential solution to this problem. In principle, rather than dumping treated wastewater into a surface water site, one can apply advanced treatment methods to reduce contaminants to a level that the water is either directly potable or sufficiently treated to recharge an aquifer.²⁹ There are a host of non-potable applications for post-treated wastewater as well such as irrigation, washing, and industrial process water. Currently, the EPA provides only guidelines for water reuse.³⁰ Actual regulations, which establish contaminant standards, are currently being developed at the state EPA level. For example California is in the process of developing guidelines for contaminant levels for a number of pollutants and microbes.³¹ These guidelines require 10 and 12 log reductions for some contaminants. Advanced water treatment methods will be needed to meet these treatment goals.

II. ADVANCED CONVENTIONAL WATER TREATMENT

In order to address water quality for applications such as water reuse, advanced conventional water treatment methods are being investigated.^{32,33} For the most part, this includes a combination of reverse osmosis (RO) and advanced oxidation. UV irradiation is typically added as well as an additional layer of protection against microbes and even some chemicals (via photolysis) such as the carcinogen *N*-Nitroso-dimethylamine (NDMA), a disinfection by product.^{34,35} Reverse osmosis (RO) is a preferential diffusion process that utilizes membranes to separate solute from water. Water, under pressure, preferentially diffuses through the membrane leading to the formation of two process streams—one of purified water and one a reject stream containing the contaminants.³⁶ Treatment costs are typically higher than conventional methods as energy is required to pump water through the membranes. Membrane pretreatment and periodic replacement also contribute to the increased processing cost. RO is followed by advanced oxidation as a second barrier of defense. Advanced oxidation refers to those chemical processes that generate large quantities of the OH radical for the purpose of decomposing a wide range of organic compounds, such as volatile organic compounds, pesticides, pharmaceuticals, and personal care products.^{35,37–40} A free radical, such as OH, is essentially a molecule with one or more unpaired electrons, which makes it particularly reactive. OH has an oxidation potential second only to fluorine, which is toxic, and twice that of chlorine. It should be pointed out that the oxidant chlorine tends to be selective in what it actually oxidizes whereas OH is indiscriminate. Table I depicts a

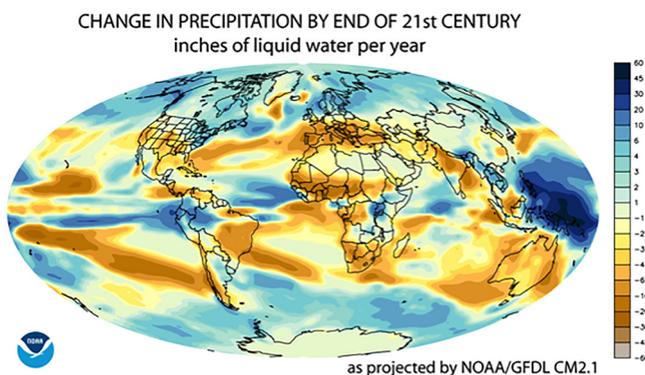


FIG. 2. Shifting precipitation patterns as projected by NOAA. Courtesy of NOAA.

TABLE I. Advanced oxidation methods.

Agent	Processes			
UV	$O_3 + UV \rightarrow O_2 + O(^1D)$; $O(^1D) + H_2O \rightarrow H_2O_2 \rightarrow 2OH$	$H_2O_2 + UV \rightarrow 2OH$	$O_3 + UV + H_2O_2 \rightarrow OH$ radicals	$H_2O + Fe^{+3} \rightarrow Fe(OH)^{+2} + H^+$ $\rightarrow Fe(OH)^{+2} + UV \rightarrow Fe^{+2} + OH$
Ozone	Ozone at pH > 8 $3O_3 + OH^- \rightarrow 2OH + 4O_2$	$2O_3 + H_2O_2 \rightarrow 2OH + 3O_2$	$O_3 + Catalyst \rightarrow OH$ radicals +Oxygen	$O_3 + Granular Activated Carbon$ $\rightarrow OH$ radicals + Oxygen
Ultrasound	Ultrasound + $H_2O \rightarrow H + OH$	$O_3 + Ultrasound \rightarrow O_2 + O(^1P)$; $O(^1P) + H_2O \rightarrow H_2O_2 \rightarrow 2OH$	Ultrasound + UV + O_3 $\rightarrow OH$ radicals	Ultrasound $H_2O_2 + UV$ $\rightarrow OH$ radicals
Other	Fenton: $H_2O_2 + Fe^{+2} \rightarrow OH^-$ + $OH + Fe^{+3}$	Shockwave + ozone $\rightarrow OH$ radicals		

partial listing of the multitude of methods that can produce the OH radical in water.^{36,37,41} The OH radical decomposes toxins in water by a series of chemical reactions such as abstraction and addition which ultimately leads to the conversion of organic compounds in solution into water and carbon dioxide along with mineral acids and salts. In this respect, the end products are essentially harmless. For example, the complete decomposition of methanol via multiple interactions with the OH radicals can be summarized as follows: $CH_3OH + OH \rightarrow CH_2OH \xrightarrow{OH/O_2} CH_2O \xrightarrow{OH/O_2} CHO - OH \xrightarrow{OH/O_2} CO_2 + H_2O$. Conventional advanced oxidation requires chemical precursors on site, which are added to the water to generate the OH as well as the infrastructure to accommodate storage. For example, an ozone-hydrogen peroxide advanced oxidation stage requires liquid oxygen storage and handling hardware as well as ozone generators in addition to hydrogen peroxide (an explosive oxidant) storage tanks. Treatment costs for conventional advanced oxidation treatment therefore exceeds that of conventional water treatment methods.

III. PLASMA AS A SOURCE OF ADVANCED OXIDATION SPECIES

The aforementioned physical processes leading to OH formation in water are also generated when a plasma is placed in contact with water. Plasma is a source of high electric fields, energetic charged particles, ultrasound, UV light, and even shockwaves, which can drive OH production in solution. Additionally, plasma chemistry driven in the gas phase produces large quantities of reactive oxygen species as well such as not only the OH radical and hydrogen peroxide (derived from water vapor) but also ozone, singlet oxygen, the nitrate radical, and super oxide (O_2^-). The energy needed to break the covalent bonds of molecules to produce these reactive species comes from plasma electrons and excited species.⁴²⁻⁴⁶ Gas phase radicals produced in the plasma enter the liquid water governed by diffusion and their respective Henry's law coefficients: $p = k_H \cdot c$, where p is the partial pressure above the liquid, c is the concentration in the liquid, and k_H is the Henry's law constant. The plasma also interacts with the liquid water directly generating reactive species at the interface.⁴⁷⁻⁵¹ This complex, interfacial interaction is shown schematically in Figure 3. In this respect, the plasma-liquid interaction is the source of the very same consumables utilized in conventional advanced oxidation, driving a range of advanced oxidation

processes, both chemical and physical. The plasma-liquid interaction offers a number of value propositions relative to conventional advanced oxidation: (1) No consumables are required. Plasmas can be generated in regular air or in the liquid itself;⁵² (2) the decomposition rates have been demonstrated to be superior to chemical methods owing to the vast array of advanced oxidation processes brought to bear in solution; (3) because consumables are not required, the associated consumables cost and infrastructure can be eliminated allowing the method to be applicable for point of use applications; for example, in underdeveloped regions lacking water treatment infrastructure; (4) the application of plasma is inherently modular and can be used as a finishing stage in a conventional water treatment system not unlike a conventional UV stage for disinfection. In this case, however, the plasma's advanced oxidation capability enables both micro-contaminant removal as well as disinfection.

