PAPER

Self-organization in 1 atm DC glows with liquid anodes: current understanding and potential applications

Self-Organization in 1 atm DC Glows with Liquid Anodes: Current Understanding and Potential Applications

John E. Foster*, Yao E. Kovach*, Janis Lai* and Maria C. Garcia**

* Department of Nuclear Engineering and Radiological Sciences, The University of Michigan, Ann Arbor 48109, USA
**Department of Applied Physics, University of Cordoba, Ed- C2, Campus de Rabanales, Córdoba, 14071, Spain

Abstract

Self-organization refers to the spontaneous generation of spatially or temporally organized patterns in an otherwise disordered system. Self-organization is ubiquitous in plasma physics particularly in the low-pressure regime as observed in astrophysical jets or plasma loaded flux loops that form on the surface of the sun. In recent times, self-organization in atmospheric pressure plasmas has captured the attention of researchers. Its occurrence has been observed in DBD discharges as well as DC 1 Atm glows with liquid electrodes. The mechanism of pattern formation is still not well understood. Here we briefly review the current understanding of pattern formation in DC glows with liquid anode, surveying past work, application areas, theories on mechanisms of formation from the context of reaction diffusion systems, current experimental work and computational progress towards predicting pattern formation.

I. Introduction

Self organization is characterized as the spontaneous and willful appearance of spatial, temporal or spatiotemporal patterns in physical systems consisting of few or many parts. Self organization occurs in many physical systems. For example, the spots on a leopard, the organization of schools of fish or flocks of birds, the geometry of the bronchial tree of the lungs, aeolian sand dunes, the hexagonal cloud pattern at Saturn's north pole as depicted in figure 1a, and Jupiter's Great Red Spot are all commonly observed self organization patterns.[1,2,3] A key attribute of such organization is that its occurrence manifests due to intrinsic microscopic processes. The appearance of self organization in plasma systems is also ubiquitous. At present no formalism has been developed to address self organizing systems generally, rather analysis is typically carried out on a case by case basis. However, there are a number of commonalities observed in essentially all self organizing systems.[2] It typically occurs in systems driven far from thermal equilibrium or in continuous flow systems with an autocatalyst.[4] Indeed, non-equilibrium thermodynamics is used to study self organizing systems.[5] Here thermodynamic state variables are used to approximate the state and evolution of

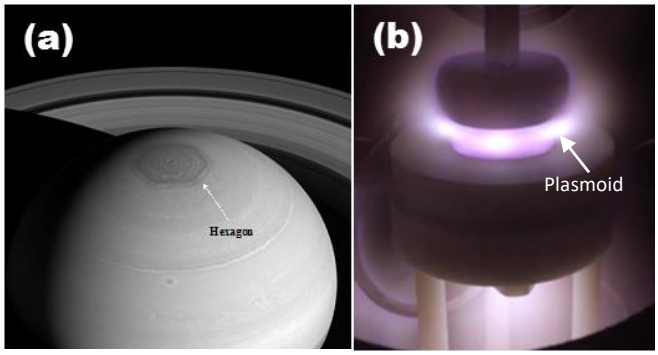

Figure 1. a) Self organized, hexagonally-shaped cloud pattern at north pole of of Saturn (NASA). B) Plasmoid formation in a parallel plate capacitive discharge

the system in the presence of structures that preclude attainment of thermodynamic equilibrium. In such systems order can appear out of apparent randomness. The appearance of patterns does not require an external excitation to the system rather the pattern formation is initiated by random fluctuations typically internal to the system in the presence of positive feedback which amplifies the pattern formation. In this respect, it is the local microscopic processes interacting that gives rise to the observed macroscopic patterns. Key to understanding pattern formation is the identification of the internal driving forces and the feedback mechanism. Systems that self organize can also be characterized by additional criteria beyond the apparent occurrence of spatially ordered patterns or temporally ordered structures. Indeed, in essentially all such systems, there is an observed local negative entropy change. It must be emphasized that the entropy change referred to here is 1) local and 2) in a system that is far from equilibrium. In such a case, locally the change in entropy can be negative but globally the change is positive.[5,6] Indeed, this local decrease in entropy in itself is a manifestation of organization. Usually one refers to free energy in the analysis of self organizing systems because it accounts for both changes in system energy content and entropy content. Here a decrease in enthalpy tends to accompany spontaneous reactions with a positive increase in entropy. Gibbs free energy which is negative for spontaneous reactions is defined as: $G = H - TS$, where H is the system enthalpy, T is the temperature and S is entropy. As a closed system relaxes toward thermodynamic equilibrium, transient oscillations in its free energy is possible. However, the thermodynamic trajectory of such a system is still stable. On the other hand, in open systems—those that are free to exchange energy and mass with the environment—such oscillations can persist so as long as reactants are constantly replenished. Under these conditions the system remains far from equilibrium. In this latter case, energy is dissipated to the surroundings so any local decrease in entropy is compensated by an increase in to the surrounding. As long input energy and mass into the system is sufficient to maintain thermodynamic instability (deviation from trajectory towards thermodynamic equilibrium), then a coherent state can persist manifesting order and structure born out of fluctuations that in the presence of sufficient positive feedback. The resulting self organized patterns themselves are called dissipative structures in contrast to equilibrium structures which are associated with homogeneity as a system tends toward thermodynamic equilibrium where free energy is minimized and entropy is maximized.[7] In such open systems maintained far from equilibrium it has been pointed out that self organization can suddenly appear.[8] In this manner, spontaneous self-organization with local entropy decrease is possible (accompanying an increase in entropy in the surrounding environment). Indeed it can be argued that the diversity of self organization appearing in the physical universe is in itself a consequence of the amplification of random fluctuations via sufficient feedback that lead to coherence and not the uniform homogeneity that would otherwise result as a system tends toward thermodynamic equilibrium.[7] In this work, we are especially interested in systems far from equilibrium.

A. Importance of self organization in the study of plasma physics

Understanding the drivers leading to the occurrence of self organization in plasma physics remains not well understood. Such an understanding is key to deciphering the collective, organizing behavior in plasmas ranging in scale from astrophysical structures to low temperature, laboratory plasma discharges. In this regard comprehension of self organization is a basic plasma science problem.[9,10,11,12,13,14,15,16,17,18,19] Self organizing patterns are also relevant to plasma-based technological applications. Thus, in fusion plasmas (for example spheromaks and FRCs) self organization leads to enhanced confinement that may one day lead to a viable fusion reactor.[20,21] Self organization also occurs in materials processing systems. For example, the appearance of stationary and rotating plasmoids has been observed in both parallel plate capacitive systems and in inductively coupled plasmas.[22] The occurrence of such self organization can impact plasma uniformity. Figure 1b depicts self organization in a parallel plate rf driven discharge. The plasmoids are observed to rotate about the axis of the reactor. In recent times there has been great interest in the application of microplasmas.[23] Microplasmas typically refer to high pressure plasmas produced over small length scales where typically the discharge volume to loss bounding surface area ratio is small, and with interelectrode gaps typically less than a millimeter. These discharges have applications in lighting, nanomaterial synthesis, plasma medicine, and ozone production. Under specialized conditions (inert gas environments at pressures in the 50-500 Torr range), arrays of well-ordered microscopic discharge spots attachments can be observed in the surface of the cathode.[24] Figure 2 illustrates the general layout of DC microdischarge along with the variation in patterns which are observed to form on the surface of the cathode as a function of operating conditions. Turing-like self organized discharge patterns observed in silent discharges near 1 atm have been attributed to the existence of a bistable, S shaped current density characteristic that allows for existence of a high and low current operating regime.[25] The field of low temperature plasmas in particular is rich with the occurrence of self organization over a broad pressure range. A detailed review of such subject matter is beyond the scope of this paper. Rather the aim of the work herein is to focus on the occurrence of self organization in a specific system: the 1 atm DC glow with liquid electrode. Such discharges have been studied to date for many years.[26,27,28,] In this work we focus on the liquid anode. This system is novel in that the return electrode is liquid

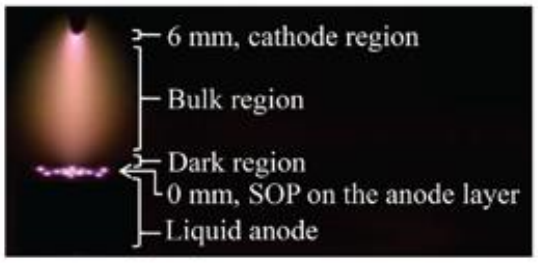

Figure 3. DC glow with liquid anode 1 atm, physics of plasma (Reproduced from [Physics of Plasmas 25, 073502 (2018], with the permission of AIP)

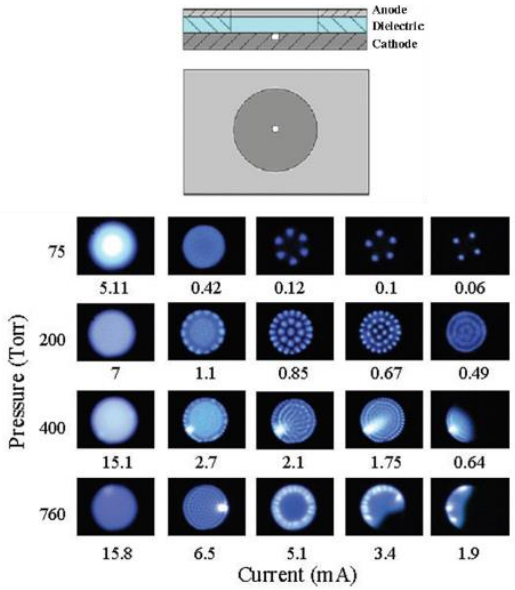

Figure 2: DC microdischarge self organization Schoenbach, K.H., Moselhy, M., and Shi, W., Plasma Sources Sci. Technol., 13, 177, 2004.

and overall the discharge is multiphase including the gas phase attachment, the liquid charge transport and the electrolytic processes taking place at the immersed return electrode. Additionally, the such discharges manifest a range of spatial and temporal patterns as operating conditions vary (including the electrochemical state of the conducting liquid). The occurrence of the self-organization pattern in this system is not well understood.[29]

B. 1 atm DC Glows with liquid anode

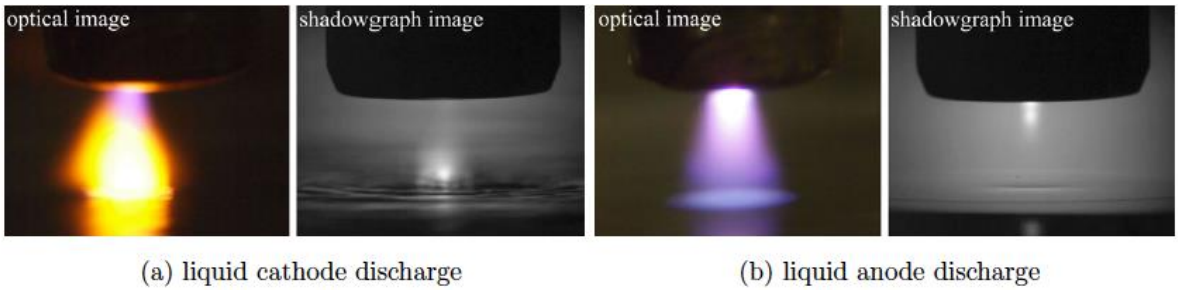

Figure 4. Comparison between morphology of plasma attachments at liquid electrode surface. Shirai, N. , Uchida, S., and Tochikubo, F., Plasma Sources Sci. Technol., 23, 054010, 2014.

