Atmospheric-pressure ionization: New approaches and applications for plasmas in contact with liquids

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Abstract. Historically, gas discharges have been difficult to stabilize at atmospheric pressure, and this has confined them to operation at low pressure under vacuum conditions. However, recent advances in plasma technology have enabled stable high pressure gas discharges up to and even exceeding atmospheric pressure. One significant advantage of operating at atmospheric pressure is that the plasma can be brought into contact with non-conventional substrates, especially soft materials such as plastics, biological tissue, and aqueous solutions. This last example is of prime interest as plasma/liquid interactions have a number of important implications in applications ranging from water purification to plasma medicine. In this paper, recent work studying the impact of electrons in the plasma inducing reactions in aqueous solutions is discussed. These studies include measurements of the bulk solution as the electrons induce long-lived species as well as interfacial measurements directly at the plasma/liquid interface to probe the behaviour of electrons traversing from the plasma into the liquid.

1. Introduction
Gas discharges or plasmas are ionized gases, and for the most part they are operated under vacuum conditions. Recently, however, new technologies using small dimensions have led to stable atmospheric pressure plasmas termed microplasmas [1]. In addition to shepherding in advances in lighting [2], gas sensing [3], and nanomaterials synthesis [4], one key advantage of operating at atmospheric pressure is that it enables the plasma to interact with non-traditional substrates. That is, plasma interactions with soft materials, ranging from plastics to biological tissue, have been uniquely enabled by atmospheric pressure operation.

One substrate that has been of significant interest over the past decade is water or aqueous solutions, where the plasma comes in direct contact with the liquid [5],[6]. One of the key features of plasmas is that they produce an abundance of reactive species including electrons, ions, radicals, metastables, and photons. The plasma therefore becomes an excellent delivery system, dissolving these reactive species into the water leading to a wide range of reactions. Recent review articles (e.g., [7]) have focused on reactive oxygen species (ROS) and reactive nitrogen species (RNS) highlighting the importance of these species in water purification and biological applications. However, one key species in both the plasma and liquid phase is the electron. This article will overview electron-driven
chemistry in plasma/liquid systems, summarizing recent studies aimed at understanding this important mechanism.

2. Historical Perspective and Recent Applications

In the mid-twentieth century, the concept of using plasmas as electrochemical reactors, often called glow discharge electrolysis, was pioneered by Hickling and his collaborators [8]. Borrowing from conventional electrochemical cells, in glow discharge electrolysis, also called contact glow discharge electrolysis, one of the electrodes was replaced by a plasma such that the electrolyte itself acted as the counter electrode under direct current (DC) conditions. Figure 1 shows two basic plasma configurations along with a conventional electrochemical cell. In a conventional electrochemical cell, two electrodes are submerged in an electrolyte solution and a DC bias is applied between them, typically on the order of ~1-10 V. In glow discharge electrolysis, either one (or sometimes both) of the electrodes can be replaced with a suspended electrode. Applying a very high voltage (~1-10 kV) causes the interstitial gas between the suspended electrode and solution to breakdown, forming a plasma. Unlike many plasma/liquid configurations where the plasma is 'remote' and formed only by electrodes external to the solution, in glow discharge electrolysis the electrolyte solution itself is an important conductive element in the entire circuit. Thus, while in remote configurations the charged electrons and ions in the plasma only pass between two external electrodes, in glow discharge electrolysis the charged particles must traverse into the solution in some manner in order to produce current. When the plasma is the cathode (Figure 1b), these charged particles are electrons entering the anodic solution. Conversely, when the plasma is the anode (Figure 1c), the charged particles are positive ions entering a cathodic solution.

