Plasma-liquid interactions

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Plasma discharges are traditionally associated with a gaseous phase; however, discharges can be generated in all phases. Plasma discharges formed in liquids and interfacing with liquids represent an emerging and fast-growing field of research, not the least because they offer unique conditions that enable decontamination of pathogens, synthesis of nanostructures, and treatment of contaminated water. With the variety of discharge regimes and types of liquids comes a rich field of multiphase phenomena to be discovered, measured, modeled, and utilized. A detailed overview of the field has been reported in [1] and extended upon in several more recent reviews and perspective articles [2-7].

In the "Plasma-Liquid Interactions" Special Topic Collection, we explore the richness and full breadth of plasma-liquid interactions and their applications. The collection contains two Perspective Articles that discuss key questions related to fundamental processes at the plasma-liquid interface. Bruggeman *et al*. [8] introduce the concept of plasma-driven solution electrochemistry (PDSE) inspired by comparing plasma-liquid interactions with conventional electrolysis and develop 10 questions that should be answered to enable researchers to make transformational advances in plasma-liquid interactions for a variety of applications. The Perspective by Vanraes and Bogaerts [9] focuses on that same plasma-liquid interface but emphasizes the gas phase processes rather than liquid-phase processes. The authors make the argument thatsheaths at liquid interfaces can have unique properties and are relatively unexplored while exceedingly important for many applications ranging from nuclear fusion to biomedical applications.

Several of the papers featured in the Special Topic Collection report on advances in plasma generation in the presence of liquids. While the breakdown in liquids has been studied for several decades, most of these studies are phenomenological in nature, and there is an urgent need for more physical insights. Phan *et al*. [10] contributed to this need for the specific case of cryogenic discharges in liquid helium. They report breakdown field data revealing that breakdown is closely correlated with Fowler–Nordheim field emission from asperities on the cathode.

While many studies have been reported on breakdown of liquid water, our knowledge remains incomplete. Competing breakdown theories focusing on direct liquid phase ionization or gaseous/low density phase generation have not been irrefutably validated experimentally. Zhang and Shneider [11] quantitatively discuss electron detachment from hydroxide as the most probably source of primary electrons that seed plasma discharges in liquid water. Their numerical study demonstrates the drift of hydrated electrons from one cavity to the next might be the rate-limiting step and sets the minimum electric field requirement for breakdown. A complementary experimental study by Grosse *et al*. [12] concludes that plasma propagation is governed by field effects in low-density regions that are created either by nanovoids or by density fluctuations in supercritical water surrounding the electrode that is created at plasma ignition. Their results suggest that plasma ignition is dominated by field effects at the electrode–liquid interface, either as field ionization for positive polarity or as field emission for negative polarity. While the conditions of Grosse *et al*. led to minor differences between positive and negative voltage pulsed at the very initial stages of the discharge, Hamdan *et al*. [13] reported optical and electrical measurements showing a major difference in the initial discharge dynamics with polarity, although for larger pulse widths. Akter *et al.* [14] investigated the effects of elevated pressure on the breakdown in liquid water in the context of the use of plasma discharges in liquids as energy-focusing devices to achieve deep earth drilling for conditions ranging from 1 to 350 atm. Korolev *et al.* [15] extended this work to conditions in highly conductive saline in which discharge generation is preceded by the formation of a vapor layer around the driven electrode, which allows to generate a glow-like plasma regime instead of the typical filamentary plasma discharges generated by pulsed discharges in liquid water. Wang *et al*. [16] developed a multiphase empirical system model to simulate breakdown in gas–liquid phase mixtures. The model considers a power law and the Meek criterion for the liquid and gas phase breakdown, respectively, and can be used to determine the deposited energy in both mixtures, which is important for the optimization of applications.