A DC 1 atm glow plasma with liquid anode is a plasma discharge with a cathode (which may be either liquid or solid) and an anode consisting of a liquid electrolytic solution with an immersed physical collector electrode that is coupled to the external circuit, which consists of a DC power supply and a ballast resistor. Such normal DC glows at 1 atm have been studied with metal electrodes.[30] The discharge manifests characteristics of a normal DC glow discharge. What distinguishes this type of discharge from arcs is that there is typically some form of stabilization that prevents the thermal instability from developing. Recall the thermal instability is initiated by localized heating which leads to reduced gas pressure and elevated E/N—which gives rise to an increase in the average electron energy. As ionization increases with increasing E/N, so does the current leading to increased localized neutral gas heating and thus further increases in E/N leading to a runaway condition that ultimately results in the formation of an arc discharge.[31] DC glows are stabilized because the liquid electrolyte limits the current that the discharge can practically support. Liquid evaporation at the anode also has a cooling effect. In such a discharge, the current is carried by ions in solution. In this respect, current continuity is driven by electron flow on the gas side of the discharge met with either positive ion flux or

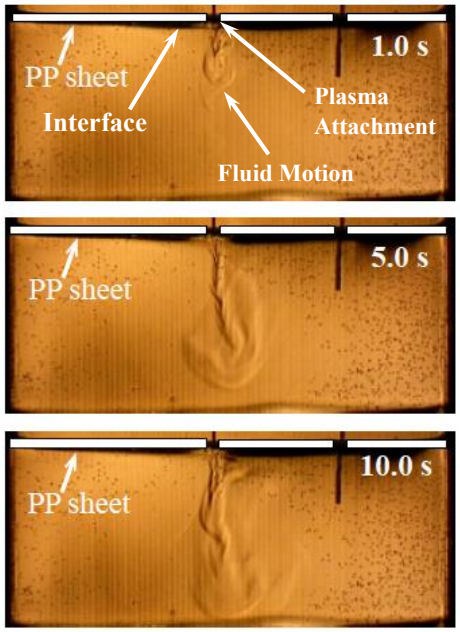

Figure 5. Development of flow in liquid due to attachment at liquid anode. Note polypropelene sheet with aperture for attachment (PP) Tochikubo, F., Aoki, T., Shirai, N., and Uchida, S., Jap. J. Appl. Phys., 56, 046201, 2017

electron driven negative ion production as well as the transport of negative ions from the gas phase into the solution. In this regard, current continuity is complex when compared to simple anodic collection with a metal anode. What is also remarkable about discharges of this type is that owing to plasma interaction with the liquid, the liquid chemistry actually changes over time as can be characterized by monitoring solution pH, conductivity or ion concentration.[32] Additionally reduction reactions at the immersed anode leads to nanoparticle production in solution.[33] The discharge is called a DC glow due to its characteristics appearance which is akin to a DC glow discharge. Figure 3 illustrates a DC glow with liquid anode complete with a positive column and cathode and anode dark spaces.[34] In general, in most cases this class of plasmas are configured with a single powered electrode and a liquid return electrode. Here a metal electrode is immersed into solution which makes the physical electrical connection with both the liquid and the power supply. Typical electrode spacings range from few mm to 1 cm with voltages ranging for 300 to 1000 V and currents up to few hundred mA.[35,36] The discharge glow can be generated with or without helium flow through the cathode. The presence of helium can stabilize the discharge owing to it high thermal conductivity which can lead to gas cooling and high ionization potential, both of which contribute to the mitigation of the ionization instability. The discharge is nonthermal. At the anode surface, there is typically a luminous plasma attachment. This attachment for all practical purposes is an anode spot structure. Within the spot, the field is locally sufficient to drive ionization and excitation processes there.[37] Above some threshold discharge current, self organization of the anode attachment at the surface of the liquid is observed. Interestingly, surface patterns have not been observed when the solution is biased negatively, suggesting a possible association between electron injection into solution as is the case for the liquid anode (which also drives electrochemical reduction processes at the interface) and pattern formation.[38,39,40,41] Indeed, Richmonds and colleagues showed clearly that reduction of a model system (ferricyanide-$Fe(CN)_6^{3-}$ to ferrocyanide-$Fe(CN)_6^{4-}$) increased with increasing discharge current for a liquid anode. In that work it was suggested that only a fraction the electrons making it to the surface participates owing the fact that in the reduction process is energy specific and in general the plasma electrons will have a distribution in energy. Figure 4 illustrates the morphological differences between the attachments of a liquid anode and a liquid cathode. As can be seen in the shadowgraph images, Shirai and colleagues found that the surface at the attachment of a liquid cathode to be in motion, essentially boiling whereas the liquid anode surface at the attachment was rather stationary in comparison. These findings are consistent with that observed by Bruggeman and colleagues which utilized a gas phase pin electrode rather than one with helium flow. In that work, they observed brighter emission near the liquid cathode surface as well as filamentous attachments.[42] This work will focus on the liquid anode configuration. While beyond the scope of this review, the formation of anode attachment pattern is often accompanied with liquid bulk circulation both in the plane of the liquid surface and in the volume (normal to the plane) which gives rise to mass transport from the interface. [43,44] An example of the development of induced flow is depicted in the Schlieren image shown in Figure 5 where a polypropylene sheet with an aperture for the plasma attachment is utilized to minimize the contact between the helium flow used in the discharge and the liquid surface. In that work, simulations suggested that the induced flow may be due to deposited momentum derived from impinging ions and electrons.[44]

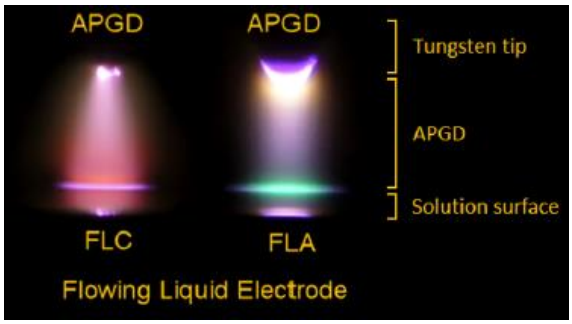

Figure 6. Comparison between atmospheric pressure glow discharge (APGD) with liquid cathode (FLC) and liquid anode (FLA). Greda, analytical chem (52)

C. 1 atm DC glow applications

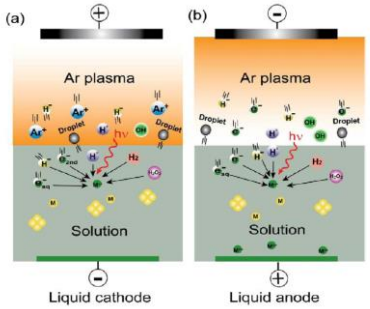

Figure 7. Nanoparticle production with liquid anode and liquid cathode Q, Chen, Applied Phys. Express, 2012

Though the underlying origin of the spatial distribution of plasma attachment on liquid electrodes is not well understood and is thus a plasma science problem, this class of discharges has a wide array of technological applications. Because the plasma is in contact with the liquid solution, aerosol generated through the plasma-liquid interaction introduces species from the liquid into the plasma. Indeed, the exchange of species between atmospheric plasmas and liquid electrodes has been previously reported.[45,46,47] Upon vaporization, electron impact of the atomic and molecular species previously in solution gives rise to electronic excitation. While this can occur with both liquid anode or liquid cathode, the liquid cathode embodiment is more widely utilized owing to the heating effects and the potential for sputtering of the liquid surface. Spectroscopic analysis of the plasma induced emission gives insight into the species content in solution. In this respect, the discharge is used as the basis for spectroscopic analysis of constituents in solution.[48,49,50,51] Figure 6 depicts emission from both a liquid anode and liquid cathode DC glow with a Tl ion electrolyte. It was shown by Greda and colleagues that the liquid anode glow had higher detection sensitivity (limit of detection) for a range of dissolved metals.[52] It was conjectured that electron reduction reactions at the interface play a key role in producing volatile metal species. During the course of the discharge operation the immersed return electrode is slowly consumed, giving rise to the formation of nanoparticles. In fact, such discharges, though typically with liquid cathode, are prolific producers of nanoparticles which can be used of a variety of applications. [53,54,55] (see figure 7). Nanoparticle size, shape and even composition can be controlled through the tailoring of the electrolyte, the immersed electrode composition, and the plasma conditions at the interface.[54] The self organization of such plasmas on liquid media such as cancerous tumors is currently being investigated as a treatment method. Owing to subtle dielectric differences between cancer cells and normal cells, selective self organization can be exploited as a tool to eradicate diseased cells. [56,57] Here it is the small variations in the external properties of the cells (cancer and normal cells) that lead to the self organization. This so-called adaptive plasma pioneered by Keidar and colleagues is a novel approach to treatment. Plasmas in contact with water generate reactive oxygen and nitrogen species such as OH radicals, ozone, hydrogen peroxide, nitrites and nitrates, which can be used to decompose organic contaminants in solution via a process known as advanced oxidation.[58] In advanced oxidation, these reactive species attack and subsequently reduce organic contaminants in solution to carbon dioxide, water, and inorganic salts via a process known as mineralization.[59,60,61] This nonselective process can be utilized in the treatment of waste

water whose conductivity is sufficient to support a discharge.[62] Such discharges produce copious amounts of reactive species such as OH radicals, hydrogen radicals, hydrogen peroxide and solvated electrons. These species drive the decomposition of contaminants in solution.[63] What is novel about such discharges in this context is that the Faradaic yield for reactive species can be nearly an order of magnitude higher than that corresponding to Faraday's electrochemical law—which states that the mass of species generated is proportional to the quantity of electricity passing through the electrolytic cell.[64,65] Such discharges have also been suggested as a means to modify the surface of immersed substrates such as polymeric films. For example, Zheng and colleagues modified the wettability of polyimide film samples immersed in an electrolyte exposed to a liquid cathode.[66]

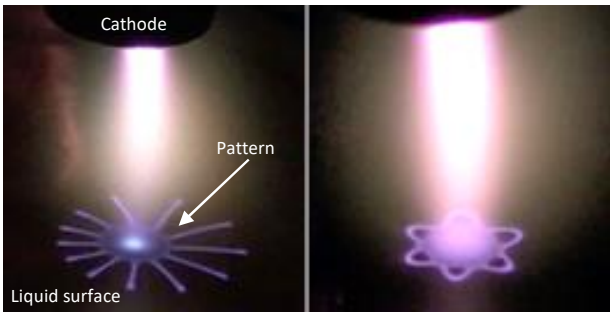

Figure 8. Self organization plasma patterns on the surface of a liquid anode liquid anode

II. Mechanisms of Pattern formation

Plasma self organization on liquid electrode surfaces is as puzzling as it is beautiful. Why does such intricate patterns appear on the surface of a liquid electrode? What energy minimization law prevails that favors this particular configuration? Figure 8 depicts two such examples. One of which is a multi-spoke pattern while the other has the shape of a star. It has to be emphasized that these patterns represent plasma induced emission at the interface. These spatially ordered attachment patterns are apparently necessary to sustain the discharge current.