Like conventional electrochemistry, the current in plasma electrolysis is maintained by reactions occurring at the electrode interfaces – reduction at the cathode and oxidation at the anode. However, in the absence of a solid electrode, the reactions occur at the plasma/liquid interface, reduction for a cathodic plasma and oxidation for an anodic plasma. This is fundamentally different from conventional electrochemistry. Hickling and his collaborators, for the most part, focused on anodic plasmas. Today, much of the interest is in using cathodic plasmas in order to understand the behaviour of electrons interacting at the solution interface. One of the most promising areas that has recently emerged is using these types of contact plasmas for the electrochemical synthesis of colloidal nanoparticles [9]. In a cathodic configuration, free plasma electrons interact at the solution interface, inducing reduction reactions. If the solution cations are metallic, the metal cation is reduced. For silver ions (Ag+) from solutions of silver nitrate (AgNO3), the silver cation (Ag+) is reduced to Ag0. In conventional electrochemistry, these reduced species adsorb onto the metal cathode, coating it with silver metal – a process called electroplating. However, if the metal cathode is replaced with a plasma cathode, there is no solid surface on to which the Ag0 can absorb, and they agglomerate to form nanoparticles. Similarly, if the initial solution contains gold chloride (HAuCl4), gold (Au) nanoparticles can be efficiently produced.

Figure 1. Schematic of electrochemical cells: (a) conventional cell, (b) plasma cathode cell, and (c) plasma anode cell.
3. The Question of Electron-Driven Reactions

Ostensibly, the simplest picture of electron-driven reactions for nanoparticle synthesis is the direct reduction of the cation by the plasma electron. For example, in the case of silver, it would be a single electron reaction ($\text{Ag}^{+} + e^{-} \rightarrow \text{Ag}^{0}$), whereas for gold reduction it is a three-electron reaction ($\text{Au}^{3+} + 3e^{-} \rightarrow \text{Au}^{0}$). However, a number of recent studies have raised the question of whether this is indeed the case. For example, Chen et al. recently showed that it is more likely the $\text{H}_2\text{O}_2$ formed in solution by the various reactive species that reduces the gold cation [10]. Thus, it is not clear if the reduction is always by plasma electron transfer, sometimes by plasma electron transfer, or never by plasma electron transfer with the reduction always through some other pathway.

A second question that is often raised is the nature of the electron transfer. Specifically, the question arises as to whether the electron initiates the reduction right at the plasma/liquid interface or if the electron penetrates into the solution, effectively becoming solvated before reacting with solution species. The solvated electron is one of the most powerful reduction agents known in chemistry, with a reduction potential of $-2.89 \text{ V}$ [11], and modern techniques typically use radiation sources (electron or gamma) to ionize the solution and causing a subsequent electron avalanche. These liberated electrons eventually thermalize in the solution as solvated electrons before reacting away [12]. The prevailing question is whether the relatively ‘low’ energy electrons escaping the plasma are injected into the solution. Recently, a number of studies have begun to narrow in at resolving these questions and unraveling the complex nature of electron chemistry at plasma/liquid interfaces.

3.1. Bulk Solution Studies

Initially studies on electron-driven chemistry focused on effects that would persist for long times and ultimately affect the bulk properties of the solution. One of the first of these studies was conducted by Richmonds et al., who studied the classic ferri/ferrocyanide redox couple [13] using a split electrochemical cell (H-cell) with separated cathodic and anodic chambers. Ferricyanide, $\text{Fe}^{3+}$, is well known to undergo a single electron reduction to form ferrocyanide, $\text{Fe}^{4+}$. Importantly, ferricyanide absorbs strongly in the blue at ~420 nm such that the color of the solution gradually turns from yellow to clear as the ferricyanide is reduced. By quantifying the absorbance using ultraviolet-visible (UV-vis) spectrosopy, Richmonds et al. were able to show that there was some inherent inefficiency. In theory, the reduction reaction should proceed Faradaically such that the moles reduced is proportional to the plasma current and the plasma processing time. While they found that the amount reduced did proceed linearly at constant current, it was less than that predicted by Faraday’s law.