IV. PLASMA SCIENCE OF NONTHERMAL, ATMOSPHERIC PRESSURE DISCHARGES

In general, plasmas generated for water purification (in contact with or within liquid water) are classified as cold, non-equilibrium discharges. Here we refer to plasmas produced at atmospheric pressure where the electron temperature is much greater than the heavy particle temperature, which is typically near room temperature.^{53,54} In such

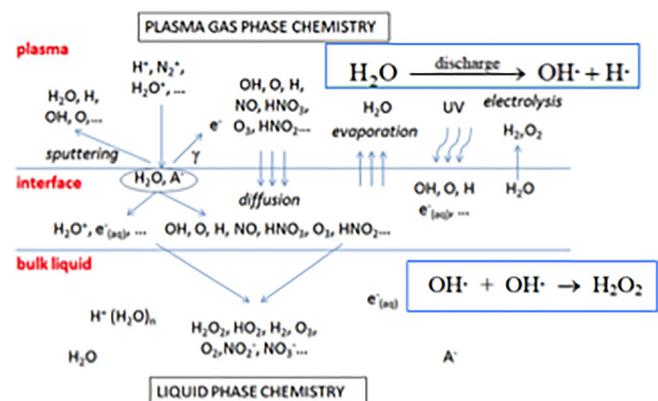


FIG. 3. Schematic depiction of physical processes taking place at the plasma-liquid interface. Reproduced with permission from Samukawa et al., J. Phys. D: Appl. Phys. **45**, 253001 (2012). Copyright 2012 IOP Publishing.

plasmas, electrical energy is channeled primarily to the electrons. Electrons via collisions excite the air, input gas or water vapor, generating copious amounts of UV and reactive oxygen and nitrogen species.^{42,43} Such plasmas have a host of applications ranging from environmental hazard mitigation to plasma medicine to the treatment of soft media.^{55–58} In general, the application of the sparking potential across an air gap (~ 30 kV/cm in 1 atm air) will result in a breakdown that transitions from avalanche to arc or spark if the applied voltage duration is sufficiently long. This transition from nonthermal ionization front to thermal discharge is a consequence of the thermal instability. Here, as the avalanche builds, the electron-neutral collision frequency increases, leading to gas heating and rarefaction of the gas, which in turn leads to an increased electric field to neutral density ratio (E/N). The increased E/N leads to greater electron energy gains between collisions and thus an associated increase in electron temperature. This increase in electron temperature increases the ionization rate, resulting in a runaway condition where, through increases in the electron-neutral collision frequency, the electron and gas temperatures merge. This so-called thermal instability leads ultimately to the formation of the arc discharge.^{53,59,60} To achieve a cold, nonthermal plasma this transition must be controlled. The transition can be mitigated by a number of ways: (1) ballasting, (2) use of dielectric barriers, depicted in Figure 4, (3) use of fast rise time, limited duration (ns) voltage pulses,⁶¹ (4) control of duty cycle, (5) use of electron beams, (6) modification of gas composition (e.g., helium), and (7) increased flow rate to enhance cooling. Perhaps two of the most common methods involve (a) the use of fast rise time, high voltage pulses that terminate (typically nanosecond to microsecond widths) before the avalanche develops into a spark or (b) the use of dielectric barriers on the electrodes, where charge deposition resulting from charge particle flow from the breakdown plasma migrates to the barriers, thereby reducing the interelectrode gap electric field below sparking strength.^{62,63} Figure 4 schematically depicts the operation of a double dielectric barrier discharge with dielectric layers on either electrode.

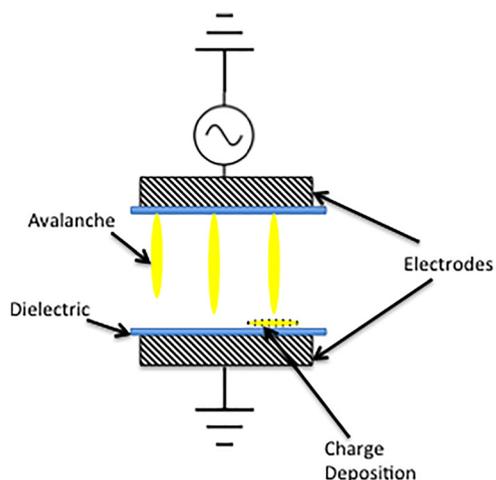


FIG. 4. Schematic depiction of the development of a barrier discharge.

A. The streamer mechanism—basis of nonthermal, 1 ATM plasmas

The basis of most cold, atmospheric pressure plasmas is the streamer discharge, shown in Figure 5. A streamer is a pre-breakdown, self propagating ionization wave that can occur in dielectric media such as air or water provided two conditions are satisfied: (1) the ionization coefficient exceeds the attachment coefficient along the track of the streamer; and (2) the space charge field associated with the avalanche head is of the order of the applied electric field magnitude (e.g., the product of the ionization coefficient and the avalanche length is of order 20—the so-called Meek's condition).^{64,65} A streamer starts as an avalanche. The avalanche is not uniform owing to the reduced mean free path at 1 Atm. The avalanche is instead filamentary with radial dimensions of order of a fraction of a mm. Owing to electron and ion mobility differences in the electric field, the resulting electron and ion charge separation gives rise to space charge formation at the head of this ionization wave. The electric field at the head of the streamer is greatly amplified (several hundred kV/cm) owing to the space charge. This high field drives ionizations upstream of the streamer allowing it to extend itself. Along the track of the streamer, reactive oxygen and nitrogen species form. These species ultimately oxidize organic contaminants in solution. Streamers typically propagate at 10^7 cm/s in air and roughly 10^6 cm/s in water.

V. PLASMA IN CONTACT WITH LIQUID WATER

Putting plasmas in contact with liquid water drives the advanced oxidation in solution. There are a number of ways to bring about this contact as shown in Figure 6.^{43–45,66} Perhaps the most direct way of achieving this end is via the direct discharge approach. Here, electrodes are immersed in liquid water. If the applied electric field of one of the electrodes reaches ~ 1 MV/cm, then a filamentary streamer discharge will form and propagate through the liquid water. The

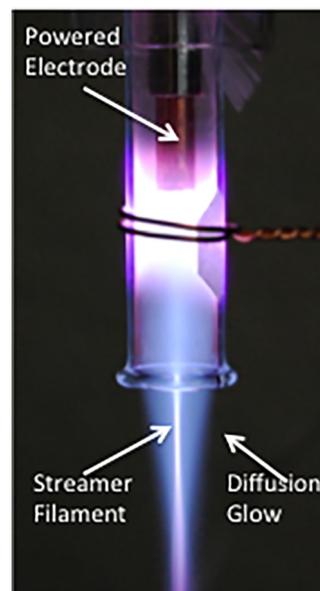


FIG. 5. Streamer discharge driven plasma jet.

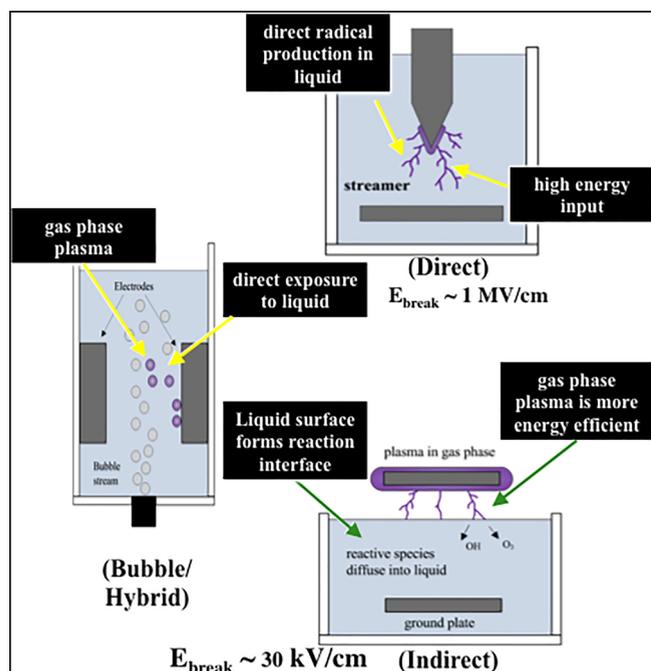


FIG. 6. Methods of bringing plasma in contact with liquid water.

ionization track of the streamer, which is typically multi-branched, is the source of reactive oxygen species. For example, the decomposition of liquid water produces OH and hydrogen. The OH production leads to longer-lived hydrogen peroxide. This direct discharge also produces shockwaves and UV, both of which can drive decomposition and ultimately the destruction of organic contaminants in solution, including microorganisms. A plasma discharge can also be generated just above the surface of the liquid water. This so-called indirect discharge approach relies on the diffusion of plasma-produced species into the bulk solution. Incident electrons on the liquid surface drive OH production. Gas phase species, such as reactive oxygen and nitrogen species, along with hydrogen peroxide diffuse into the water via Henry's law. The voltage required for the initiation of the indirect discharge is reduced in comparison to the direct discharge as plasma is produced in the gas phase, albeit at 1 ATM. The third method is the so-called bubbling method. Here, plasma is produced inside bubbles injected in the water. In this case, bubbles serve as mass transporters of reactive oxygen species. Generating plasma in liquid water monodisperse with bubbles greatly increases the plasma liquid contact surface area.^{43–45} By tailoring the composition of the bubbles, one can also modify induced chemistry. These approaches constitute the basic building blocks of plasma water purifiers.