It is interesting to note that the appearance of pattern formation akin to those observed on the surface liquid anodes has been observed and studied for some time in chemically active systems.[67,117] These patterns in chemical systems may provide insight into the occurrence of self organization in plasma/liquid systems as well. The self organization in chemical systems takes the form of spatial, temporal or spatiotemporal variations in chemical properties of the reacting solutions. For example, spatial islands of a specific pH or species concentration can appear. These patterns are typical of nonlinear systems described by reaction-diffusion kinetics, as first predicted by Turing.[68] Here reactions take place locally but in the presence of diffusion gives rise to a set of n coupled nonlinear differential equations (two shown here for illustrative purposes):

1) $\frac{\partial c_1}{\partial t} = r_1(c_1, c_2) + D_1 \nabla^2 c_1$

2) $\frac{\partial c_2}{\partial t} = r_2(c_1, c_2) + D_2 \nabla^2 c_2$

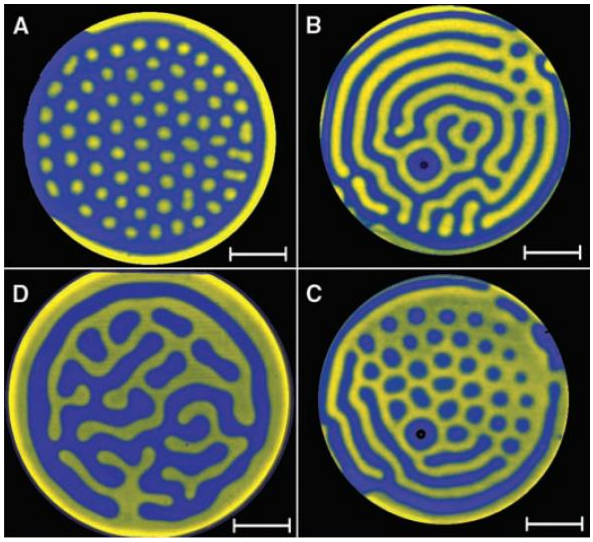

Figure 9. Stationary patterns in a chemically active reaction diffusion system. Scale bare corresponds to 4 mm long. (Horvath, 2009)

where c_1, is the concentration of species one, D_1 is the diffusion coefficient associated with c_1 and $r_1$is the reaction rate between the species present in the system. Solutions to this system of equations include wavefronts, clustering, spatiotemporal chaos and composite patterns. A key aspect of such systems is that the diffusion rates of the reacting species are different and some form of feedback is present in the system to amplify the pattern development. Figure 9 depicts an example of stationary patterns in a reaction diffusion system.[69] The patterns typically take the form of spots or stripes. In figure 9, the yellow regions represent areas of low pH. Because the liquid anode solution in a 1 atm DC glow is chemically active, it is not unreasonable to assume that at least locally, at the attachment point, plasma injection drives chemical processes such redox reactions as well as local acidification. These local chemical changes ultimately spread throughout the volume via convection, both plasma-induced as mentioned previously and thermal. Locally in particular at the plasma attachment point the liquid is chemically active with reactions induced by the plasma and diffusion also taking place in regards to reagents to the active zone and intermediates out of the region—thus making the region a reaction diffusion system and equations similar to 1 and 2 must apply. This chemical reaction diffusion system present could provide the seed template for spatial variations in parameters such as ion concentration and conductivity which in turn may play a crucial role in the evolution of the observed anode plasma patterns. It should also be pointed out that reaction diffusion systems under isothermal conditions can occur in so-called autocatalytic systems.[70,71] Such systems, named after the investigators Gray and Scott, feature a catalyst that converts one reactant into another at for example a quadradic or cubic rate: A+B→2B or A+2B→3B and with B→C, where C is inert. Even though the equations represent irreversible processes as long as A is continuously feed into the system and B removed as in a continuous flow reactor, this system is describable by reaction diffusion equations which can give rise to stable limit cycles and pattern formation. In this case the feedback mechanism is due to the presence of the autocatalyst B which converts A to B and is thus not thermally driven. A key consideration applying the reaction diffusion model to plasma systems is the identification of the activator and inhibitor (or autocatalyst as in the case of a Gray-Scott system) along with the feedback source. For example, current has often been identified at the activator of the pattern with voltage serving as the inhibitor.[72,] Consider for example a discharge between two electrodes at atmospheric pressure. Here a single filament may form at a given applied voltage. With increasing voltage, current increases but eventually exceeds the magnitude for which can be collected practically at the surface. This is particularly the case for a resistive surface. In this case multiple filaments are required to support the current. In this manner, the attachment becomes more complex and perhaps seeds the self organization. A predator-pray formulation can be used to describe at least why more filament are necessary. This formulation is nonlinear and can lead to complex a solution for the spatial distribution of the attachment. For a simplified insight into the physical processes leading to the need for more complex collection surface area, consider a single filament attached to an electrode with finite surface resistance. Such an approach has been used to formulate reaction diffusion for DC filaments on semiconducting surfaces.[73] In the present formulation, the current can be modeled as the "prey" and the boundary layer resistivity can serve as the "predator." It must be kept in mind that the resistivity discussed here is local—the attachment is highly localized and thus the current transport is also local and can be expected to be subject to localized saturation; that is, the current in principle should be limited by the local diffusion of ions to and through the double layer to the attachment point to complete the circuit (in the case of a liquid electrode). Indeed, the nature of the liquid double layer below the attachment has the effect of shielding these local processes from the surrounding fluid is the same manner as

the Debye sheath shields electrodes from the rest of the plasma in the gas phase. The conductivity in this localized region and the double layer properties below the attachment depends on local field strength and ion formation processes associated with the plasma as depicted in figure 10. Here ions travel through the liquid to the attachment point to neutralize incoming electron charge. The relevant system of equations describing the predator-prey relationship between current I and resistivity ρ can thusly be written:

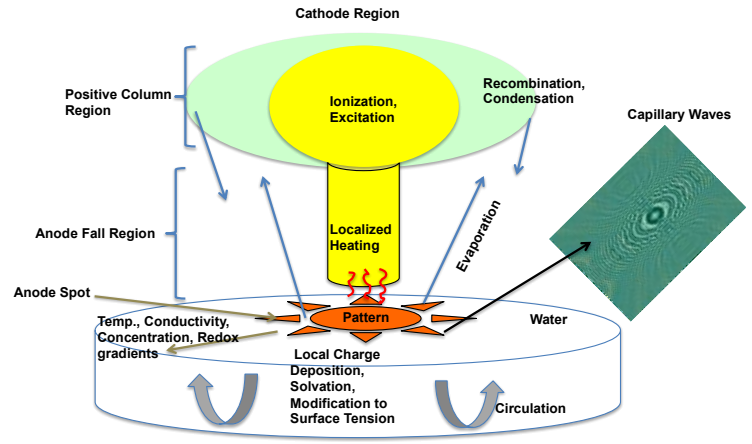

Figure 10a. Physical processes prevailing at the interface influencing local resistivity and charge transport.

3) $\frac{dI}{dt} = aI - bI\rho$

4) $\frac{d\rho}{dt} = -c\rho + dI\rho$

Here, the time variation in the current I would increase exponentially without a limit if the solution can handle the transport. The second term represents the limiting factor of local resistivity, which in this case scales as the power deposited in the local attachment volume. a,b are constants. The second of the coupled equations represents the resistivity variation. It tends to decay with increasing resistivity as its increase ultimately limits the amount of current collected (a type of feedback) and thus the amount of ion production both in gas phase and in local interface region. Reductions in resistivity reduces depletion as well. Resistivity on the other hand increases with more power locally deposited into the area near the attachment. This system of equations gives at least qualitative insight into why more area or filaments are needed. It is also a system of nonlinear equations that can give rise to spatial and spatial temporal solutions. A single filament will ultimately always be limited by the local resistivity derived from a lack of additional charge carriers for example. Simply put, the plasma can supply more current than the electrolyte can support. The nonlinear discharge column response relative to the linear conductivity response of the bulk can lead to instability. The plasma interaction with the liquid can enhance conductivity locally but continuity and ultimately the discharge current that is possible is determined by diffusion from the bulk. Current therefore can only

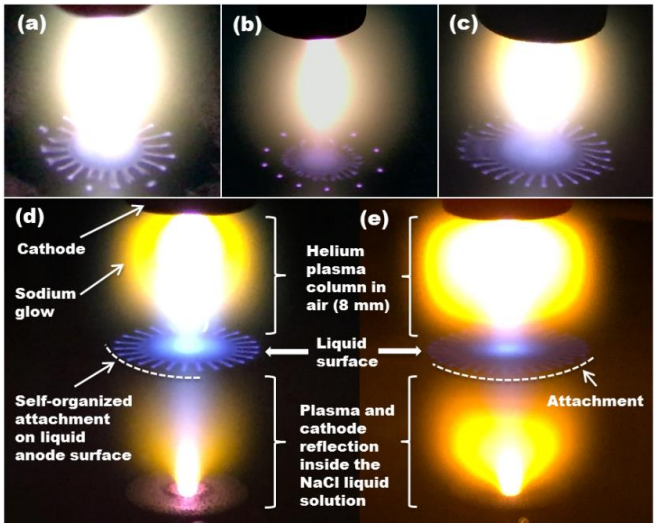

Figure 10.b. Observed self organization patterns with different electrolytes (a-c) along with an illustration (d-e) of the interplay between solution derived species (yellow sodium cloud) and the gas phase plasma of an NaCl electrolyte solutions. Kovach, TPS, 2019.

increase if there are more attachment points-more filaments or increasing discharge complexity to sustain the current. Similar depletion processes are also observed in batteries when operating at higher currents. In such a case, near electrodes (in an electrolyte solution) ions are removed or generated giving rise to temporal and spatial variations in conductivity.[74] Motion of the attachment at the interface is another mechanism that can manage such depletion as the local conductivity with a liquid electrode can actually change. In this case the attachment can simply rotate or displace to pristine solution where more carriers are abundant, thereby leaving the region of temporarily localized depletion—or inhibition zones. The translation time of such oscillatory can be expected to be on the time scale of depleted region recovery which should be of order the characteristic diffusion time of the solution. It should also be pointed out that the plasma attachment is not point-like but rather extended and thus the attachment shape (regions of charge injection) can be expected to change spatially during such predator-prey oscillations.