Many plasma applications involving liquids do not involve the generation of a plasma in the liquid phase but involve plasma generation between a metal electrode and a liquid electrode. Hoft *et al*. [17] reported on the unique aspects of a less-studied approach of plasma formation between an electrode covered with a dielectric layer and liquid water, which shows distinct differences compared to the extensively studied metal-liquid electrode geometries. While the dielectric-covered electrode was able to prevent spark formation very similar to dielectric barrier discharges, it remarkably can –for certain conditions– even prevent a volume discharge. When electrodes are heated excessively, for example in welding, a solid electrode can become a liquid electrode without a liquid initially being introduced in the plasma reactor. This process is also relevant for breakdown studies at low pressure, where so-called explosive emission centers, explosions of micro-protrusions on electrode surfaces, inject metal and electrons in the plasma. This process can involve the melting of these protrusions due to the high local energy deposited. This intriguing process is modelled in the contribution of Barengolts *et al*. [18].

An alternative approach to electrically generated plasmas both in gas and liquid phase are laser-produced plasmas. Dell'Aglio *et al*. [19] compared the unique differences between laser-induced plasma (LIP) in liquid water and air. Their experimental results reveal that plasma under water remains much longer in a high-density state than in air due to the confinement effect of the surrounding water. It is argued that these differences allow LIP in liquid and gas to be used in a wide variety of applications, ranging from analytical chemistry to nanomaterial production. Young *et al*. [20] reported on the memory effects in repetitive laser-induced breakdown in water near a solid target, and explained these effects through particle inclusion concentration changes and microbubbles in the laser path.

Three contributions of the “Plasma-Liquid Interactions” Special Topic Collection focus on reactions and transport of reactive species at the plasma-liquid interface. Solvated electrons are suggested to be an important plasma-produced species in liquid, although the detailed processes of the transfer of electrons from the gas to the liquid phase are not well understood. Akiyama *et al*. [21] report Monte Carlo simulations of electrons in liquid water, assuming the dense gas approximation, to investigate the production of hydrated electrons and radical species by low-energy electron irradiation of the water surface from an atmospheric-pressure plasma. Delgado *et al*. [22] determined the characteristic lifetimes and penetration depth of solvated electrons and hydroxyl radicals at the plasma-liquid interface based on mathematical scaling of the reaction–diffusion equations. These effects lead to transport limitations for secondary chemical reactions that are exceedingly important for many applications. Sgogina *et al*. [23] studied these same transport effects near the plasma-liquid interface for atomic oxygen reactions with phenol and showed the important impact of Henry’s law solubility constant and near surface reactions due to the surfactant character of phenol molecules.

While previous studies focus on diffusion in boundary layers, convection in the liquid phase can contribute to species transport in the liquid phase more dominantly than in the gas phase, as diffusion in the dense liquid is much slower than in the gas phase and hence Peclet numbers are typically large. Dickensen *et al*. [24] found that the dominant mechanism driving the liquid flow in the absence of imposed gas convection is correlated with the charge relaxation time of the liquid. For liquids with a charge relaxation time longer than the characteristic time of the plasma, such as de-ionized water, the liquid behaves as a dielectric, and the electric surface stresses dominate the flow in the liquid phase. For liquids with a charge relaxation time shorter or in the same order of the plasma characteristic time, such as tap water, the liquid behaves as a conductor, and the EHD flow induced in the gas phase dominates the flow in the liquid phase. Yang *et al*. [25] found correlations between self-organized anode layers at the plasma-liquid interface and the plasma-induced flow field. Their results showed that self-organization led to non-static flow structures and generation of a strong swirl flow hypothesized to be due to electrohydrodynamic forces.

An approach to mitigate transport limitations of reactive species is the use of highly dispersed liquid phases in the plasma such as droplets and sprays with a high surface-to-volume ratio. This highly multiphase environment leads to additional complexities for diagnostics. Janda *et al*. [30] used a cost-effective diagnostic technique based on planar laser light attenuation for online monitoring of electrospray microdroplets, which enables simultaneous and synchronized electrical and optical diagnostics of an electrical discharge, and can be used to estimate the speed and size of microdroplets. Nonetheless, droplets can also impact the safety of high voltage transmission lines. To this end, Zhang *et al*. [31] performed particle-in-cell simulations of streamer discharges on the conductor surface in the presence of raindrops.