Plasma properties of these discharges vary depending on whether the plasma is generated directly in liquid water or in air (bubbles or above the liquid). Direct discharges in water tend to possess high channel gas temperatures $\sim 1000\text{--}3000 \text{ K}$ with electron temperatures around 1 eV. These plasmas are also highly ionized and owing to collisionality, local thermal equilibrium (LTE) prevails. Plasma streamers in water produce large amounts of OH radicals and are a source of shockwaves (channel formation and

channel collapse). Plasma densities approach $10^{24}/\text{m}^3$, which translates into ionization fractions approaching 1. Indirect and bubble discharge tend to range in density between 10^{20} and $10^{21}/\text{m}^3$ with electron temperatures in the 2–3 eV range. Gas temperatures for these discharges are typically around room temperature. Ionization fractions are low ranging between 10^{-5} and 10^{-6} . Both discharge types are sources of UV radiation though the direct discharge produces broadband UV.⁶⁷

A. The solvated electron: The fate of plasma electrons in liquid water

Plasma in contact with liquid water invariably leads to the interaction of electrons directly with liquid water. Upon entry into water, the electron rapidly thermalizes via elastic and inelastic collisional processes and is ultimately "solvated." By solvation, we refer to the process by which an electron is captured in a potential well formed by clusters of water molecules. Here the electron resides essentially in a "cage" formed by 6 hydrogen bonded water molecules.⁶⁸ The theoretical binding energy of this "cage" ranges between 1.5 and 4 eV.⁶⁹ At the surface of the water, binding is incomplete and thus the potential well depth is shallower. The solvation process, which occurs on a ps time scale, in part, prevents the development of an avalanche in liquid water. The injected electron quickly thermalizes and forms the solvation complex as depicted in Figure 7. This complex is reactive.⁷⁰ The complex, whose lifetime is \sim microseconds, leads to the decomposition of water molecules: $e^- \rightarrow e_{\text{therm}}^- \rightarrow e_{\text{aq}}^-$ and $e_{\text{aq}}^- + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}_{\text{aq}}^-$.⁷¹ Solvated electron physics is still not well understood. For example, a complete theory explaining the absorption spectra, binding energy, and local electron distribution around a solvated electron does not exist. The presence of solvated electrons modifies water's absorption spectrum, giving rise to the appearance of a broad absorption peak around 700 nm. The binding energy of the solvated electrons has recently been measured via photo-detachment methods.⁶⁹ Here, a laser beam focused on water jet was used to form photoelectrons while a second tunable laser source was used to liberate them so that their energy spectrum could be measured using a time of flight electron spectrometer. The presence of solvated electrons generated by plasma in contact with water has also been measured. In this case a DC atmospheric pressure glow, featuring a pin cathode and a liquid anode (electrolytic

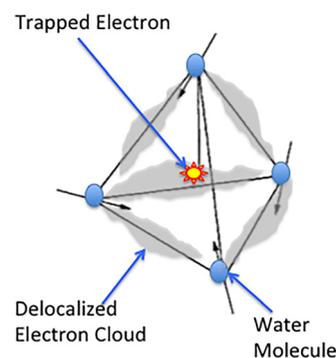


FIG. 7. Artist conception of solvated electron trapped in potential well complex with only 4 of the 6 water molecules shown.

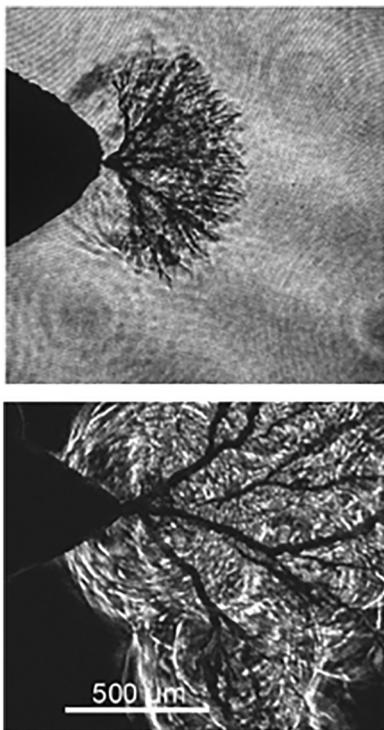


FIG. 8. Shadowgraph images of streamers propagating in water (dark filaments) emanating from pointed electrode. Reproduced with permission from An *et al.*, *J. Appl. Phys.* **101**, 053302 (2007). Copyright 2007 AIP Publishing.

solution), was used to form a plasma attachment on the surface of a liquid water solution. A tunable laser was then used to trace the absorption peak at the point of plasma attachment. It was observed that the solvated electron absorption peak was blue-shifted, suggesting possible a Stark effect shift. The origin of the field producing this shift has not been identified though factors such as ion density and the presence of a local voltage drop (sheath) at the liquid surface may play a role. In that work, an estimated 1 mM of solvated electrons was produced locally in the vicinity of the attachment.⁷²

B. Theories of plasma ignition in liquid water

The direct streamer discharge in liquid water can be observed in a point to plane geometry at fields of order of a MV/cm, which is considerably lower than the threshold field required for the propagation of a direct avalanche in solution.⁷³ The physical mechanism by which streamers form and propagate through liquids is still not well understood.^{74,75} There are a number of compelling theories that have been put forth to date to explain the mechanisms of breakdown in liquid water. The majority of these theories suggest the presence or production of bubbles or a low-density gaseous state as a key prerequisite to breakdown, with the actual discharge forming in this medium.⁷⁶ The discharge itself tends to manifest itself as bush-like disturbance with many branches emanating from the powered electrode as shown in Figure 8. The dark channels in the shadow graph indicate regions of lower density, in contrast with lighter regions of water. Here we briefly review four theories that have been put forth as the physical mechanism for direct breakdown in liquid water. These include: (1) the thermal mechanism, (2) the bubble mechanism, (3) crack or fissure formation, and (4) the nanopore mechanism.

1. Thermal mechanism for breakdown

The basis of the thermal mechanism for breakdown is vapor state formation at the electrode, which can be driven by conduction or dissipation processes at the electrode as depicted in Fig. 9. Because the thermal mechanism involves vaporization, it is typically a slow process (ms to s for mm scale electrodes with few W of power dissipation). The dissipation leading to vaporization can occur via two modes: (1) Ohmic heating in the liquid phase via ion drag and (2) localized heating of asperities on the electrode surface which in turn leads to localized heating of the surrounding liquid. In this case the non-uniform field at the electrode can lead to localized dissipation (S) where $\vec{J}_{cond} = \sigma_{cond}\vec{E} \rightarrow S = \int_o^r \vec{J}_{cond} \cdot \vec{E} dt$. This mode requires some level of conduction in the liquid. This

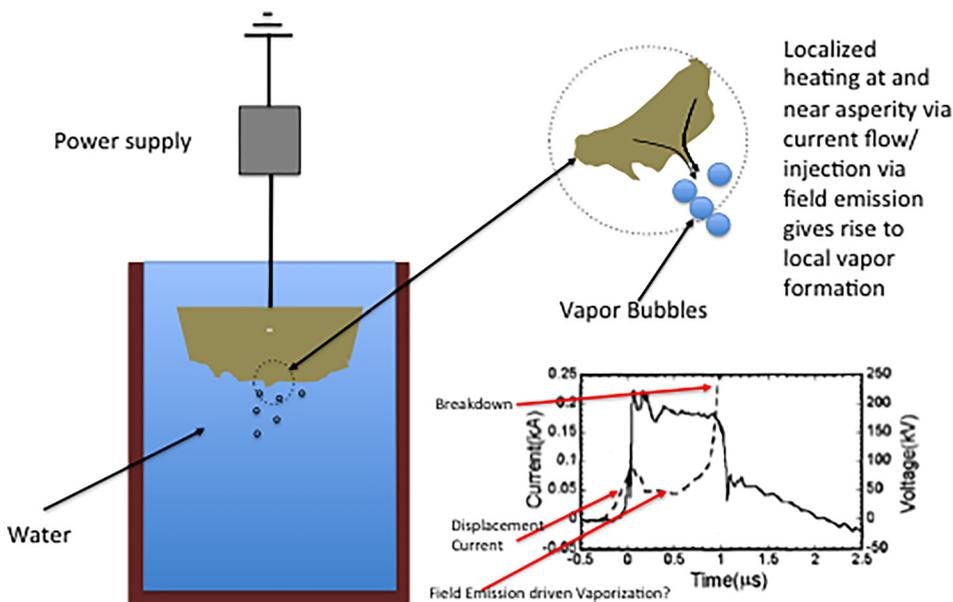


FIG. 9. Thermal mechanism basis for breakdown in water. Reproduced with permission from Lisitsyn *et al.*, *IEEE Trans. Dielectr. Electr. Insulation* **6**, 351 (1999). Copyright 1999 IEEE Publishing.