Localized conductivity variations can be attributed to a host of physical processes that have the potential to influence the morphology of the discharge pattern. We review a few of these processes here. Figure 10a and 10b illustrate the complex interplay of physical processes that can occur during discharge operation. Localized evaporation at the attachment point affects conductivity of plasma column at the attachment and in the positive column, e.g collisionality and negative ion formation. The localized heating at the interface along with the plasma induced changes in ionic concentration can lead to localized gradients in the surface tension which in turn leads to induced flow such as Marangoni.[75, 76,77] Such induced flow can entrain ions from regions removed from discharge attachment location thus providing enhanced transport into regions that would otherwise deplete. The complex interplay between the electrolytes in the liquid phase actually determines in part the color of the discharge itself as is illustrated in figure 10b, where in this case sodium ions from a salt water electrolyte appear in positive column emission at increased discharge current. Charge flow in the electrolyte to the attachment point consists of induced convection, electromigration, and diffusion: $j_i = u \cdot c_i - \mu_i \cdot c_i \cdot \nabla\emptyset - D_i \cdot \nabla c_i$, where $c_i\, is$ the concentration, D_i is the diffusion coefficient, u is the flow velocity, μ_i is the ion mobility, and $\emptyset$ is the electrostatic potential.[74] Localized carrier depletion (demand exceeds availability in electrolyte locally) leads to increased resistance and thus an increase in voltage drop in this layer. If sufficiently large at least on the gas phase side the anode sheath can breakdown thereby effecting the spatial distribution of the attachment. In this case, the anode spot plasma provides the additional charge carriers to support the required current. While these physical processes can influence local conductivity, they can also contribute to spatial gradients in ion concentrations and pH as well which in turn can serve as templates for patterns.[78] The excitation of capillary waves at the interface can also contribute to complex pattern formation. Capillary waves are mechanical waves that oscillate normal to the liquid surface while propagating along the interface/surface. These waves can be excited by plasma contact (e.g. streamers) with

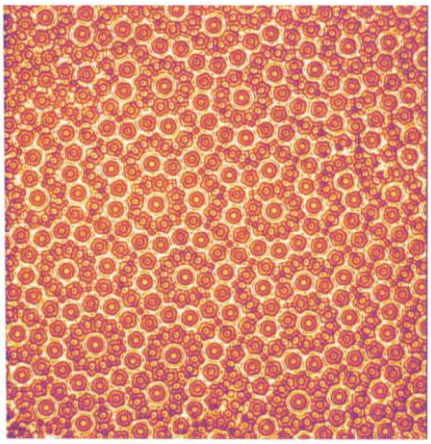

Figure 11. Surface standing wave pattern associated with liquid excited at two different frequencies (Gollub and Langer, 2006)

the interface which can give rise to a normal oscillation which seed capillary wave development. Standing wave patterns formed by capillary waves interacting at different frequencies produce ordered structures over a range of characteristic length scales. Figure 11 illustrates a complex pattern generated on the surface of a liquid due to standing wave formation with multiple frequencies.[7980] Such complex spatial patterns has the potential to influence the morphology of the discharge attachment. It is known that such waves can couple with the occurrence of streamer strikes.[81] The interfacial perturbations depending on the structure can alter the intensity of the local electric field which can affect the breakdown and the plasma spatial distribution.[82] The presence of capillary waves can also greatly contribute to the uptake of gas phase species into the liquid.[83] In the case of plasmas, not only reactive species but also ion mass transport can therefore be enhanced, which in turn influences the spatial distribution of charge carries in solution. This effect can also be expected to influence pattern formation.

Adding to the complexity of pattern formation are the prevailing physical processes in the solution, particularly the double layer region. The electric field in the double layer facilitates electromigration. Interestingly, the thickness of the double layer region depends on the ionic strength of the liquid, a measure of the total ion species. Depletion effects can greatly affect the value of the local ionic strength. This means that the spatial extent of the double layer is dependent on local conditions at the interface (e.g. charge injection and production).[84] Studies also show that the field in the double layer also influences reaction rate constants there which again can influence local conductivity.[85,86] Finally pH stratification in the double layer affects advanced oxidation reactivity there as well. All these physical processes taken together influence overall reaction rates and diffusion both in the gas and liquid phase and thus may play a role in pattern formation.

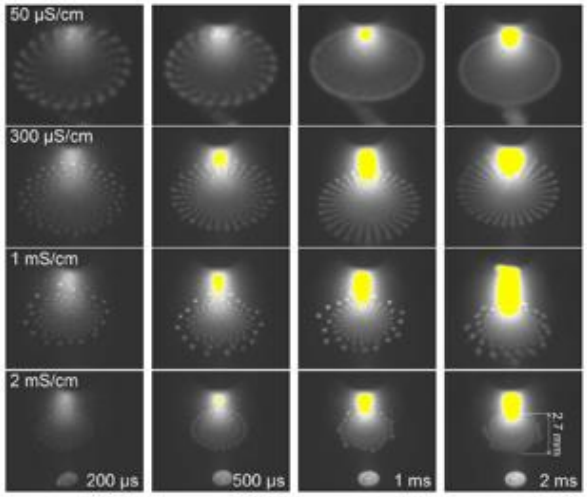

Figure 12. From Leys et al, variation in pattern complexity and size with conductivity and time (Verreycken, J. Applied Phys, 2009)

Reaction diffusion models may provide insight into pattern formation, but the species equation must be expanded to include solvation of species and investigate which generation or loss rates are the driving terms. For example, solvation of species may dominate species density over diffusion and local reactions. Experiments aimed at providing specific evidence of pattern formation where the aforementioned processes can be at least tracked would greatly improve our understanding of the applicability of the reaction diffusion formalism to the observed self organization. Another design parameter is the structure of the plasma discharge column, i.e., how many contact spots are created at the liquid electrode surface? This would be another term or boundary condition in a spatially resolved species equation and thus an important experiment. A model that takes into account these physical processes is necessary to truly understand the formation process of such complex patterns on the liquid anode surface.

III. State of Affairs: What we currently know via experiment

To date there is a healthy body of experimentally-derived insight regarding the conditions under which self organization occurs. These experiments elucidate the importance of key variables but the underlying mechanism of formation remains elusive. Leys and colleagues found that self organization pattern size on liquid anode increases with increasing discharge current, suggesting that contact larger area and presumably accompanying spatial complexity is required to support the discharge current.[87] In the case of higher solution electrical conductivity, there are more ions per unit volume to neutralize incoming electrons and thus the attachment reduces in size. Here the solution effectively "shorts out" the pattern. Because electrolytic processes take place at the immersed electrode and at the plasma liquid interface where plasma chemical driven processes such as oxidation, electron solvation, and acidification occur, the solution anode is chemically reactive and changes over time. Indeed, conductivity tends to increase with time. Such temporal variations may obscure the underlying processes that lead to pattern formation since the chemistry is irreversibly changing. Over time the infinite boundary approximation (open system approximation) fails as the chemistry of the entire receptacle changes, approaching that of the region local to the plasma attachment in the limit of long time scales. Additionally, the presence of induced convection observed in liquid of such discharges would tend to hasten this convergence. Leys and colleagues found that the pattern tended to evolve over time presumably due to these effects. Figure 12 illustrates these variations in pattern complexity with both time and conductivity. [88] Attempts to circumvent these changes and thus fix the chemistry of the solution by utilizing a continuous flow has been explored. Here, the electrolyte is continuously replenished by pumping in new solution from a reservoir. Cserfalvi and colleagues for example studied liquid cathode attachment phenomena using such an approach which also allows for continuous analysis of waste water.[89] Methods such as this are crucial to understanding what the key control variables are and the relative important of solution chemical changes on pattern formation.

Shirai and colleagues have extensively studied pattern formation on liquid anodes. They identified a threshold current that was required for a given interelectrode spacing to observe pattern formation. Furthermore, they observed that at low helium flows, the pattern was unstable while at high flows, the gas flow "presses on" the surface disrupting pattern formation. The group also identified the role of steam evolution from the surface and pattern formation. Finally, it was observed that patterns tended to favor formation in presence of electronegative gases (see Fig. 13). It was found that in contrast to operating in regular air, when a curtain of nitrogen was used to minimize air diffusion into the discharge, the pattern was absent. Additionally, they found that the ratio injected oxygen to air could be used to control the patterns observed. The role of negative ions in pattern formation is suggested in this work.[90,91] In general, it is well established that the presence of negative ions in discharges can lead to a type of ionization instability, which may play a role in the formation of the patterned anode spots. In fact, role of negative ions has been alluded to in the formation of self organized plasmoids in low pressure

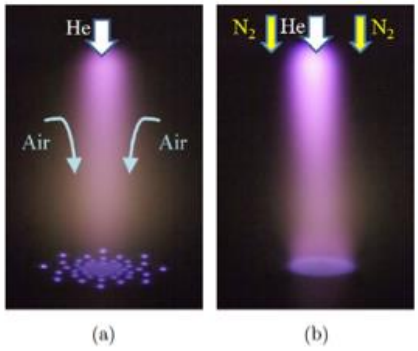

Figure 13. The effect of electronegative gases on pattern formation. A) in ambient air B) with nitrogen curtain (Shirai, psst 2014)

plasmas as well. An attachment instability can occur when the relative negative ion concentration is high. In this case, the attachment rate can increase with electron temperature due to an increase in the effective E/N, where N is the uncharged neutral gas density. This allows for an increase in average electron energy an increasing higher ionization rate leading a runaway condition. The recombination instability is also possible. In the presence of an increasing electric field, ionization of recombining ions can lead to an increase in heavy, charged molecules. Coupled with attachment associated with recombination electron mobility is reduced thereby leading to a reduction in the local ionization rate and thus a perturbation to the local electron density. [92] Such a process may play a role in the formation of anode attachments since significant evaporation takes place at the surface of attachment in liquid anodes, leading to the introduction of attaching species via for example plasma driven disassociation of water. Negative oxygen ions can interact with oxygen to generate O_2 molecules for example: $O^- + O \rightarrow O_2 + e$.

Zheng and colleagues investigated pattern formation with a pin-to-plane (liquid anode) configuration.[93] They observed a pronounced anode dark space when using acid electrolytes that contained fluorine or chlorine. Here it is conjectured that gas phase F or Cl derived from the solution, attaches electrons locally above the anode, giving rise to a prominent dark space, again highlighting the role of negative ions. Interestingly, hydrogen lines were not observed in the emission spectra. This was attributed to the production of H_2 gas by energetic electrons: $2H^+ + 2e- \rightarrow H_2(g)$. Hydrogen emission however has been observed near the surface in other studies albeit at reduced intensities in contrast to the liquid cathode configuration. The observed weak emission may be attributed to the large amount of water vapor present near the surface. [94] In liquid anodes, the water plays a key role in stabilizing the discharge.