Plasma discharges formed in liquids and interfacing with liquids can exhibit strong differences in morphology and modes. Some studies, like the work of Marjanović *et al*. [26], are performed in highly controlled conditions that allow for detailed comparison with modeling, nonetheless a lot of studies focus on more complex electrode geometries motivated by applications. Marjanović *et al*. [26] report on different discharge modes in four different alcohol vapors covering Townsend, normal glow, and abnormal glow regimes with a focus on distinct transitions between the normal and abnormal glow regimes, while Yuan *et al*. [27] reported three discharge modes (streamer mode, glow-like mode, and abnormal glow/arc mode) in an oxygen discharge with liquid electrode plasma. Gershman and Belkind [28] extended this work to a study of the plasma properties of discharges generated in gas bubbles in hydrogels, which allowed them to assess the impact of dielectric constant and conductivity. Additional complexity can also be introduced when discharges are transient, particularly self-pulsing, spark-like discharges as reported by Sretenović *et al*. [29].

Several of the papers in the “Plasma-Liquid Interactions” Special Topic Collection are directly linked to a specific application or its underlying process. While nanomaterial synthesis with plasmas interacting with liquids has been around for more than a decade, a recently renewed interest in this area is reflected in six contributions in the collection. The general idea is that a broad range of metal ion precursors can be reduced by plasma-produced solvated electrons and the resulting large concentrations of reduced metal atoms nucleate to form nanoparticles. This approach has been studied in detail for noble metals in the last decade. The study of Thai *et al*. [32] suggests that the ability to form nanoparticles is strongly dependent on the redox potential and is driven by equilibrium processes. While the most common approach to generate nanoparticles is using a gas phase glow discharge with a solution anode, Čechová *et al*. [33] showed that silver and gold nanoparticles could also be effectively produced in a pinhole discharge in which the discharge is generated in a vapor bubble, which is formed due to the constriction of current in the solution at the position of the pinhole. While single-phase particles have been produced by plasma-liquid interactions for many materials, an outstanding challenge is the formation of bimetallic particles, which is the focus of Merciris *et al*. [34]. Nomine et al [35] extensively reviewed the basic physics of nanoparticles’ synthesis by discharges in liquids with the metal precursor introduced from the electrode. Furthermore

Chao-Mujica *et al*. [36] showed the production of fluorescent carbon quantum dots (CQDs) by a submerged arc discharge in water, and Égerházi *et al*. [37] utilized exploding wire discharges for the synthesis of copper oxide particles. In many applications it is important to adhere nanoparticles on a substrate. Dos Santos *et al*. [38] report in this context on the electrical discharge-enhanced deposition of TiO_2 nanoparticles on cotton fabric.

Plasmas in and in contact with liquid water produce an abundant amount of hydroxyl radicals and thus have great potential for wastewater treatment. While plasma technology for water treatment has been investigated for several decades, the treatment of newly emergent pollutants like pharmaceutical residues and perfluorooctanoic acids (PFOAs) remains a topic of further investigation. Nau-Hix et al [39] report on the treatment of PFOA and rhodamine B showing that for a surface spark discharge the dominant decomposition is not due to hydroxyl radicals but by the formation of hypochlorous acid in the presence of NaCl and photolysis. Brault *et al*. [40] use molecular dynamics simulations to elucidate reaction steps of hydroxyl radical interaction with the paracetamol molecule in water. There is renewed interest in discharges in hydrocarbons that have been studied extensively in the past in the context of electrical insulation but are now investigated in the context of upgrading low-grade fuels or the production of value-added chemicals. Hamdan *et al*. [41] demonstrated the use of microwave discharges in liquid heptane to produce ethylene and acetylene, which showed significantly different products than expected from a chemical equilibrium composition, and Adámková *et al*. [42] studied the conversion of ethanol in pinhole discharges in ethanol–water solutions.