type of heating is associated with the real part of the complex permittivity. Even if electrical conductivity is small, the local electric field can be substantial, giving rise to the localized heating.^{77–79} If this deposited energy minus conduction losses exceeds the heat of vaporization for water driven to 100 °C, then vapor bubbles will form. There is a spread in the reported energy per pulse for such discharges ranging from a few mJ to 1 J per pulse.^{80–83} Another mechanism for localized vaporization and plasma formation is the heating of asperities on the surface of the electrode followed by an explosive release of electrons, vapor, and plasma. This so-called “ecton” mechanism is akin to that observed in cathode spots.^{84,85}

Lisitsyn and colleagues studied the waveforms and optical field near the tip of the powered electrode in a coaxial pin to plane configuration.⁸⁶ In this work, a detailed analysis of the current waveform was carried out. The results showed that the pre-discharge current and voltage (Fig. 9) was consistent with the input power required to vaporize the surrounding water to form the streamer. The evaporation rate can be converted into the power required for initial streamer channel formation: $P = H_{vap} \cdot \pi r^2 \cdot v \cdot \rho_w$, where H_{vap} is the heat of evaporation, v is the streamer velocity, ρ_w is the density of water, and r is the radius of the streamer. Power measurements via analysis of the pre-discharge waveform were in excellent agreement with this relatively simple calculation. In this respect, ignition occurs via localized vaporization effects and once the streamer forms, it is the plasma flow from the streamer into the surrounding water that provides the low-density volume to propagate.

Strong experimental evidence along with accompanying computational analysis supports the thermal mechanism for breakdown in highly conductive solutions such as saline. Schaper and colleagues investigated plasma formation at the surface of a powered electrode immersed in a saline solution (~0.9% NaCl in distilled water).⁸⁷ This work focused on understanding plasma formation mechanisms in saline solution for medical applications. The discharge geometry was essentially pin-to plane, with all but the tip of the pin covered in dielectric. The voltage pulses were up to –500 V with 20 ns rise times and widths up to 10 ms. No working gas was injected into the gap. In this work, it was found that the discharge formation occurred in stages. At early times <5 μ s, double layer formation was observed. Subsequent to the double layer formation, a regime where the discharge current was relatively constant was observed. This stage, lasting for a fraction of a ms, was attributed to Ohmic heating leading to vapor formation around the electrode. The vapor formation time was dependent on water initial temperature, with the electrode attaining fully vapor coverage in a shorter time period if the starting water temperature is higher. The formation of the vapor layer was correlated with the waveform using time-resolved shadowgraphy, which indicated vapor thickness and coverage. With vapor coverage, the current drops as much of the electrode tip is insulated from the conductive fluid. The subsequent voltage rise across this insulating vapor layer ultimately ends in the breakdown and the associated formation of microdischarges. Figure 10 illustrates the current and voltage variations observed along the way to breakdown. In this work, the time dependent heat

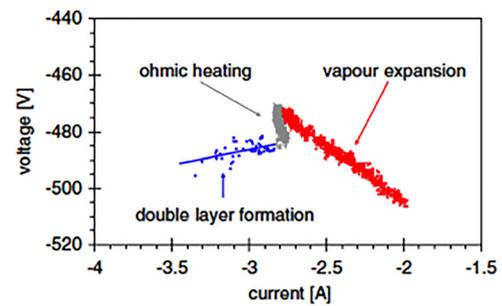


FIG. 10. Current and voltage response of electrode immersed in saline solution just before breakdown. Reproduced with permission from Schaper *et al.*, *Plasma Sources Sci. Technol.* **20**, 034003 (2011). Copyright 2011 IOP Publishing.

conduction equation was solved for the region near the electrode to predict the theoretically expected vapor layer formation using COMSOL. It was found that the simple model was in general agreement with the observed vapor layer formation. In summary, it was found that localized superheating of the liquid in the vicinity of the electrode ultimately creates a low-density vapor region. When the local E/N is sufficiently high, gas phase, short-lived streamers are formed. In this respect, the discharge forms locally in a low-density medium.^{87,88}

Similar vapor bubble formation has been observed in a coaxial dielectric barrier discharge (DBD) underwater discharge without gas injection.^{52,89} In this case, the water was deionized with a starting conductivity of ~6 microsiemens/cm. Vapor bubble formation and subsequent plasma formation was observed to occur on a millisecond time scale. Because the bubbles are observed to form at the electrode tip at early times, it is clear that electrode processes likely play a role. In this case, the electrode is ac excited between 4 and 5 kHz.

2. Bubble mechanism for breakdown

The thermal mechanism is supported by experimental observations for long pulses. For pulses of duration below a microsecond, however, localized heating is too slow to render the medium locally to the vapor state.⁹⁰ Bubbles in solution however need not be thermally derived. Water in its natural state contains dissolved gas. Additionally, it has been postulated that it is possible for micron-sized bubbles to stably exist in liquid water.⁹¹ A monodispersion of such bubbles in liquid water can explain a wide array of observed breakdown related physical processes in water, such as streamer branching and streamer luminosity spots. Indeed, Monte Carlo simulations carried out by Joshi and colleagues suggest that breakdown in microbubbles is a compelling mechanism leading to discharge ignition in liquid water.⁹² Joshi *et al.* were also able to show that electric field enhancement at the electrode could initiate field emission, which in turn could ignite discharges in microbubbles. In that work, Joshi *et al.* showed that the source of the electric field enhancement at the bubble is associated with large reductions in the dielectric constant in the medium. In this case, field enhancement naturally occurs near the electrode independent of surface roughness.⁹³ This enhancement is a consequence of localized water polarization, which leads to a field enhancement at the boundary. In fact, based on this

model, the field enhancements are sufficient to locally reduce the dielectric constant, thereby further enhancing the local electric field, increasing the likelihood of field emission. Qian and colleagues further assert that it is this field emission at the electrode or at the bubble-liquid interface that gives rise to nascent electrons that drive the avalanche process in the bubbles.⁹⁴ In this case, the postulated microbubbles themselves are therefore the source of electrons and localized breakdown. Liquid streamer branching, current spikes, and pressure effects are explained by this theory. For example, following breakdown, the resulting electric field collapse gives rise to increased electric field in adjacent bubbles. This leads essentially to what would have the appearance of discharge hopping from one bubble to the next. The so-called streamer hopping phenomenon suggested by Qian and colleagues is supported by simulations that were later carried out by Babaeva and Kushner.⁹⁵ Here, the electric field and UV photon emission from a streamer propagating in an adjacent bubble is of sufficient magnitude to initiate breakdown. The process repeats itself—hopping from bubble to bubble as depicted in Figure 11(a).^{95,96} Secondary processes such as bubble shape distortion, which can enhance the electric field locally, can also contribute to the bubble hopping mechanism.^{97,98} There exists experimental evidence in support of this mechanism. The initiation of breakdown of an isolated bubble (ultrasonically trapped) near (but not in contact with) a streamer has been observed by Sommers and Foster as depicted in Figure 11(b).⁹⁹ Here, presumably field and photon flux from the streamer initiate breakdown in the isolated bubble.