One obvious culprit is that some percentage of the electrons injected by the plasma go directly to water electrolysis, rather than reduction of the reagent. In acidic solutions, electrons will directly recombine with protons to produce hydrogen gas ($\text{H}_2$) via

$$2\text{(H}^{+})_{\text{aq}} + 2e^{-} \rightarrow \text{(H}_2)_{\text{g}}.$$  \hspace{1cm} (1)

which is the well known hydrogen evolution reaction. This cathodic reaction at the plasma interface is complemented by an oxidation reaction at the anode that produces oxygen ($\text{O}_2$) gas via

$$\text{H}_2\text{O} \rightarrow (\text{O}_2)_{\text{g}} + 4\text{(H}^{+})_{\text{aq}} + 4e^{-}.$$  \hspace{1cm} (2)

These electrolytic effects can be measured in multiple ways, either via changes in the local pH of the solution or by detecting the subsequent gas products (e.g., $\text{H}_2$). The author’s group took advantage of this to confirm that in fact the plasma does drive hydrogen evolution via electrolysis [14]. Using a split H-cell, with separated cathodic and anodic chambers, and a 0.001 M solution of hydrochloric acid (HCl) with 1.0 M potassium chloride (KCl) for conductivity, they both measured the pH change in the solution and the ($\text{H}_2$) using an isotope mass spectrometer. As expected, the reduction proceeded linearly, but like Richmonds et al. [13] it was less than that predicted by Faraday’s law.
Follow up studies focused on understanding these electrolytic processes further. In particular, it is well known that other reactive species formed in the plasma also dissolve into the solution, changing the bulk chemistry. Therefore, there is potentially an inherent competition at the plasma/liquid interface – chemistry driven by electrons (electrolytic) and chemistry driven by dissolved species. In order to resolve this inherent competition, the author’s group studied electrochemical processes in solutions of sodium chloride (NaCl) as opposed to the acidic solutions studied earlier [15]. Because electrolytic reactions in NaCl lead to excess OH\(^{-}\), the pH increases. However, in nitrogen/oxygen-rich environments, such as air, the plasma forms nitric oxides (NO\(_x\)), and these plasma products dissolve in to the solution to form nitrous (HNO\(_2\)) and nitric (HNO\(_3\)) acid, which lowers the pH. By measuring pH variation in different plasma environments (pure Ar, O\(_2\), N\(_2\), and air), Rumbach et al. [15] revealed conditions where electrolytic reactions dominate the chemistry and conditions where dissolved plasma species dominate the chemistry. Importantly, they also showed that the electrolytic and that dissolved species pathways can couple with each other to fundamentally alter the chemistry in the solution.

### 3.2. Interfacial Studies

While these bulk studies confirmed the electrolytic activity driven by cathodic plasmas, they did not directly address one persistent question – do the plasma electrons solvate before reacting or do they react right at the plasma/liquid interface? The author’s group has developed a novel approach to directly measuring solvated electrons at the interface of the plasma and liquid, taking advantage of the absorption behavior of solvated electrons [16]. It is well known in the radiolysis community that solvated electrons absorb strongly in the red [17], with a peak near 700 nm that shifts further into the red as the solution temperature increases [18]. Therefore the strategy was to probe the interface with a red laser and measure the absorption signal as shown in Figure 2. If the electrons do solvate at the interface, then there would be a measured absorption. However, a number of technical challenges make this measurement particularly difficult. In the absence of anything that reacts directly with electrons, such as a cation like Ag\(^+\), solvated electrons eventually diffuse to each other and react via

$$2(\text{e}^-)_{aq} + 2\text{H}_2\text{O} \rightarrow 2(\text{OH}^-)_{aq} + (\text{H}_2)_{g},$$