Zheng and colleagues also investigated the formation of patterns on the surface of a liquid electrode by exciting a pin to plane (liquid) geometry with AC voltge up to 14 kHz rather than DC.[95] Here again, air was the working gas. In this work, patterns only occurred when the liquid electrolyte was at anode potential, consistent will all DC tests. This indicates the importance of an electron collecting liquid. Interestingly, in this work, the sodium from the electrolyte was not observed in the gas phase nor was OH radicals. The authors attributed the absence of these species near the surface to reduced localized vaporization in this discharge. Note that the patterns only appeared for a short time on a half cycle, so the localized power deposition is greatly reduced for similar currents and voltages in comparison to the DC case. Additionally, it was observed that at high currents, the patterned attachment becomes diffuse. The diffuse attachment can be expected at increased current. As the size of the filaments increase, the relative inter-filament spacing decreases. When this occurs, lateral inhibition is overcome via diffusion and intricate structures will blur, melding into a single diffuse attachment.[72]

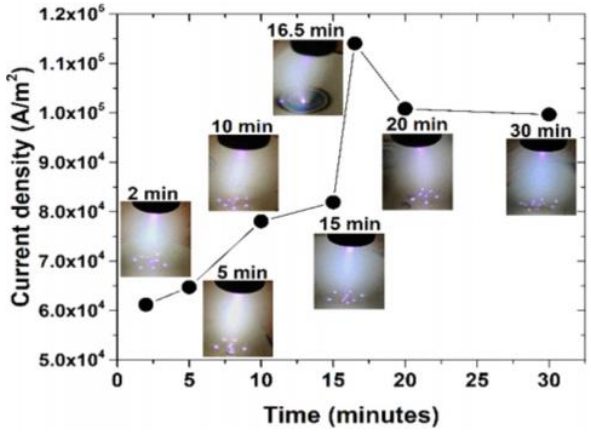

Figure 14. Discharge pattern changes on metal anode (Kovach, J. Vac. Sci. A, 2019)

As a side note, while this survey focuses on anode patterns on liquid electrodes, these patterns are also observed on metal anodes in 1 atm as well. Technically these are 1 atm DC glows as well. Observation of self organization on metal electrodes at low pressure has been observed dating back to the late 1920s.[96] Self organization here remains not well understood either. At 1 atm the discharges take the form of a patterned array of spot attachments. Like liquid anode patterns, the metal patterns also depend on gap length, helium flow rate, and glow discharge current, suggesting similar physics may prevail.[97] There are notable differences however in that the composition of the bulk metal does not change as the liquid solution change with time. The patterns do evolve over time as shown in figure 14. The study by Kovach and colleagues, the surface also evolves over time, essentially nanostructuring in morphology as shown in figure 15.[98] Such structuring affects local heat transfer (thermal conductivity) and also greatly enhances the collection surface area.[99,100]Additionally, as the discharge was in air with helium cathode flow, the surface did show some oxidation which would also affect surface resistivity. These factors may be analogues to the aforementioned processes taking place locally at the attachment point in the case of the liquid anode. The nanostructuring observed is similar to that observed in fusion tungsten fuzz experiments, suggesting the possible presence of energetic helium ions. Such energetic ions if present could form if the potential of the anode is below local plasma potential in the anode spot and perhaps exceedingly thin. This in fact can occur in an ion sheath double layer structure.[37] Such as structure also accommodates the acceleration of electrons to ionization potential to form the spot itself. The condition for the formation of such a sheath structure (at least in the low pressure case) depends on the ratio of the plasma attachment area to the electrode attachment area: $\frac{A_S}{A_E} < 0.6\sqrt{\frac{T_{eI}m_i}{2\pi T_{eS}m_e}} - 1$, where T_{eI} is the electron temperature of the electrons born in the spot, while T_{eS} is the total electron temperature (average of bulk and ionization produced electrons). If such a structure exists, then in the case of the liquid anode, ions could sputter the liquid surface which could explain in part the presence of observed metal ions such as sodium in the gas phase. Further research is necessary to elucidate the role energetic ions may place in both discharge interactions.

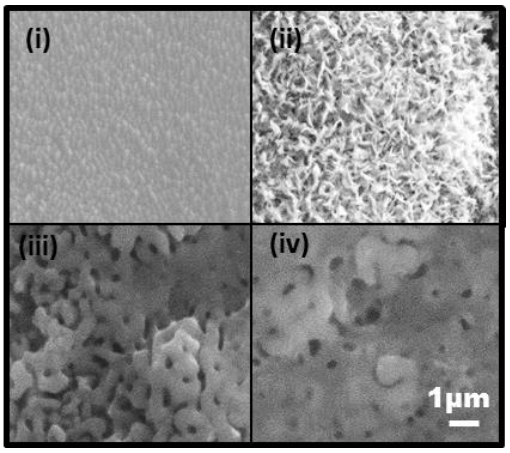

Figure 15. Anode nanostructuring observed on metal anode with DC glow

IV. Recent Experimental Insight into Plasma Self organization on liquid anode

Using an experimental apparatus similar to that utilized by Shirai and colleagues, additional insight regarding anode plasma self organization on liquid anode has been gleaned. For example, spatially resolved spectroscopic analysis revealed a stark change in positive column emission upon the onset of plasma self organization at the anode surface. For example, prominent OH emission was observed coincident with pattern formation, presumably from evaporated water.[101] This observation highlights the interplay between water in the liquid and gas phases and how this interplay plays a role in discharge impedance changes. Indeed, based on spectroscopically measured temperature near the interface, the evolution of water vapor flux due to evaporation was found to exceed the helium gas flow rate by a factor of 10. The water vapor dominates the discharge dynamics, as inferred by the noticeable reduction in nitrogen emission relative to OH. Also observed in this work was the presence of sodium in the positive column. The sodium can be derived from direct sputtering or droplet formation if localized boiling occurs at the attachment point. Figure 16 depicts the dramatic evolution in the discharge color to yellow (sodium emission) and overall shape as current is increased.

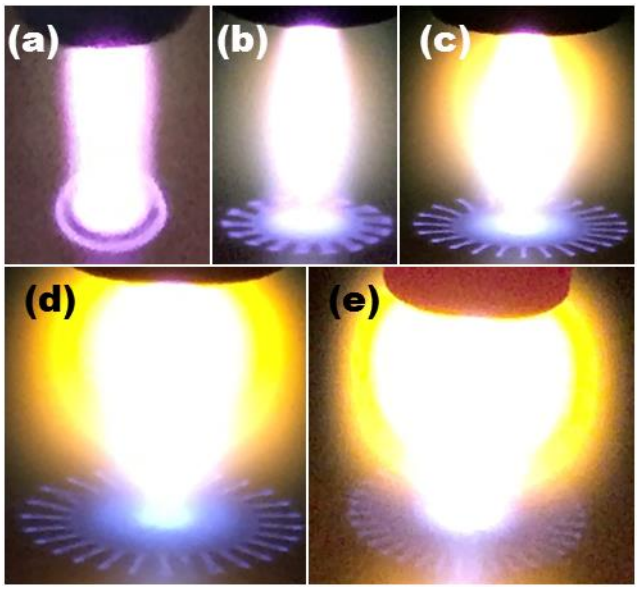

Figure 16. Variation in discharge and attachment color and structure with increasing current (a-e) from 30 mA to 105 mA. (Kovach, TPS 2019)

The presence of electrolyte ions in the gas phase such as sodium suggests that the electrolyte may play an important role in discharge properties and perhaps self organization of the anode attachment. Zheng and colleagues as mentioned previously alluded to the role of negative ions derived from the solution in the formation of the dark space. Such an interaction suggests that current transport is not only dependent on ion concentration in solution (and of course depletion processes) but also solution derived species that make it into the gas phase which can also affect charge transport there as well. This gives rise to the question of does electrolyte type effect anode pattern morphology? A survey of 13 electrolytes with similar initial mass concentrations dissolved in deionized water was carried out to ascertain the impact of solution type on self organization pattern. Two

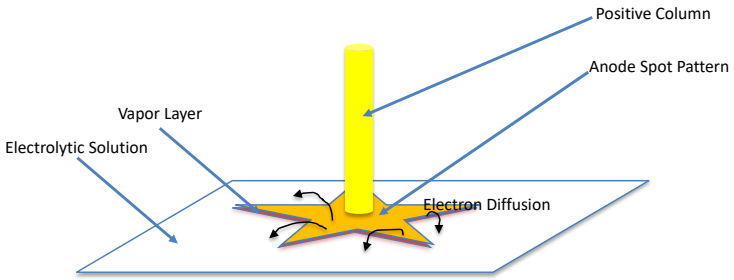

Figure 17. Schematic depiction of electron collection via diffusion from pattern anode spot plasma to electrolyte solution

important findings resulted from that work. Regardless of the solution type the discharge voltage behaved quadratically with discharge voltage, decreasing with increasing current at low currents only to increase monatonically at higher currents beyond the voltage minimum. The pattern tended to appear near the voltage minimum with organization increasing with further increases in current suggesting a distinct impedance change (from negative to positive resistance). This behavior (above the voltage minimum) is akin to abnormal glow where discharge voltage rises with increasing current. The anode attachment is analogous to anode spots observed in low pressure plasma discharges.[102] Such spots form on the surface of the anode under conditions where the gas phase ionization processes are too small to sustain the discharge. The spots themselves are double layer structures containing high electric fields that can drive ionization locally and thus maintain the discharge. As mentioned earlier, the minimum in the I-V characteristic of the glow with liquid anode is coincident not only with pattern formation but also with the appearance of a water dominated discharge. Evaporation just below the attachment leads to the formation of vapor barrier which would tend to impede the flow of electrons. It is not surprising therefore that anode spots form on the surface of the water. These structures may be necessary to sustain the discharge. In such attachments, excitation and ionization processes are present. These contribute to current flow. Indeed, the spots can serve as plasma contactors which provide a low impedance plasma bridge between the vapor saturated positive column and the electrolyte surface. The anode spot therefore can be thought of as an enhanced collection structure at the surface necessary to support the current. Indeed, anode spots have been shown to greatly increase electron surface area by more than 50 times. [102] In the case of the liquid anode however, the spot is a distributed pattern. Because it is the spot attachment itself is the source of the vapor, current collection may also occur between attachment structures and so structures such as spokes may very well be the simplest structure that optimizes pristine collection surface area and the discharge production region. This would be consistent with the reality regarding the reduced electrical conductivity of the evaporation layer immediately below the spot compared to reduced vapor region above the conductive anode electrolyte surface nearby. This scenario is depicted schematically in figure 17. It is therefore of high importance to spatially map the electric field structure near the surface of the attachment. Measurement of the electric field in the positive column has been performed using the optical spectroscopy technique proposed by Paris and colleagues.[103] This method is based on the measurement of the intensity ratio of two nitrogen spectral bands: the first negative system of N_2^+ (band head at 391.4 nm) and the second positive system of N_2 (band head at 394.3 nm). An estimation of E/N can be done using the following expression:

$$R_{391/394} = 46 \exp\left[-89 \left(\frac{E}{N} \right)^{-0.5} \right]$$

where E/N is a dimensionless quantity that numerically equals the field strength expressed in units of 10^{-21} Vm^2. Finally, considering the gas temperature values already measured by Kovach and colleagues [104], the E can be obtained. Figure 18 shows the electric field in the positive column

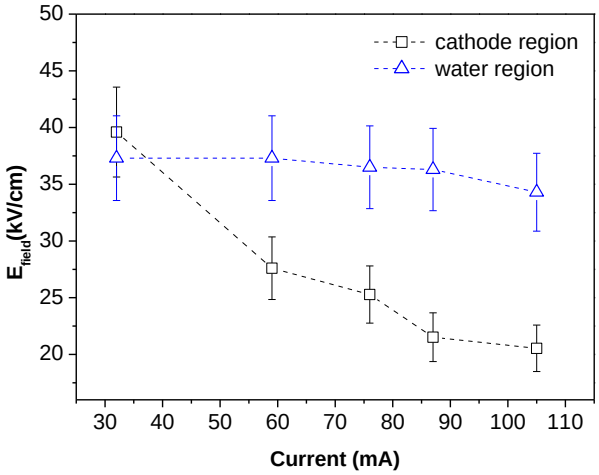

Figure 18. Electric field in the plasma column of a 1 atm DC helium glow discharge with a liquid anode for different experimental conditions.

measured both near the cathode and near the water, in the discharges shown in figures 16a-e. The experimental setup used to acquire the spectra has been described elsewhere.[105] Line integrated emission spectra corresponding to these two axial positions were collected and focused onto an optical fiber using an achromatic lens (at 1:1 magnification). For each experimental condition, the spectrum was recorded three times. As shown in Fig. 18, the electric field near the liquid anode surface has a value around 37.0 kV/cm for the five cases studied. As can be seen here, at least for this work, the local electric field estimated is above the ionization threshold for a 1 Atm air discharge.