3. Crack mechanism for breakdown

Lewis suggests that a low-density phase in liquid water can be produced by the so-called crack formation in direct analogue to fissure formation in solids under stress. In general, in liquid water, the water molecules are not densely packed, but rather a large part of its volume actually consists of voids (molecule volume to space occupied = 0.49).¹⁰⁰ In

this case, the electric field-derived ponderomotive-driven mechanical stress essentially “unzips” the liquid water producing a fissure of connected voids—essentially an extended “crack” region.¹⁰¹ The large field for crack formation can be estimated given that the theoretical tensile strength of water is 10^8 Pa.¹⁰² Equating this to the electric field pressure, one finds that the local field required “unzip” water must be at least of the order of 5 MV/cm. Here, the electric field effect on the local dielectric constant is ignored in this estimate. As is observed in fissure formation in dielectric media, it is posited that charges exist in the fissure just as that which occurs in solid fissures. The combination of the free charge and applied field in the void gives rise to the formation of a propagating streamer. Indeed, the characteristic length scale of the cracks (10^{-7} m) combined with the field strengths of interest (10^8 V/m) has the potential to accelerate electrons to near the ionization potential (~ 10 eV). The short time scale of streamer development is postulated to be related to fluctuation in the population of the voids formed under electric field-driven stress. In this case, the ignition pathway is fissure formation followed by streamer inception. Anode and cathode-directed streamers can be explained at least qualitatively with the crack model. In either case, space charge enhances the local electric field, essentially seeding the growth of new cracks, taking on a mushroom-like appearance akin to that observed in underwater streamer discharges (e.g., Fig. 8). Very high-resolution optical diagnostics will be required to test this potential breakdown mechanism.

4. Nanopore mechanism for breakdown in water

The aforementioned theories all hinge upon the production of a low-density state in order for breakdown to develop. Lewis’s crack theory involves the formation of low-density channels for streamer development and even the formation of bubbles at the ends of fissures that allow for continued streamer propagation. The development of a discharge in the liquid water itself has largely been dismissed owing to the high collisionality and the extremely short solvation time of an injected electron. Recently however, the prospect of bubble-free ionization in the liquid state has been proposed. This mechanism requires the application of high voltage, sub-nanosecond pulses.¹⁰³ With such a short pulse, it is possible that local to the electrode, a region monodisperse with nanopores or ruptures in the liquid water can be formed via electrostriction. If the local field is high enough, the condition for streamer formation can be satisfied in the nanopore. Electrons in the nanopore can be accelerated to energies necessary to ionize water at the interface and drive an avalanche in the liquid between nanopores. A requirement for this mechanism is that the pulse rise time on the electrode be shorter than the pressure equilibration time—which determines the lifetime of the pores. Experimental evidence suggests that this mechanism is possible.¹⁰⁴ In some respects, the distribution of nanopores is likened to the cracks and voids formed under electrostriction forces described in the Lewis theory. The theories differ in that in the crack theory, the streamer is essentially confined to the field-induced fissure.

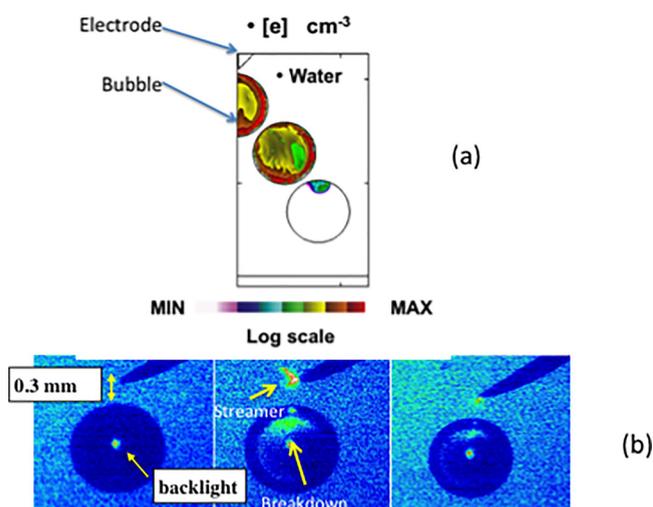


FIG. 11. (a) Streamer hopping from bubble to bubble and (b) experimentally observed streamer to bubble hopping event. Reproduced with permission from Sommers and Foster, *J. Phys. D: Appl. Phys.* **45**, 415203 (2012). Copyright 2012 IOP Publishing.

VI. DEMONSTRATION OF FUNCTION

To date, there exists a large number of published studies demonstrating the efficacy of plasma discharges for the purpose of water decontamination. These studies have focused on a wide array of contaminants. Many of these tests, particularly the early tests, focused on recalcitrant dyes, such as those used in the textile mills. Decoloring dyes using plasma methods show directly observable effects such as the transformation of a colored solution to a clear one, as shown in the plasma treated methylene blue solution in Figure 12. From an environmental standpoint, textile dyes represent a significant pollution problem particularly in underdeveloped countries.^{105–107} Such dyes can become carcinogenic when assimilated in the ecosystem.¹⁰⁸ There is therefore a big push to decompose such dyes efficiently. An early study of the effectiveness of a plasma discharge in water to decompose dyes was reported by Clements *et al.*¹⁰⁹ In that work it was shown that bubbling oxygen into the discharge, which produced ozone, resulted in increased decomposition. Since that work, a number of researchers have reported on the effectiveness of plasmas in the decomposition of a range of dyes.^{84,110–114} Organic micro-pollutants, such as the aforementioned CECs found in drinking water and waste water, are currently of concern. Advanced oxidation methods can be used to remove these contaminants. Advanced oxidation, driven by plasmas, has demonstrated the capacity to remove a range of these contaminants as well. In a number of these works, phenol, which contains an aromatic ring, has been used as a surrogate for more complex organics to test decomposition effectiveness by plasmas.^{115–119} Hazardous chemicals in water have been directly decomposed by plasmas as well. These include pesticides, dioxin, PCP, and TNT.^{120–123} Jiang *et al.* reviewed the application of plasma discharges for the removal of pollutants in waste water including pharmaceuticals.¹²⁴ In small-scale experiments, it has been shown that plasma-driven advanced oxidation can decompose a range of contaminants of emerging concern, including BPA—the cancer causing contaminant in some plastics, personal care products as well as pharmaceuticals (antibiotics, anticonvulsants, contrast media, hormones, anti-hypertensives, and analgesics).^{125–127} Magureanu *et al.* point to the need to be able to identify intermediates that form during plasma advanced oxidation so as to enable the assessment of toxicity.¹²⁸ Complete mineralization of the compound is desired ideally. Advanced oxidation is relatively indiscriminant and thus can be used to degrade biological-derived molecules as well. Advanced oxidation can therefore disinfect through the degradation of bacteria and viral particles. Here,



FIG. 12. Plasma-driven decomposition of methylene blue dye.

the cell membrane and cellular genetic material are attacked by reactive oxygen and reactive nitrogen species.¹²⁹ Dors *et al.* showed that *Escherichia coli* laden river water could be sterilized using plasma.¹³⁰ Liu and colleagues utilized a direct current discharge in liquid water to remove *Staphylococcus aureus* in solution.¹³¹ Microcystin, a hepatotoxin, produced by cyanobacteria can also be degraded by plasma methods.¹³² This toxin is of concern to the drinking water plant managers because conventional methods do not directly address this toxin, as demonstrated with the imposition of a brief water ban in Toledo, Ohio, in 2014.¹³³

A. Decomposition efficiency

As mentioned previously, the plasma–water interaction can be made in at least three fundamental ways. The question that naturally arises is of course which one is most efficient. Because plasmas can decompose a wide array of organic contaminants, the question must be narrowed to a specific contaminant as a comparison reference for the various methods. Additionally, a suitable metric to quantify the efficiency is also required. An attempt to answer this question was made by Malik.¹³⁴ It turns out that a large number of past plasma decomposition studies have featured organic dyes as the test contaminant. It has been observed that decomposition interference due to competition with intermediates (decomposition by-products) is minimal with dyes, making it a reasonable test chemical for efficiency comparison. Malik then defined a decomposition efficiency: the power required for a 50 percent reduction in contaminant level measured in grams per kW hour. This investigation found that those plasma reactor geometries that feature the interaction of thin layers of water or water aerosol (mist) with plasma were the most efficient, likely resulting from significant reactive oxygen species loading into these thin layers. While this realization does point to practical reactor designs, those designs would have a inherently low throughput because the water is injected via low mass transport methods. Furthermore, while the specialized efficiency parameter used in this work is suitable for comparison purposes within the plasma treatment community, the conventional advanced oxidation water treatment community quantifies efficiency in terms of the electrical energy required to reduce a contaminant one order of magnitude.¹³⁵ It is recommended that future plasma water purification studies utilize this unit for direct comparison with conventional advanced oxidation water treatment methods.