which is referred to as 2\(^{nd}\)-order recombination. At the concentrations expected from a typical cathodic plasma operating at \(~1\text{--}10\ \text{mA}\), the timescale for recombination is on the order of \(\mu\text{s}\), such that the change in signal due to absorption is only \(I/I_0 \sim 0.999999\), which is exceedingly low. Thus any sources of random noise, such as through electromagnetic pick-up, or systematic effects that cause spurious reflections, could swamp the measured absorption signal. To overcome these limitations, an alternative configuration was used where the laser passed through the solution at an angle less than the critical reflection angle, such that all the laser light that is not absorbed is captured by the photodetector, mitigating spurious reflections. This total internal reflection configuration, shown in Figure 2, also included modulating the plasma between low current and high current states at a known frequency of 20 kHz. Locking in the photodetection at this same modulation frequency filtered out any incoherent noise generated by the experiment, allowing for the very high signal-to-noise ratio required to detect solvated electrons.

Figure 3 shows a series of absorption measurements taken in aqueous solutions of NaOH using diode lasers of various wavelengths. Consistent with the absorption spectrum measured from radiolysis [18] shown as a solid line, there is peak in the red near 700 nm confirming that plasma electrons do in fact solvate in the solution. Interestingly, the spectrum appears to be blue-shifted from those measured via radiolysis. There are various effects that could cause this shift, including a Stark effect due to the high electric field at the interfacial double layer, space charge in the double layer, or even stratification due to localized heating by the plasma. What the blue shift does suggest is that the plasma generates solvated electrons under conditions distinct from other methods such as radiolysis, and these conditions impact their behaviour.
Rumbach et al. [16] also confirmed that these electrons are solvated by introducing additional species that are known to react with electrons, scavenging them and reducing the absorption signal. That is, for the reaction

\[(e^-)_{aq} + S \rightarrow S^{n-1}, \]  \hspace{1cm} (3)

as the concentration of scavenger S increases, reaction (4) dominates reaction (3) and extinguishes the absorption signal. By varying the concentration of cationic (H\(^+\)), anionic (NO\(_2^\), NO\(_3^\)), and neutral scavengers (H\(_2\)O\(_2\)), they showed that the signal decreases as \(I_0/I_0 \propto [(S)_{aq}]^{-1}\), confirming that the electrons are solvated before reacting away. Adding even greater confidence to their results, Rumbach et al. [16] extracted reaction rate coefficients from these scavenger experiments, and they were consistent with known values from the radiolysis literature.

![Figure 2.](image1.png)

**Figure 2.** Total internal reflection absorption spectroscopy configuration where the plasma is generated using a stainless steel capillary with a diameter \(~100 \mu m\) suspended \(~1-2 mm\) above the solution surface biased negatively relative to a submerged platinum electrode. The plasma current is modulated at 20 kHz and lock-in amplification is used to mitigate sources of noise, including spurious reflections from the liquid interface mechanically deforming beneath the plasma.

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![Figure 3.](image2.png)

**Figure 3.** Measured plasma-generated solvated electron absorption spectrum using a solution 0.163 M NaClO\(_4\). Adapted from [16].

Ultimately, these recent interfacial measurements confirm that cathodic plasmas inject electrons into the liquid phase. This has important implications, as the solvated electron is one of the most powerful reducing species with a reduction potential of -2.89 V. Thus while much is known about the impressive chemical effects of dissolved plasma species, it is clear that plasma electrons can have a
significant impact on liquid chemistry, with implications on applications ranging from plasma medicine to water purification.

4. Conclusions
It is well understood that the way that plasmas and gas discharges interact with liquids is very complex. Recent developments in using plasmas for nanomaterials synthesis have raised questions about how plasma electrons, in particular, interact with liquids. It is now becoming more evident that the plasma can act as a source of solvated electrons, and that these solvated electrons will subsequently drive reduction chemistry in the liquid. However, it is also clear that the many other plasma species also induce liquid chemistry that can often times be in direct competition with the electron-driven chemistry. Looking toward the future, it is necessary to continue to parse and understand all these reaction paths in order to design plasma/liquid systems that are truly optimized toward a specific application, whether that be materials synthesis, water purification, or biomedical in nature.

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