Glow discharge plasmas with liquid cathode (and anode) have been extensively studied in the analytical chemistry field as a tool for trace elemental analysis. The plasma not only enables the transfer of the solute into the plasma phase, but also the excitation of the atomic species, thereby allowing the detection by atomic emission spectroscopy or alternatively act as an ionization source of the atoms for mass spectrometry detection. In this context, Walton *et al*. [43] showed that changing the composition of the cathode solution alters analytical performance (similar to electrospray ionization) and used these observations to provide more detailed insights into analyte ionization and fragmentation processes within the glow discharge. Hazel *et al*. [44] studied the effect of magnetic fields on the operation of such glow discharges and they report that perturbation of the plasma in the magnetic field is predominantly a structural change, as opposed to a change in overall electrical or spectroscopic characteristics.

The last application topic that is covered by the “Plasma-Liquid Interactions” Special Topic Collection is the use of plasmas in medical, agricultural and food cycle processes. This remains an important and hot topic of our research field. Several years ago, it was shown that the treatment of water by air-containing plasmas lead to so-called plasma-activated water (PAW) that has long-term (hours to days, depending on conditions) bactericidal activity enabled by plasma-produced reactive oxygen and nitrogen species (RONS). This early work has led to a bulk of research that uses not only PAW but also a variety of other plasma-activated solutions for many disinfection applications and even cancer treatment. Weihe *et al*. [45] use PAW for conveyor band cleaning relevant for applications in the food industry. Their work suggest that PAW offers an extensive spectrum of possible sanitizers for specialized cleaning demands in a food production line. Furthermore, Rathore *et al*. [46] assess the impact of key process parameters on PAW generation to allow for system optimization, while Wartel *et al*. [47] showed that the presence of compounds in tap water can greatly impact PAW properties. Takahashi *et al*. [48] showed that PAW with adjusted pH can be used as a nutrient solution for cultivating cucumber plants in a hydroponic system and extended this study to show the effect of the presence of allelochemicals (organic compounds that have auto-toxic effects on plant growth) in PAW.

The biological impact of plasma treatment on pathogens, cells and tissues is mediated by RONS or electric fields. Nonetheless, we currently do not have a detailed understanding of the dominant species and reaction pathways for many treatment conditions and modalities due to the complex composition of many different RONS produced by plasma. Chien *et al*. [49] verified in this context that short-lived species in plasma inhibit skin cancer cells more than normal skin cells. Wenske *et al*. [50] reported on the chemical modifications of biomolecules by plasma that are believed to be crucially impacting physiological processes and hence linking plasma science directly with biological processes.

In summary, the "Plasma-Liquid Interactions" Special Topic Collection includes both more fundamental studies on plasma-liquid discharges (by modeling and diagnostics) as well as applied studies in a wide range of application fields. It therefore provides a good overview of the current state of research in this domain.

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References:

[1] 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. Machala, 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. Wilson, K. Yasui, G. Zvereva, Plasma-liquid interactions: a review and roadmap, Plasma Sources Sci. Technol. 26 (2016) 053002

[2] P. Rumbach, D. B. Go, Top. Catal. 60, 799–811 (2017).

[3] J. E. Foster, Phys. Plasmas 24, 055501 (2017).

[4] P. Vanraes, A. Bogaerts, Appl. Phys. Rev. 5, 031103 (2018).
[5] F. Rezaei, P. Vanraes, A. Nikiforov, R. Morent, N. De Geyter, Materials 12, 2751 (2019).