VII. PLASMA REACTOR FIELD TESTING

As mentioned earlier, plasma-based water purification methods have demonstrated performance superior to conventional advanced oxidation methods for small treatment volumes, typically less than a few liters. Why then have such systems not been integrated into water treatment systems? The key problem is throughput and treatment volume. Scale up has proven to be quite elusive for plasma-based water purifiers. Water treatment systems for municipalities process treatment volumes at a rate of order 1000 gallons per min. The average American family uses roughly 400 gallons per day.¹³⁶ For practical applications such as this or even low

throughput, specialty industrial waste water pretreatment needs, a plasma purifier must be able to process water within this flowrate range. Conventionally, 5 gallons/min can be taken to be the threshold to be useful in a practical sense. Here at these flow rates the plasma must inject advanced oxidation doses comparable to conventional advanced oxidation methods. For example for the advanced oxidation hydrogen peroxide-ozone treatment method, doses of 1–5 mg/l of ozone with 5 mg/l of hydrogen peroxide are required.¹³⁷ Meeting or exceeding this lower throughput limit has proven elusive. The throughput problem is related to the plasma-liquid interface problem. Reactive species must diffuse into the bulk solution to process contaminants. These rates tend to be slow which in turn means water flow rates have to be correspondingly slow for adequate contact time.^{138,139} Methods that increase the diffusion rate and surface dose of reactive species can greatly enhance the performance of plasma reactor. Once this hurdle has been surmounted, the devices must demonstrate economic feasibility. Additionally, water treatment costs must be comparable with that of conventional methods. In the USA, the cost for conventional drinking water treatment is currently around 2 dollars per 1000 gallons.¹⁴⁰

Despite scale-up challenges, in recent times a number of plasma purifier ventures have been initiated in an attempt to commercialize plasma water reactors. In general, after laboratory demonstration, the next step toward commercialization is the demonstration of the approach in relevant environment under relevant conditions. This so-called piloting approach involves the operation of the reactor at a water treatment facility using actual effluent for the direct treatment. One notable piloting demonstration was carried out by Aquapure.¹⁴¹ The Aquapure reactor design is faithful to the recommendations suggested by Malik.¹³² Here, a thin layer of wastewater effluent is subjected to a surface barrier discharge. Water flows under the plasma discharge assemblies in conveyer belt-like fashion. Reactive oxygen species are produced both in the gas phase and at the liquid-plasma interface. In the Aquapure piloting exercise, the reduction in two contaminants was demonstrated at two wastewater treatment facilities: Aerojet General Corporation and the Southern Nevada Water Authority. The tests targeted trichloroethylene (TCE), a toxic industrial solvent and methyl tertiary butyl ether (MTBE), a gas additive. It was found in that work that the plasma system was more efficient than the conventional UV-hydrogen peroxide advanced oxidation method both in energy required to reduce the contaminant level in 1000 gallons of wastewater by one order of magnitude and in cost. This piloting test, which demonstrated function, was largely successful with treatment flows ~few gallons/min. Symbios markets a plasma reactor for water treatment that features a multiplicity of low current arcs.¹⁴² Figure 13 depicts the operation of this device. The device features a rotating shaft of air-fed cathode potential nozzles. As water flows through the device, an arc is struck between the cathode potential nozzles and the cylindrical, grounded enclosure (anode). The arcs form in the unsteady bubbles that essentially bridge the gap. The rotation serves two functions: (1) prevention of localized deposition of cathode material onto the anode which would otherwise lead to

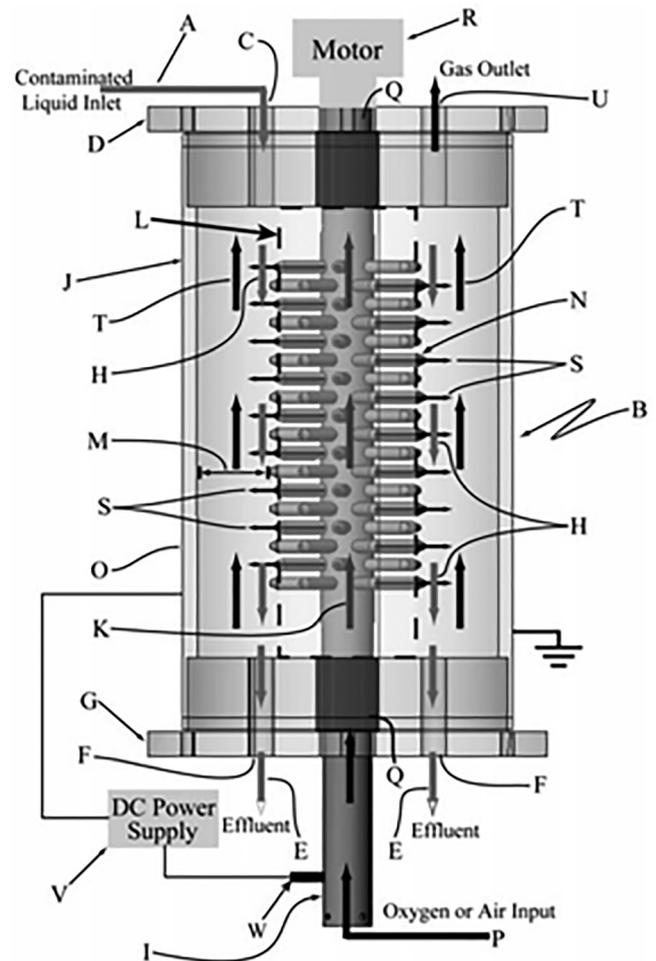


FIG. 13. Symbios water treatment reactor depicting rotating cathode shaft (H). Reproduced with permission from Johnson *et al.*, *Desalination and Water Treatment* **57**, 8097 (2016). Copyright 2016 Taylor and Francis Group Publishing.

preferential arcing in one location and (2) liquid agitation, which enhances mixing. Typical operating discharge voltages range between 600 and 900 V with total current of few Amps. Rotation speeds are in the 1000 Hz range. The unit in static (not flow through) configuration was used to achieve a 6 Log reduction in a solution of water containing *Acidithiobacillus ferrooxidans*, a sulfate reducing iron pipe biofouling bacteria (leads to pipe corrosion). Pellucid Water LLC markets a plasma water treatment device based on the dense plasma medium reactor.¹⁴³ This unit features a rotating plasma applicator as well. Discrete plasma discharges form between the rotating head and the return electrode. The revolution of the plasma filaments generates a quasi-continuous shell-like volume of plasma. The more densely packed the filaments, the closer to the idealization of a dense plasma medium. The inventors assert that precipitation is the dominant contaminant removal mechanism rather than advanced oxidation. In this approach, the sediment resulting from the plasma treatment can then be removed by conventional filtration. NASA has also developed a plasma water treatment method featuring an underwater plasma jet. The device is essentially an air fed coaxial dielectric barrier discharge. The water plays the role as the additional dielectric

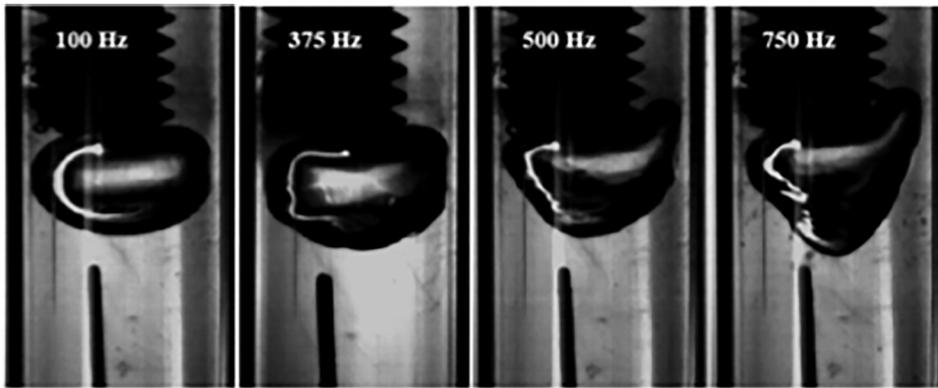


FIG. 14. Streamer propagation along bubble water interface. Reproduced with permission from Sommers *et al.*, *J. Phys. D: Appl. Phys.* **44**, 082001 (2011). Copyright 2011 IOP Publishing.

barrier. Plasma production in the bubble formed at the exit nozzle of the device well as through plasma contact with the liquid-gas interface produces reactive oxygen species. This technology is currently being field tested by interested, potential users.¹⁴⁴ A multi-layer barrier discharge reactor with the water to be treated serving as the dielectric layer is also currently being investigated as an approach that addresses throughput.¹⁴⁵ It should be pointed out that currently numerous ventures investigating the possibilities of plasma based water purification are being explored in diverse areas ranging from industrial wastewater pre-treatment to the treatment of hydraulic fracturing waste water.