Sensitivity of pattern formation to electrolyte. A number of studies have explored the effect of electrolyte on pattern evolution. For example, the work of Zhang and colleagues showed the importance of electrolyte species that can become negative ions in solution which was found to enhance the thickness of the anode dark space. In that study a range of acid electrolytes were explored. The stronger acid HCL showed patterns only at low conductivity while the weaker sulfuric acid manifested patterns over a broad range In this study, the solution electrical conductivity was controlled.[93] In general, it is the ionic strength and ultimately the activity of the electrolytes that determine the nature of charge transport in the solution. Ionic strength is a measure of the density ions present in the solution. Activity takes into account electrostatic effects so that when combined in ionic strength gives the effective ionic concentration. Locally, the solution ion distribution has contributions not only from the solution electrolyte but

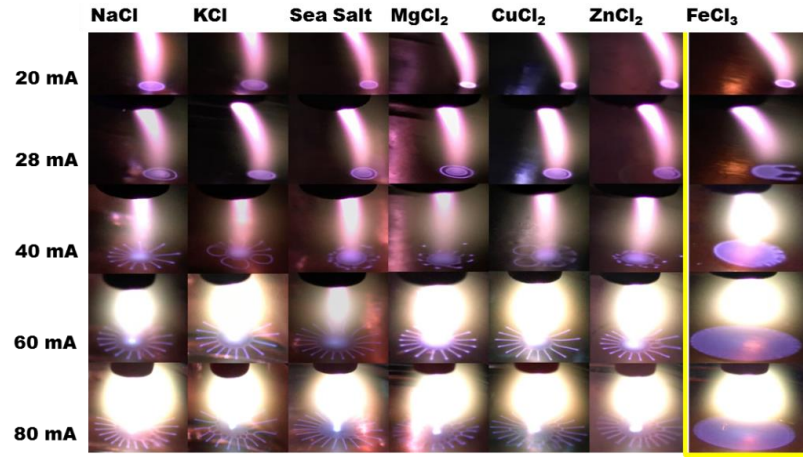

Figure 19. Variation in pattern evolution with discharge current for a range of electrolytes. Note evolution of high oxidation state $FeCl_3$.

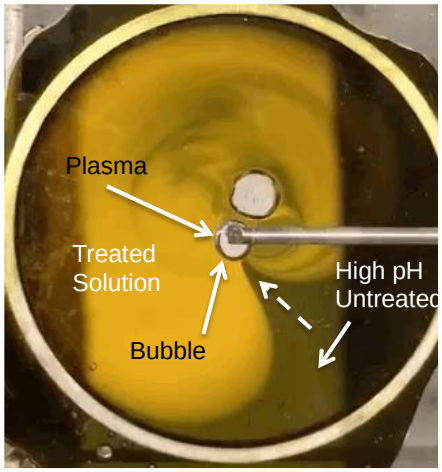

Figure 20. Convection cells induced by plasma interaction at the interface of a 2-D bubble.

also the diffusion of plasma generated ions and ions generated by electron or excited species impact at the interface. The presence of the plasma derived ions affect equilibria locally can actually enhance the solubility and thus local conductivity. Such changes may not be detectable by macroscopic conductivity measurements since the changes are local. In a recent study, an attempt was made to explore the impact of ionic strength on pattern formation for a range of electrolytes. Here a total of 13 electrolytes were investigated. Electrolytes with sulfate anions and chloride anions were investigated. It was found that the in all cases, the discharge increased in complexity with increasing current regardless of electrolyte, evolving from a disk attachment to spokes at the higher current investigated (~100 mA). It was found however that higher oxidation state cation electrolytes tended to be more unstable and overall evolution did not differentiate into complex patterns, rather continuously evolved into a larger disk attachment. This solution also had the lowest molar concentration of the solutions presented. In this case the charge on the cation is larger leading to reduced activity which suggests a decrease in the ions hydrated radius and thus the reduced effect of the surrounding solution. The decreased activity suggests locally an increase in the local conductivity. The lack of a pronounced pattern formation with the solution of reduced activity suggests that the local conductivity that may be important in determining patterns. Pattern formation is likely a means of maintaining discharge continuity when there is a mismatch between the local conductivity in solution and the demanded discharge current as suggested earlier. Figure 19 illustrates the variation in pattern formation for the chloride anion family. In general, the patterns evolve similarly regardless of electrolyte type for at least this family.

Self Organization and Fluid effects

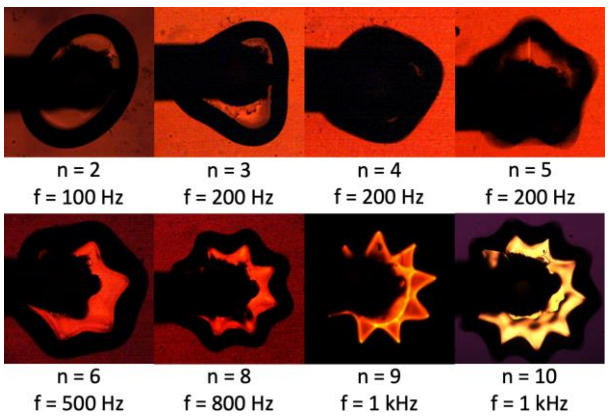

Figure 21. 2-D bubble interfacial perturbation driven by streamer attachment. (Lai, Foster PSST, 2019)

Induced fluid motion typically accompanies the interaction of plasma with liquid water. This has been seen in DBD plasma jets as well as DC glows with liquid electrode.[106,107] Such plasma-induced fluid motion has also been studied in systems with plasmas produced in bubbles. Here Marangoni flow appears to be the mechanism at play that gives rise to fluid circulation. In this case the plasma locally induces a gradient in the surface tension at the interface associated with localized heating or the development of a concentration gradient as a result of the production of chemically active

species, which subsequently drives the flow.[108,109] Fluid motion adds to the complexity of interpreting plasma pattern formation. While reaction-diffusion formalism has been applied in part to understand plasma self organization on liquid surfaces, the presence of fluid motion means that a convective term must also be added, thereby greatly enriching the solution set and its associated complexity.[110] This coupling of fluid motion to the plasma liquid interaction giving rise to spatial ordering of the discharge has been observed in 2-D bubble systems. In the 2-D bubble apparatus, a thin layer of water is captured between two closely spaced quartz plates. A flat, essentially 2D bubble is injected in the water layer between the two plates. A discharge is then generated in this "2D" bubble through the application of a voltage pulse to an electrode located at the center of the bubble. Streamer discharges arise and make contact with the bubble interface when the electrode is excited repetitively with high voltage pulses (~10 kV). In this system, evidence of fluid plasma coupling has manifested itself in two distinct ways: Case 1) formation of circulation cells as a result of Marangoni flow and Case 2) coupling of streamers with induced capillary oscillations excited at the bubble boundary. In the former case, the plasma incident on the interface drives Marangoni convection. If a chemical probe such as a pH sensitive dye is placed in solution, then entrained solution will then be circulated past the interface with plasma contact and thus chemically reacts and changes color which facilitates the imaging of the organizing patterns in the solution beyond the bubble as shown in figure 20.

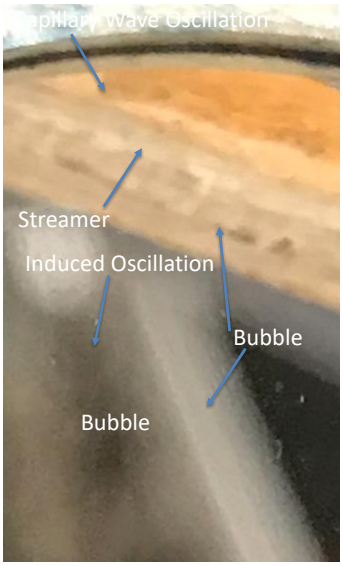

Figure 22. Streamer self-organization and the transmittal of acoustic noise to adjacent bubble. Lai and Foster, PSST, 2019

Case 2 suggests the possibility of coupling between plasma induced fluid effects (capillary oscillations) and the spatial ordering of the streamer attachments. This scenario has been also observed in the 2-D bubble. Its occurrence is intriguing in that it suggests the prospect of exploiting induced fluid effects to actually increase the plasma-liquid contact surface area. It is this contact surface area that serves as the source of the production and propagation of reactive species into the solution. The maximation of this contact area is therefore key to scaleup for a range of plasma engineering applications such as water purification. The observed coupling is initiated by the plasma induced generation of capillary waves on the interface of the bubble. It was observed that subsequent streamers to interface attachments are synchronized with the capillary wave leading to wave driven organization of the spatial distribution of the streamers. Figure 21 depicts capillary waves induced at the interface due to streamer strikes at the interface. The streamers tended to strike only in the regions of the crest of the capillary waves as can be seen in figures 21 and 22. In this respect, the spatial organization of the streamers is driven intrinsically via feedback from the microscopic interactions of the streamer with the interface which sets it into motion. Since the appearance of the pattern develops from a condition with seemingly random streamer strikes at the interface, the observed subsequent spatial and temporal structuring of the streamer strikes may be thought of as a form of self organization as well.[111] Here, the role of positive feedback is being played by the oscillating interface. Only certain oscillations modes are possible depending on the size of the bubble so the system also contains resonances. Figure 21

illustrates the interfacial shape perturbations as a function of voltage pulse frequency and the formation of capillary waves at the interface. Interestingly, the acoustic noise from the capillary waves can be transmitted to nearby bubbles giving rise to sympathetic oscillations along the interface of nearby bubbles as well. In this respect, one observes a local cluster of bubbles that oscillate in unison as well.[112] This can be seen in Figure 22.