[6] A Khlyustova, C Pierre Labay, Z Machala, M P Ginebra Molins, C Canal Barnils, Frontiers of Chemical Science and Engineering 13 (2), 238-252 (2019)

[7] A Stancampiano,T Gallingani, M Gherardi, Z Machala, P Maguire, ,V Colombo, J-M Pouvesle and E Robert, Appl. Sci. **2019**, 9(18), 3861

[8] P. J. Bruggeman, R. R. Frontiera, U. R. Kortshagen, M. J. Kushner, S. Linic, G. C. Schatz, H. Andaraarachchi, S. Exarhos, L. O. Jones, C. M. Mueller, C. C. Rich, C. Xu, Y. Yue, Y. Zhang, Journal of Applied Physics **129**, 200902 (2021)

[9] P. Vanraes, A. Bogaerts, Journal of Applied Physics **129**, 220901 (2021)

[10] N. S. Phan, W. Wei, B. Beaumont, N. Bouman, S. M. Clayton, S. A. Currie, T. M. Ito, J. C. Ramsey, G. M. Seidel, Journal of Applied Physics **129**, 083301 (2021)

[11] X. Zhang and M. N. Shneider, Journal of Applied Physics **129**, 103302 (2021)

[12] K. Grosse, M. Falke, A. von Keudell Journal of Applied Physics **129**, 213302 (2021)

[13] A. Hamdan, J. Gorry, T. Merciris, J. Margot, Journal of Applied Physics **128**, 033304 (2020)

[14] M. Akhter, J. Mallams, X. Tang, D. Staack, Journal of Applied Physics **129**, 183309 (2021)

[15] Y. D. Korolev, I. A. Shemyakin, V. S. Kasyanov, V. G. Geyman, N. V. Landl, A. V. Bolotov, Journal of Applied Physics **129**, 043304 (2021)

[16] K. Wang, S. I. Bhuiyan, Md A. Hil Baky, J. Kraus, C. Campbell, H. Jemison, D. Staack, Journal of Applied Physics **129**, 123301 (2021)

[17] H. Höft, M. Kettlitz, R. Brandenburg, Journal of Applied Physics **129**, 043301 (2021)

[18] S. A. Barengolts, I. V. Uimanov, V. I. Oreshkin, K. V. Khishchenko, E. V. Oreshkin, Journal of Applied Physics 129, 133301 (2021)

[19] M. Dell'Aglio, V. Gardette, S. C. Jantzi, A. De Giacomo, Journal of Applied Physics **129**, 233303 (2021)

[20] A. Young, W. G. Graham, T. J. Morgan, L. Hüwel, Journal of Applied Physics **129**, 183303 (2021)

[21] N. Akiyama, Y. Nakagawa, S. Uchida, F. Tochikubo, Journal of Applied Physics **129**, 163304 (2021)

[22] H. E. Delgado, G. H. Brown, D. M. Bartels, P. Rumbach, D. B. Go, Journal of Applied Physics **129**, 083303 (2021)

[23] K. Sgonina, G. Bruno, S. Wyprich, K. Wende, J. Benedikt, Journal of Applied Physics **130**, 043303 (2021)

[24] A. Dickenson, J. L. Walsh, M. I. Hasan, Journal of Applied Physics **129**, 213301 (2021)

[25] Z. Yang, Y. Kovach, J. Foster, Journal of Applied Physics **129**, 163303 (2021)

[26] J. Marjanović, D. Marić, G. Malović, Z. Lj. Petrović, Journal of Applied Physics 129, 143303 (2021)

[27] H.Yuan, J. Feng, D.-Z. Yang, X.-F. Zhou, J.-P. Liang, L. Zhang, Z.-L. Zhao, W.-C. Wang, Journal of Applied Physics **128**, 093303 (2020)

[28] S. Gershman, A. Belkind, Journal of Applied Physics **128**, 133302 (2020)

[29] G. B. Sretenović, M. Saleem, O. Biondo, G. Tomei, E. Marotta, C. Paradisi, Journal of Applied Physics **129**, 183308 (2021)