VIII. RESEARCH DIRECTIONS

The physical processes taking place at the boundary between the plasma and the liquid water are not well understood. It is the general belief that the physical processes prevailing there is key to understanding how plasma-induced reactivity is transmitted into the bulk liquid.⁶⁷ This understanding is key to understanding and ultimately optimizing the performance of plasma reactors for water purification. Progress in understanding this region lies in the fact that interrogating this region is inherently difficult. The presence of the water all but eliminates electrostatic probes. The intervening water makes optical diagnosis of the interfacial region difficult. Compounding matters is the plasma-induced fluid dynamical effect, which makes the interfacial region unsteady. Fluid dynamical, plasma, and chemical effects need to be tracked simultaneously to obtain a full picture of production and subsequent transport. In an attempt to understand interfacial processes, single bubble studies have been implemented. This approach is reasonable since many plasma reactors feature plasma production in bubbles. Streamers formed in bubbles in liquid water tend to propagate along the interface of the bubble. This is illustrated in Figure 14, which shows a propagating streamer on an electrode-attached bubble despite bubble shape changes. This interfacial propagation is a consequence of the differences in dielectric constants of the water and the air. The electric field tends to refract toward the region of the lower dielectric constant. The electric field is therefore amplified at the interface, where the normal component of the electric field follows from: $\hat{n} \cdot (\epsilon_{water} \cdot \vec{E}_{water} - \epsilon_{air} \cdot \vec{E}_{air}) = \sigma_f$. Note that charge deposition, σ_f , associated with the plasma can

further enhance this effect. Tian and colleagues have modeled plasma propagation along the interface as well as the production of reactive species at the interface.⁵¹ Such simulations feature a fixed bubble boundary. In general, the spherical shape of the bubble is a consequence of the balance between surface tension and internal bubble pressure. The surface tension provides the restoring force to any interfacial perturbation. If the interface is perturbed, a bubble will oscillate at a characteristic frequency called the Minnaert frequency, named after Minnaert who first formulated this resonant frequency: $\omega_m = \frac{1}{R_0} \sqrt{\frac{3\gamma p_0}{\rho}}$. So the interface is actually not static, but rather in constant motion. The application of a time varying electric field will drive both shape and volume mode oscillations as well. Here, electrohydraulic forces distort the interface. The various modes can be found by solving the Rayleigh–Plesset equation, which yields spherical harmonic solutions. Interfacial capillary wave propagating modes are also possible as well.¹⁴⁶ The motion of the interface is important in that such oscillations affect not only the local electric field at the bubble and thus breakdown, but because both internal pressure and surface area change during forced oscillation (both volume and surface capillary wave modes), mass transport is affected, which in turn has implications for the delivery of reactive species into solution.^{147,148}

In addition to local fluid dynamical effects at the interface, it is known that plasma in contact with liquid water can also drive large-scale convection patterns in solution.^{147,149–151} The origin of this convection is still not well understood. Figure 15 illustrates convection driven patterns in liquid water under the influence of a plasma jet. The convection patterns flow direction was acquired using laser scattering

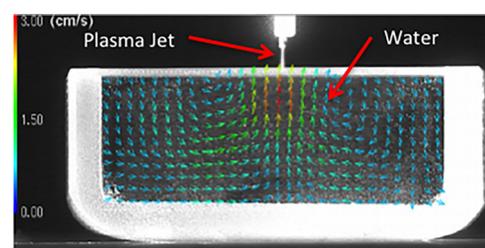


FIG. 15. Particle velocity imaging (PIV) of convection in water induced by plasma jet impingement. Reproduced with permission from Shimizu *et al.*, *New J. Phys.* **13**, 053025 (2011). Copyright 2011 IOP publishing.

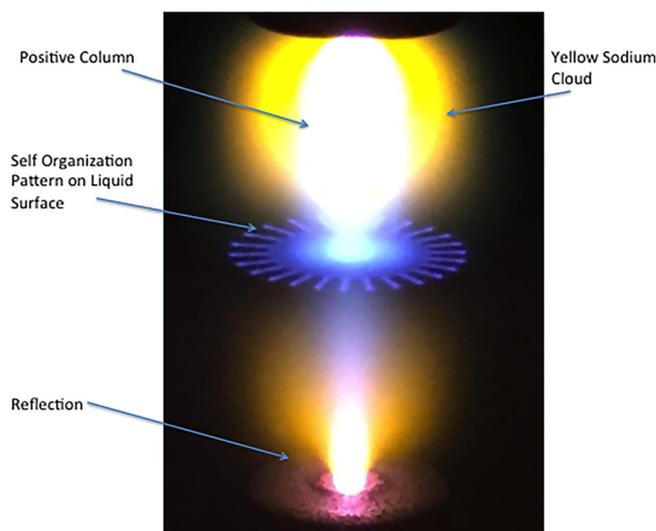


FIG. 16. In-house photograph of a self-organization pattern formed on the surface of a liquid water anode in an atmospheric pressure DC glow.

methods. Such induced convection can greatly enhance the flow of reactive species into the bulk solution. In so-called DC atmospheric pressure glows, a plasma can be formed between an electrode and the surface of an electrolytic solution where a grounded electrode is immersed.^{53,152} In such discharges, large-scale convection is also observed. Such plasma at the surface also tends to self organize into a moving, patterned plasma attachment as shown in Figure 16.^{153–157} The effect of non-uniform plasma attachments combined with the induced convection influences mass transport as well.

As mentioned earlier, the physical processes taking place at the interface are difficult to assess in practice. In order to elucidate the physical processes taking place at the interface, a 2-D bubble apparatus has been investigated.¹³⁸ In this case, a flattened bubble in liquid water is formed and trapped between two quartz plates. Internal to the trapped bubble is a central electrode excited with ns, high voltage pulses that initiates plasma formation into the bubble. The

plasma-liquid interface and the surrounding fluid are amenable to interrogation by optical diagnostics, such as emission/absorption spectroscopy, schlieren, and particle velocity imaging (PIV) diagnostics. Additionally, by doping the liquid with colorimetric chemical probes, one can track the transport of radicals from the bubble interface into the solution.

It is interesting to note that based on such studies, the rate of reactive oxygen species propagation into the bulk solution is highly dependent on the type of plasma present in the bubble or more generally the type of plasma in contact with the interface. If the plasma is locally produced at the central electrode, then reactive species must diffuse to the bubble interface and enter the solution in accordance with Henry's Law. Such a discharge and the resulting diffusion of radicals in water doped with a pH sensitive solution (methyl orange) is shown in Figure 17(a). The solution darkens as the pH is reduced due to the transport of reactive nitrogen species (e.g., NO_3) that leads to acidification.¹⁵⁸ The transport rates inferred from experiments such as this match in magnitude those predicted in 1-D diffusion models.⁴⁷ It was found that if a streamer discharge is formed in the 2-D bubble and makes contact with the interface, the interface is significantly perturbed. The motion of the acidification front which indicates the transport of reactive species into solution is much more rapid. This appears to be a consequence of fluid dynamical effects that lead to large-scale circulation in solution as can be seen in Figure 17(b). The velocity flow field induced at the interface due to the presence of a streamer discharge in the bubble was also measured using PIV as shown in Figure 18, which indicates significant velocity shear at the interface. The origin of the force leading to this shear is not known at this time. It is this force that drives the enhanced transport. These effects ultimately determine the efficiency of the plasma reactor. The importance of including such convection effects in modeling plasma-liquid interactions was illustrated by Lindsay and colleagues.⁴⁹ They were able to show that by