V. Computational Insight: Progress in Modeling Self Organization Patterns

While the bulk of this review has focused on liquid water anodes, models describing aforementioned patterns on solid electrodes may provide some insight into pattern formation more generally. One early such model for the formation of anode spot patterns on solid electrodes was proposed by Muller.[113] In that work, the existence of a bistable layer (sheath and near electrode plasma) in contact with the anode can give rise to spatial plasma attachment patterns. Here it is assumed that the voltage-current characteristic of this layer is "S" shaped which in turn allows for three regimes of charge flow—a high current mode, a medium current and a low current mode existing at some critical voltage. It is the existence of these multiple states at a given critical voltage along with repulsive columbic interactions that gives rise to solutions consisting of spatially varying current distributions on the anode—patterned spots. In this case, the low mode is associated with a diffuse glow while the high mode is associated with spot transition. It should be noted that. The existence of a bistable layer is consistent with liquid anode. The water anode surface is inherently resistive since conductivity depends on ionic production and transport in the liquid and thus is a function of the current itself. The electrical conductivity of the liquid also depends locally on temperature as well, generally increasing with increasing temperature.[114] The anode surface can be perturbed as well which modifies both the local electric field and collection area. Localized vaporization can greatly effect ionization processes and given the local magnitude of the electric field can give rise to anode spot formation. These processes given rise to nonlinarities in the current voltage response which in turns varies spatially at the surface with the current distribution. In this respect, a bistable layer model in principle is consistent with conditions at the anode. Insight into pattern formation on anodes can also be gleaned from cathode attachment studies aimed at elucidating similar self-organization phenomena. Almeida, Benilov and Faria have shown computationally that patterns on the surface of the cathode can be described using bifurcation analysis.[115,116] Here, owing to the fact that the discharge possesses axial symmetry, a continuum of possible solutions at a given discharge current exists. Perturbations can lead to branching or bifurcation which in turn leads to spatial mode changes and self-organization. By applying such analysis to a simple, self-consistent glow discharge model that also includes drift diffusion, Almeida and colleagues observed multiple steady-state solutions corresponding to 2D and 3D patterns. 2-D patterns were observed even when diffusion losses were turned off in the model. These patterns were discovered by locating the points of bifurcation which branch off from the expected fundamental mode where the attachment is uniform. Perturbing the solution around the bifurcation point in the radial direction allows for the 2D mode to be located. The range in current or voltage over which these states exist was then further elucidated by varying the current or voltage. Such an approach featuring a glow discharge model with local approximation may applicable to the prediction of patterns on the surface of liquid anodes though local charge transport processes at the interface and through the liquid add additional complexity. Plasma patterns appearing on the surface of solid anodes in arc discharges have been observed in computational models and appear to agree at least qualitatively with that observed in experiment.[117] Some of these patterns are similar to those observed on liquid anodes. Computational modeling of 1 atm

pressure discharges with liquid anodes on the other hand has proven elusive. Some success in at least qualitatively understanding pattern formation in DBD discharges has been realized by applying an equivalent circuit model in which coupling between filaments is modeled using resistor. The system of equations transformed into a set reaction diffusion equations—the solution of which yields patterns.[118,119] Self organization of anode spots DC low pressure glows has been successfully qualitatively modeled. This work utilized a drift diffusion model with local field approximation coupled and Poisson's equation.[120] In that work it was acknowledged that to address patterns quantitively, the model must incorporate plasma chemistry, nonlocality of electron energy, gas heating, collisions and neutral flows. More recently, a reaction diffusion model has been put forth that has been able to successfully predict the onset of pattern formation.[121] In this work, Rumbach and colleagues treats local electron impacts resulting in ionization as an autocatalytic reaction which produces more electrons. Recombination and attachment are treated as inhibitors. The model assumes the patterns form in a thin sheath layer just above the liquid water. Two dimensional profiles predicted by this model are similar to experimental measurements as shown in figure 23. While the model does not treat nonlinear feedback associated with ionization, the electric field and gas heating, it represents a very important first step towards understanding the occurrence and form of self-organization patterns on the liquid anode.

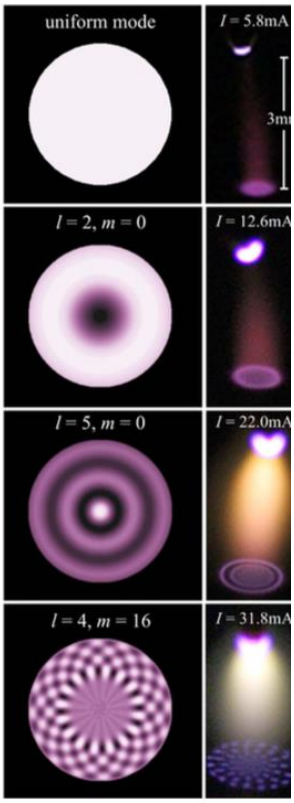

Figure 23. Comparison with model predicted modes (left) and experimentally observed patterns (Rumbach. 2019)

VI. Future prospects

Self organization is a fundamental physical process ubiquitous in nature. Self organization of plasma on liquid or solid surfaces at one atmosphere remains not well understood. Comprehension of plasma self organization in the 1 atm regime may yield insight into this general problem with applicability not just in plasma physics but over a wide range of disciplines. Understanding self organization of these plasmas is not just a basic plasma science question. A range of technological applications featuring such plasmas are currently under study or development. To have a better understand of the nature of such plasmas and ultimately control the self organization process is therefore important. Experiments to date have given a great deal of insight into conditions for pattern formation and evolution. These experiments provide guidance into how perhaps one can maximize plasma contact surface area—a problem key to scale up. Key experiments however remain to be carried out. For example, a detailed spatial mapping of the plasma properties in the attachment itself (e.g. temperature and density) as well as the electric field within would provide great insight into understanding the formation and maintenance of these attachments. Are the attachments true double layers? Furthermore, the liquid surface at the attachment locally is not well characterized. Is this surface superheated or boiling? What role does plasma induced chemistry and the liquid double layer play in the self organization process? Is surface charging important in pattern development? Plasma induced fluid motion is known to occur in these systems, but the precise role it plays in discharge maintenance and self organization

remains a mystery. Such processes have not be extensively explored experimentally but if measured can contribute to completing the picture of the interplay between the plasma, the electrolyte and ultimately pattern formation. Modeling efforts have lagged somewhat though excellent progress is being made in this arena as well. For example, reaction diffusion along with bifurcation analysis appear to hold a great deal of promise in the prediction of the onset of and ultimately the evolution of the patterns. Incorporating complex liquid phase chemical processes and convection into such a model remains to be carried out. Advanced computational tools may be necessary to solve the seemingly simple discharges as in reality it involves a multitude of both liquid and gas phase chemical reactions and collision driven physics in the anode sheath—coupled to fluid dynamical effects. Once fully developed, such a model can be used as not only a design tool for applications, but also serve as a guide to experiments to fully elucidate the physics prevailing within the beautiful surface plasma patterns of the 1 atm DC glow with liquid anode.

Acknowledgement

This work was supported by the Department of Energy: DOE DE-SC0001939 and DOESC0018058

References

[1] Serna, H. and Barragan, D., Rev. Acad. Colomb. Cienc. Ex. Fis. Nat. 41,(160), 349, 2017.

[2] Aschwanden, M.J., Scholkmann, F., Bethune, W., Schmutz, W., Abramenko, V., "Order out of Randomness: Self-Organization Processes in Astrophysics", Space Science Reviews, March, 55, 214, 2018.

[3] Kocurek, G. and Ewing, R.C., Geomorphology, 72, 94, 2005.

[4] Pearson, J.E., Science, 261, no 5118, 189, 1993.

[5] Epstein, I.R. and Pojman, J.A., An Introduction to Nonlinear Chemical Dynamics, Oxford University Press, 1998.

[6] Nicolis, G., and Prigogine, I. (1971). Fluctuations in nonequilibrium systems. Proceedings of the National Academy of Sciences, 68(9), 2102-2107.

[7] Nicolis, G., and Prigogine, I, Self Organization in Nonequilibrium Systems, John Wiley and Sons, 1977.

[8] Prigogine, I., Thermodynamics of Irreversible Processes, Wiley, New York, 1955.

[9] Yang, G., and Heberlein, J. (2007). Anode attachment modes and their formation in a high intensity argon arc. Plasma Sources Science and Technology, 16(3), 529.

[10] Yang, G., Cronin, P., Heberlein, J. V., and Pfender, E. (2006). Experimental investigations of the anode boundary layer in high intensity arcs with cross flow. Journal of Physics D: Applied Physics, 39(13), 2764.

[11] Benilov, M. S. (2008). Bifurcations of current transfer through a collisional sheath with ionization and self-organization on glow cathodes. Physical Review E, 77(3), 036408

[12]Chirokov, A., Gutsol, A., Fridman, A., Sieber, K. D., Grace, J. M., and Robinson, K. S. (2006). A study of two-dimensional microdischarge pattern formation in dielectric barrier discharges. Plasma chemistry and plasma processing, 26(2), 127-135.

[13] Fridman, A., Chirokov, A., and Gutsol, A. (2005). Non-thermal atmospheric pressure discharges. Journal of Physics D: Applied Physics, 38(2), R1.

[14] Abolmasov, S. N., Tachibana, K., and Shirafuji, T. (2011). Mechanisms of pattern formation in dielectric barrier discharges. IEEE Transactions on Plasma Science, 39(11), 2090-2091.

[15] Babaeva, N. Y. and Kushner, M. J. (2014). Self-organization of single filaments and diffusive plasmas during a single pulse in dielectric-barrier discharges. Plasma Sources Science and Technology, 23(6), 065047.

[16] Trelles, J. P. (2016). Pattern formation and self-organization in plasmas interacting with surfaces. Journal of Physics D: Applied Physics, 49(39), 393002.

[17] Mokrov, M. S., & Raizer, Y. P. (2018). 3D simulation of hexagonal current pattern formation in a dc-driven gas discharge gap with a semiconductor cathode. Plasma Sources Science and Technology, 27(6), 065008.
[18] Klarenaar, B. L. M., Guaitella, O., Engeln, R., & Sobota, A. (2018). How dielectric, metallic and liquid targets influence the evolution of electron properties in a pulsed He jet measured by Thomson and Raman scattering. Plasma Sources Science and Technology, 27(8), 085004.
[19] Martinez, L., Dhruv, A., Lin, L., Balaras, E., & Keidar, M. (2019). Interaction between a helium atmospheric plasma jet and targets and dynamics of the interface. Plasma Sources Science and Technology, 28(11), 115002.
[20] Rajkovic, M., Milovanovic, M., and Skoric, M. M., Phys. Plasmas, 24, 052303, 2017.
[21] Yamada, M., AIP Conference Proceedings, 1721, 020005, 2016.
[22] McCarter, A.J., PhD thesis, "Quantifying self-organization in fusion Plasmas," Dublin City University, 2005.
[23] Becker,K.H., Schoenbach, K.H., and Eden, J.G., J. Phys. D: Appl. Phys. 39, R55, 2006.
[24] Schoenbach, K.H., Moselhy, M., and Shi, W., Plasma Sources Sci. Technol., 13, 177, 2004.
[25] Breazeal, W., Flynn, K.M., and Gwinn, E.G., Phys. Rev. E., 52, 52, 1995.
[26] Hickling, . and Ingram, M.D., Transactions of the Faraday Scoiety, 60, 1964.
[27] David Staack, Bakhiter Farouk, Alexander Gutsol and Alexander Fridman Plasma Sources Sci. Technol. 14 700, 2005
[28] N. Shirai, S. Ibuka, S. Ishii, "Self-organization pattern in the anode spot of an atmospheric glow microdischarge using an electrolyte anode and axial miniature helium flow", Appl. Phys. Express, vol. 2, no. 3, Mar. 2009.