[30] M. Janda, M. E. Hassan, V. Martišovitš, K. Hensel, M. Kwiatkowski, P. Terebun, J. Pawłat, Z. Machala, Journal of Applied Physics **129**, 183305 (2021)

[31] X.-c. Zhang, F. Wang, N.-n. Liu, A.-q. Li, W.-l. Fan, Journal of Applied Physics **129**, 183306 (2021)

[32] V.-P. Thai, H. Furuno, N. Saito, K. Takahashi, T. Sasaki, T. Kikuchi, Journal of Applied Physics 128, 043305 (2020)

[33] L. Čechová, F. Krčma, M. Kalina, O. Man, Z. Kozáková, Journal of Applied Physics **129**, 233304 (2021)

[34] T. Merciris, F. Valensi, A. Hamdan, Journal of Applied Physics **129**, 063303 (2021)

[35] A. V. Nominé, Th. Gries, C. Noel, A. Nominé, V. Milichko, and T. Belmonte, Journal of Applied Physics **130,** 151101 (2021)

[36] F. J. Chao-Mujica, L. Garcia-Hernández, S. Camacho-López, M. Camacho-López, M. A. Camacho-López, D. Reyes Contreras, A. Pérez-Rodríguez, J. P. Peña-Caravaca, A. Páez-Rodríguez, J. G. Darias-Gonzalez, L. Hernandez-Tabares, O. Arias de Fuentes, E. Prokhorov, N. Torres-Figueredo, E. Reguera, L. F. Desdin-García. Journal of Applied Physics **129**, 163301 (2021)

[37] L. Égerházi, B. Kovács, T. Szörényi, Journal of Applied Physics **129**, 195902 (2021)

[38] V. F. dos Santos, L. C. Fontana, J. C. Sagás, M. E. P. Missner, D. Becker, Journal of Applied Physics **129**, 123302 (2021)

[39] C. Nau-Hix, T. M. Holsen, and S. Mededovic Thagard, Journal of Applied Physics **130**, 123301 (2021)

[40] P. Brault, M. Abraham, A. Bensebaa, O. Aubry, D. Hong, H. Rabat, M. Magureanu, Journal of Applied Physics **129**, 183304 (2021)

[41] A. Hamdan, J.-L. Liu, M. Suk Cha, Journal of Applied Physics **129**, 043303 (2021)

[42] B. Adámková, F. Krčma, S. Chudják, Z. Kozáková, Journal of Applied Physics **129**, 143304 (2021)

[43] C. L. Walton, A. J. Schwartz, J.T. Shelley, Journal of Applied Physics **130**, 043305 (2021)

[44] N. Hazel, J. Orejas, S. Ray, Journal of Applied Physics **129**, 183301 (2021)

[45] T. Weihe, U. Schnabel, H. Winter, T. Möller, J. Stachowiak, S. Neumann, O. Schlüter, J. Ehlbeck, Journal of Applied Physics **129**, 223304 (2021)

[46] V. Rathore, S. K. Nema, Journal of Applied Physics **129**, 084901 (2021)

[47] M. Wartel, F. Faubert, I. D. Dirlau, S. Rudz, N. Pellerin, D. Astanei, R. Burlica, B. Hnatiuc, S. Pellerin, Journal of Applied Physics **129**, 233301 (2021)

[48] K. Takahashi, S. Kawamura, R.Takada, K. Takaki, N. Satta, T. Fujio, Journal of Applied Physics **129**, 143301 (2021)

[49] P.-C. Chien, C.-Y. Chen, Y.-C. Cheng, T. Sato, R.-Z. Zhang. Journal of Applied Physics **129**, 163302 (2021)

[50] S.Wenske, J.-W. Lackmann, L. M. Busch, S. Bekeschus, T. von Woedtke, K. Wende, Journal of Applied Physics **129**, 193305 (2021)