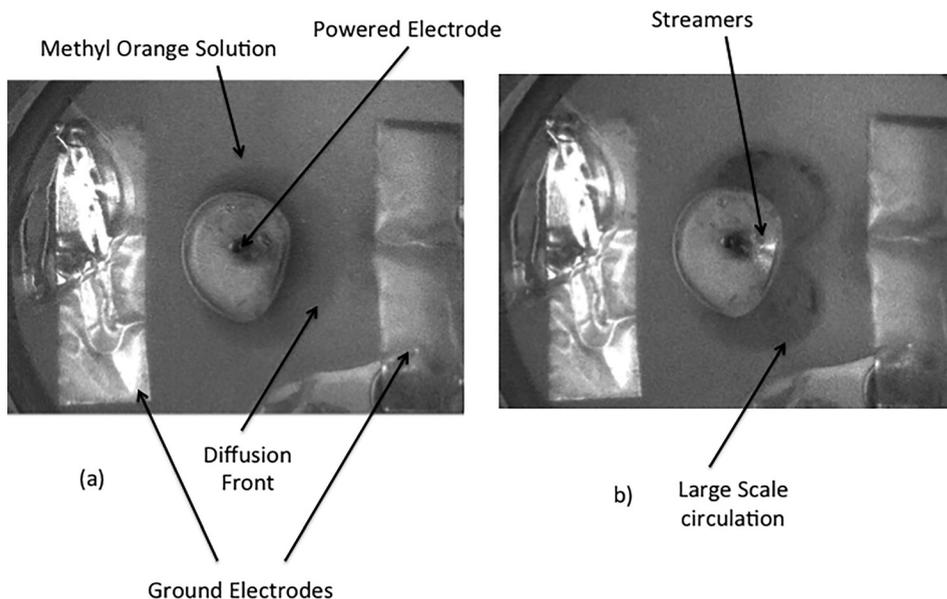


FIG. 17. Response of reactive species transport in 2-D bubble apparatus operating with (a) discharge localized at the central electrode and (b) with streamer discharge that emanates from central electrode and terminates at the interface.

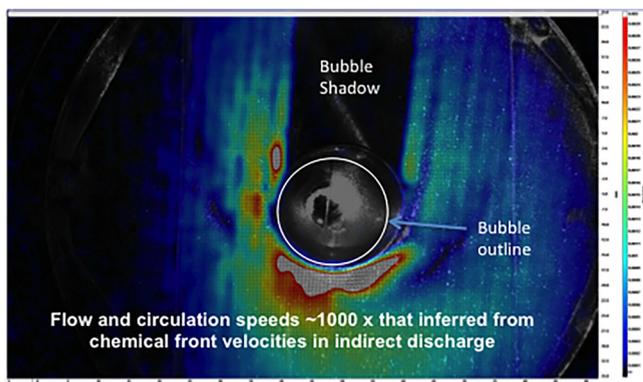


FIG. 18. PIV image of the induced velocity flow field in liquid water in 2-D bubble apparatus driven by streamer action at the bubble interface.

adding convection to the model, the uptake of hydrophobic species greatly increased. Additionally, the spatial distribution of radicals is greatly affected by the presence of solution convection as illustrated dramatically in Figure 19. These findings clearly show the importance of fluid effects.

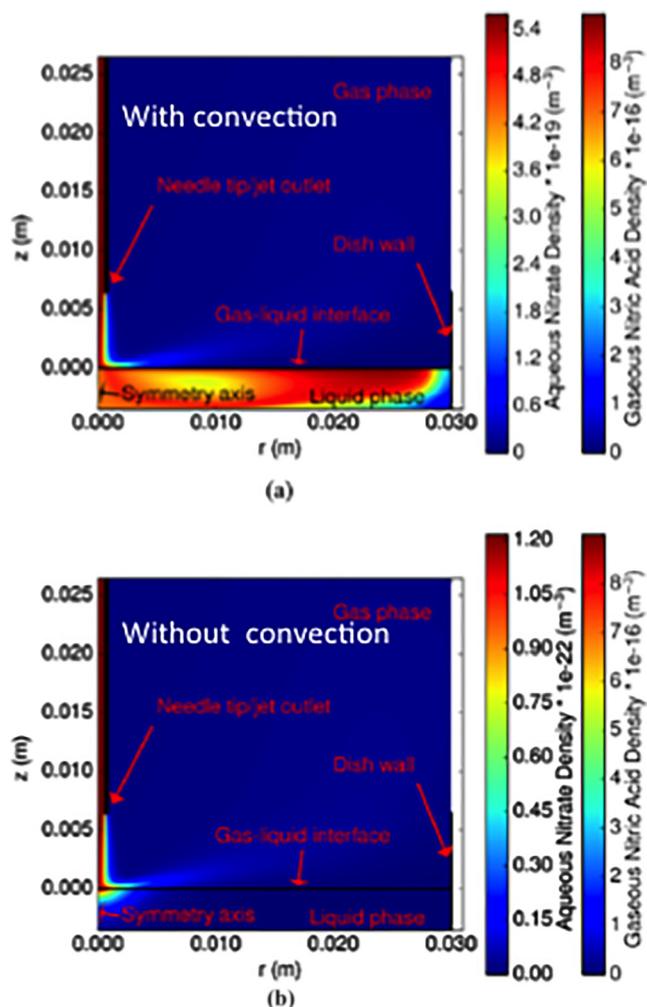


FIG. 19. Spatial Distribution of nitrate ion concentration in solution with and without convection included in model. Reproduced with permission from Lindsay *et al.* J. Phys. D: Appl. Phys. **48**, 424007 (2015). Copyright 2015 IOP Publishing.

IX. DIAGNOSTICS ADVANCES

Broadly speaking, gas phase diagnostics of atmospheric pressure plasmas has advanced considerably over the past 10 years. These diagnostics are primarily optically-based featuring emission and laser absorption. It is now possible to measure plasma density, gas temperature, and electron temperature of these cold plasmas.¹⁵⁹ Plasma density can be assessed using Stark broadening or Thompson scattering. Gas temperature is typically obtained from either nitrogen or OH molecular emission. Electron temperature has also been measured using Thompson scattering. The gas phase plasma contributes to the flow of reactive oxygen and nitrogen species into the liquid. The magnitude of these fluxes can be obtained optically as well. OH, peroxide, NO, and other radicals can be measured in the gas phase using laser-induced fluorescence. A thorough review of these optical techniques can be found elsewhere.^{159–164}

Advances in liquid-phase diagnostics have lagged behind the gas phase tools. In the liquid phase, chemical probes are typically used to assess species concentration. Dye decomposition studies suggest that spectrophotometry can faithfully match mass spectroscopy measurement of chemical breakup.¹¹⁴ On the other hand, while there exist chemical probes that can measure species concentration of important radicals such as NO₃, hydrogen peroxide, OH, and ozone, it is not clear at all how well the response of these probes map with actual species concentration. The plasma-activated solution is complex and can even attack the probes. Resolution of this question is key to obtaining a fuller understanding of plasma-induced chemistry in liquid water.

X. CONCLUDING REMARKS

Plasma-based water purification as demonstrated in small-scale experiments clearly illustrates the promise of this technology. Scale-up remains perhaps the biggest challenge. A better understanding of the physical processes taking place at the interface and how to best control them are key to further advances in reactor efficiency. For example, radical transport and production rates in the bulk solution are not well understood. Fluid dynamical effects are clearly important as they determine transport rates. Electric field-driven effects have not sufficiently been explored either in regards to local transport or even field-driven decomposition of water. Plasma-driven water purification is an advanced oxidation method. The fate of intermediates is not clear. The production of unwanted products is to be avoided in general. This is a more general question that faces advanced oxidation methods overall but it is one that requires additional exploration. To gain insight into these complex processes it is important that models take into account not only relevant chemistry but also fluid dynamical effects. Such modeling efforts should be coupled to simplified experiments to isolate and ultimately elucidate salient physics. The future of plasma-based water treatment will depend on parallel efforts of fundamental studies along with exploratory piloting activities, which together address key issues head on. In closing, plasmas in liquid water is a challenging arena including non-equilibrium physics with all the states of matter involved,

one that has the potential to revolutionize the way we treat water. In this regard, the potential and outlook of this technology is bright.

ACKNOWLEDGMENTS

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