[29] Trelles, J.P., J. Phys. D. Appl. Phys., 49, 393002.
[30] Staack, D., Farouk, B., Gutsol, A., and Fridman, A., Plasma Sources Sci and Technol., 17, 025013, 2008.
[31] Staack, D., Farouk, B., Gutsol, A., and Fridman, A., J. appl. Phys., 106, 013303, 2009.
[32] Tochikubo, F., Shirai, N., and Uchida, S., Journal of Physics: Conference Series 565, 012010, 2014.
[33] Chen, Q., Li, J. , and Li, Y., J. Phys. D. Appl. Phys., 38, 424005, 2015.
[34] Zhang, S. and Dufour, T., Physics of Plasmas, 25, 073502, 2018.
[35] Shirai, N., Uchida, S., Tochikubo, F., and Ishii, S., IEEE Trans. Plasma Science, 39, 2652, 2011.
[36] Kovach, Y.E., Garcia, M.C., and Foster, J.E., IEEE Trans. Plasma Sci., 47, 3214, 2019.
[37] Scheiner, B., Barnat, E.V., Baalrud, S.D., Hopkins, M.M., and Yee, B.T., Phys. Plasma, 24, 113520, 2017.
[38] Bruggeman, et al, J. Phys. D: Appl. Phys. 41, 215201, 2008.
[39] Shirai, N. , Uchida, S., and Tochikubo, F., Plasma Sources Sci. Technol., 23, 054010, 2014.
[40] Richmonds, C., Witzke, M., Bartling, B., Lee, S.W., Wainright, J., Liu, C.C., and Sankaran, R.M., J. Am. Chem. Soc., 133, 17582, 2011.
[41] Rumbach, P., Bartels, D.M., Sankaran, R.M., and Go, D.B., Nature communications, | 6:7248 DOI: 10.1038/ncomms8248 | www.nature.com/naturecommunications
[42] Bruggeman, P. et, J. Phys. D: Appl. Phys., 41, 215201, 2008.
[43] Bruggeman, P.J. et al, Plasma Sources Sci. technol. 25, 053002, 2016,
[44] Tochikubo, F., Aoki, T., Shirai, N., and Uchida, S., Jap. J. Appl. Phys., 56, 046201, 2017.
[45] Lietz, A. M., and Kushner, M. J. (2016). Air plasma treatment of liquid covered tissue: long timescale chemistry. Journal of Physics D: Applied Physics, 49(42), 425204.
[46] Martinez, L., Dhruv, A., Lin, L., Balaras, E., and Keidar, M. (2019). Interaction between a helium atmospheric plasma jet and targets and dynamics of the interface. Plasma Sources Science and Technology, 28(11), 115002.
[47] Bruggeman et al, Plasma Sources Sci. Technol.,25, 053002, 2016.
[48] Couch, D. E.; Brenner, A. J. Electrochem. Soc. 1959, 106, 628-629.
[49] Marcus, R.K., and Davis, W.C., Anal. Chem., 73, 2903, 2001.
[50] Webb, M.R. et al, J. Analytica Atomic Spectrometry, 11, 1218,2005
[51] Webb, M., and Hieftje, G.M., Analytical Chemistry, 81, 3, 867, 2009.
[52] Greda, K., Swiderski, K, Jamroz, P., and Pohl, P., Anal. Chem. 88, 17, 8812.
[53] Chen, Q., Kaneko, T., and Hatakeyama, R., Applied Physics Express, 5, 086201, 2012.
[54] Chen, Q., Li, J., and Li, Y. J. Phys. D:Appl. Phys. 48, 434005, 2015

[55] Shirai, N., Uchida, S., and Tochikubo, F., Japanese Journ. Appl. Phys., 53, 046202, 2014.
[56] Keidar, M., Phys. Plasmas, 25, 083504, 2018.
[57] Chen, Z., Zhang, S., Levchenko, Beilis, I.I. and Keidar, M., Scientific Reports, 7, 12163, 2017.
[58] Foster, J.E., Phys. Plasma, 25,4, 055501, 2017.
[59] Munter, R., Proc. Estonia Acad. Sci. Chem., 50, 2, 59, 2001.
[60] Glaze, W.H., Kang, K.W., and Chapin, D.H., Ozone: Sci. Eng., 9, 335, 1987.
[61] Wang, X., Zhou, M., and Jin, X., Electrochimica, Acta, 83, 501, 2012.
[62] Gao, J. et al, Water Research, 37, 267, 2003.
[63] Lu, Q., Yu, J., and Gao, J., J. Hazard. Mat. , B136, 526, 2006.
[64] Sengupta, S. K., Singh, R., and Srivastava, A.K., J. Electrocem. Soc., 145, 7, 2209, 1998.
[65]A. R. Denaro and A. Hickling, J. Electrochem. Soc. 105, 265 (1958)
[66] Zheng, P. et al, Applid Surface Science, 259, 494, 2012.
[67]Epstein, I.R. and Showalter, K., J. Phys. Chem., 12132,1996.
[68] Turing, A.M.,, Philos. Trns. R. Soc London, B237, 37, 1952.
[69]Horvath, J., Szalai, I., and De Kepper, P., Science, 324,773, 2009.
[70] Gray, P. and Scott, S.K., Chemical Engineering Science, 39, 1087, 1984.
[71] Gray, P. and Scott, S.K., Chemical Engineering Science, 38, 29, 1983.
[72] Radehaus, C., Dirksmeyer, T., Willebrand, H., and Purwins, H.G., Physics Letters A, 125, 2/3, 92, 1987.
[73] Niedernostheide, F.J., Ardes, M., Or-Guil, M., and Purwins, H.G., Phys. Rev. B, 49, 49,1994.
[74] Palko, J.W et al, J. of Power Sources, 397, 252, 2018
[75] Tadmor, R., J. Colloid and Interface Science, 332, 451, 2009.
[76] Foster, J.E., and Lai, J., IEEE Trans. Plasma Science, 44, 1137, 2016.
[77] Lai, J., Petrov, V., and Foster, J.E., IEEE Trans. Plasma Science, 46, 875, 2018.
[78] Horvath et al, ACC. Chem. Res., 51, 12, 3183, 2018.
[79] Gollube, J.P. and Langer, J.S., Reviews of Modern Physics, 71, 2, S396, 1999.
[80]Mutabazi, I., Wesfreid, J.E., and Guyon, E., Dynamics of Spatio-Temporal Cellular Structures, Springer Verlag,2006.
[81] Sommers, B.S., Foster, J.E., Babaeva, N., and Kushner, M.J., J. Phys. D: Appl. Phys. 44, 082001, 2011.
[82] Sommers, B.S., and Foster, J.E., J.Phys. D: Appl. Phys., 49, 415203,2012.
[83] Szeri, A., J. Fluid Mech., 332, 341, 1997
[84] Smith, A.M., Lee, A A., and Perkin, S. J. Phys. Chem. Lett. , 7, 2157, 2016.
[85] Lin, C. et al, Phys. Chem. Chem. Phys., 18, 9829, 2016.
[86] Nurnberg, H.W., Discuss. Faraday Soc.,39, 136, 1965.
[87] Verreycken, T., Bruggeman, P., and Leys, C., J. Appl. Phys., 105, 083312, 2009.
[88] Verreycken, T., Bruggeman, P., and Leys, C., J. Applied Phys., 105, 083312, 2009.
[89] Cserfalvi, T., Mezei, P., and Apai, P., J. Phys.D: Appl. Phys. 26, 2183, 1993.
[90] Shirai, N. et al, plasma sources sci. technol. 23 054010, 2014

[91] Shirai, N. Applied Physics Express, 2, 036001, 2009.
[92] Johnson, J.A., and Ramaiah, R., Phys. Rev. A, 36, 774,1987.
[93]Zhang, S, and Dufour, T, Physics of plasma 25 , 073502, 2019
[94] Bruggeman, P. et al, J. Phys. D: Appl. Phys., 41, 215201, 2008.
[95] Zheng, P. et al, Plasma Sources Sci. Technol., 24, 015010, 2015.
[96] Thomas, C.H., and Duffendck, O.S., Phys. Rev. 35, 73, 1930
[97] Shirai, N., Satoshi, U., Fumiyoshi, T., and Shozo, I., IEEE Trans. Plasma Science, 39, 11, 2653, 2011.
[98] Kovach, Y.E., Zhang, F., Gao, F., and Foster, J.E., J. Vac. Sci. Technol. A., 37, 011301, 2019.
[99] Nakamura, Y., Sc. Tehnol. Adv. Mater., 19, 31, 2018.
[100] Toprak, M.S., Adv. Funct. Mater, 14, 1189, 2004.
[101] Kovach, Y., Garcia, M.C., and Foster, J.E., IEEE Trans Plasma Science, 47, 3214, 2019
[102] Song, B., D'Angelo, N., and Merlino, R.L., J. Phys. D: Appl. Phys, 24, 1789, 1991.

[103] Paris, P., Aints M., Valk F., Plank T., Haljaste A., Kozlov K.V. and Wagner H.E., J. Phys. D: Appl. Phys. 38 (2005) 3894–3899,

[104] Kovach, Y., Garcia, M.C., and Foster, J.E., IEEE Trans Plasma Science, 47, 3214, 2019
[105] Kovach, Y., Garcia, M.C., and Foster, J.E., IEEE Trans Plasma Science, 47, 3214, 2019
[106] Foster J.E. 2017, Physics of Plasmas. 24(5).
[107] P.J. Bruggeman, M.J. Kushner, B.R. Locke, J.G.E. Gardeniers, W.G. Graham, D.B. Graves, R.C. Hofman-Caris, D. Maric, J.P. Reid, E. Ceriani, D. Fernandez Rivas, J. E. Foster, S.C. Garrick, Y. Gorbanev, S. Hamaguchi, F. Iza, J. Kolb, F. Krcma, P. Lukes, Z. Macha-la, I. Marinov, D. Mariotti, S. Mededovic Thagard, D. Minakata, E. Neyts, J. Pawlat, Z.Lj. Petrovic, R. Pfieger, S. Reuter, D.C. Schram, S. Schroter, M. Shiraiwa, B. Tarabová, H. Tresp, P. Tsai, J. Verlet, T. von Woedtke, E. Vyhnankova, K.R. Wil-son, K. Yasui, G. Zvereva, .Plasma Sources Science and Technology, 25,1, 2016
[108] Lai, J., Petrov, V., and Foster, J., IEEE Trans. Plasma Sci., 46, 4, 875, 2018.
[109] Berendsen, C.W.J., van Feldhuizen, E.M, Kroesen, G.M.W., and Darhuber, A.A., J. Phys. D.: Appl. Phys. 48, 025203, 2015
[110] Nicolis, G., and De Wit, A., Scholarpedia, 2(0), 1475, 2007.
[111] Lai, J. and Foster, J.E., " Experimental observations of interfacial oscillations and self organization derived from streamer driven mechanical perturbation of a gas liquid boundary," Accepted for publication Plasma Sources Science and Technology , Oct, 2019.
[112] Lai, J., and Foster, J.E., PSST, 28, 125003, 2019.
[113] Muller, K.G., Physical Review A, 37, 12, 4836, 1988.
[114] Kuyucak, S. and Chung, S-H., Biophysical Chemistry, 52, 15, 1994.
[115] Almedia, P.G.C., Benilov, M.S., Cunha, M.D., and Faria, M.J., J. Phys. D.: Appl. Phys., 42, 194010, 2009.
[116] Almeida, P.G.C., Benilov, M.S., and Faria, M.J., Plasma Sources Science and Technol., 19, 025019, 2010.
[117] Trelles, J.P., Plasma Sources Sci. Technol., 22, 025017, 2013
[118] Purwins, H.G. et al, Adv. Phys., 59, 485, 2010.
[119] Callegari, T., Bernecker, B., and Boeuf, J.P., Plasma Sources, Sci. Technol., 23, 054003, 2014.
[120] Bieniek, M.S., Almeida, P.G.C., and Benilov, M.S., Plasma Sources Sci. Technol. 27, 05LT03, 2018.
[121] Rumbach, P., Lindsay, A.E., and Go, D.B., Plasma Sources Sc. Technol, https://doi.org/10.1088/1361-6595/ab45e4, 2019.