# Single Liquid Aerosol Nano-Impact Electrochemistry: Accessing the Droplet | Air Interface

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## Environmental Significance Statement:

Liquid aerosols and their physicochemical properties (e.g., charge, pH, evaporation rates) have great importance in environmental science. Very few techniques can make measurements on single aerosol droplets with 100s of nanometer dimensions. We provide the community with a new platform for studying single aerosol droplets on nanoelectrodes, opening up electroanalytical methods to study single liquid aerosol droplets, one at a time. By using dual-barrel nanoelectrodes, we are able to observe the stochastic collision of single liquid aerosol droplets and observe their evaporation in real-time. Furthermore, with the emerging evidence that chemistry changes in microdroplets, it is critical to develop tools that can elucidate fundamental environmental questions at the nanoscale. This communication does just that.

# Single Liquid Aerosol Nano-Impact Electrochemistry: Accessing the Droplet | Air Interface

Philip J. Kauffmann, Jeffrey E. Dick*

**ABSTRACT:** Over the past decade, many groups have shown that chemistry changes drastically in confined volumes compared to large volumes. As a robust analytical chemistry tool, electrochemistry has augmented to the discussion because of its ability to study reactivity of single atoms, molecules, and nanoparticles, one at a time. Unfortunately, this field of science, known as nano-impact electrochemistry, has been limited to studying sub-femtoliter liquid droplets suspended in oil because measurements require at least two electrodes. Here, we develop a miniaturizable platform for the nano-impact electrochemical study of single liquid aerosol droplets. We achieve detection by the miniaturization of laser-pulled, dual-barrel ultramicroelectrodes, where two Pt ultramicroelectrodes are separated by a distance of a few micrometers. When aerosols (radius ~ 500 nm) loaded with a 1:1 solution of 300 mM hexacyanoferrate (II/III) are nebulized, discrete transients, indicative of single aerosol droplet collisions with the nanoprobe, can be observed in the amperometric *i*-t trace. Using finite element modeling, we demonstrate the amperometric signal depends on the aerosol droplet geometry at the nanoprobe. Our results push the limit of what is measurable by taking electroanalysis to the single aerosol level. These experiments also allow access to the study of chemical reactions at the droplet|air interface.

**Environmental Significance Statement:** Liquid aerosols and their physicochemical properties (e.g., charge, pH, evaporation rates) have great importance in environmental science. Very few techniques can make measurements on single aerosol droplets with 100s of nanometer dimensions. We provide the community with a new platform for studying single aerosol droplets on ultramicroelectrodes, opening up electroanalytical methods to study single liquid aerosol droplets, one at a time. By using dual-barrel ultramicroelectrodes, we are able to observe the stochastic collision of single liquid aerosol droplets and observe their evaporation in real-time. Furthermore, with the emerging evidence that chemistry changes in microdroplets, it is critical to develop tools that can elucidate fundamental environmental questions at the nanoscale.

Chemistry in tiny volumes (droplets) differs drastically from bulk phases. Cooks and Zare have demonstrated chemical reaction acceleration in droplets generated by electrospray and nebulization[1-4]. Many groups, such as Griffiths, Pielak, and ours, have demonstrated changes in chemistry in droplets suspended in an oil continuous phase[5-10]. Marcus has indicated experiments are necessary that rigorously elucidate how chemical reactions change as a function of droplet size[11]. The most robust way to study such chemistry is on a droplet-by-droplet basis, where droplet size heterogeneity can be rigorously accounted for. Such experiments are currently difficult because measurement tools are not yet available to probe kinetics and thermodynamics in sub-femtoliter volumes at the single droplet level. These experiments represent a great challenge and opportunity for analytical chemistry.

Stochastic electrochemistry has emerged as a reliable means by which reactivity can be measured on single particles, one at a time[12,13]. Ultramicroelectrodes have been used to probe the heterogeneous electrocatalysis of single atoms and nanoparticles[14,15] as well as measure reactions in small droplets and vesicles[16-20]. Electrochemistry's key measurement requirement is two electrodes. We have successfully used stochastic electrochemical techniques to demonstrate enzymatic rates are accelerated in sub-femtoliter volumes, and rates scale with the inverse of droplet radius[8] (an experimental observation predicted by Marcus[11]). However, to meet the two-electrode requirement, nanodroplets were suspended in oil. This is a limitation considering most observations of reaction acceleration and curious chemistry in droplets have entailed the droplet|air interface[21-24]. This interface is much more realistic, as the droplet|air interface is ubiquitous in nature. This Communication serves to develop a platform to overcome this significant limitation using electrochemistry.

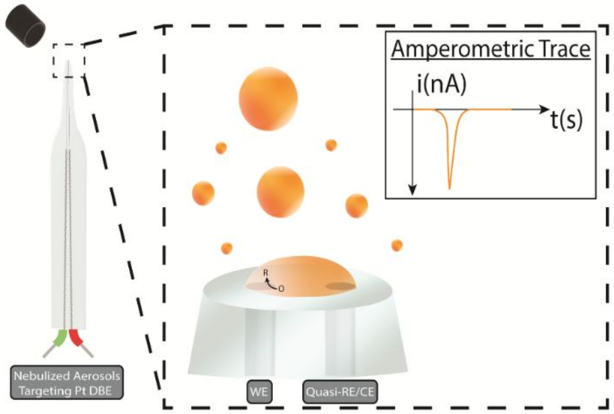

**Figure 1.** Illustration of an aerosol spanning the distance between platinum disks and producing a transient of current from an electrochemical reaction, recorded via an amperometric *i*-t trace. The typical transient is on the order of a second.

Here, we further the reach of stochastic electrochemistry towards single aerosol events. This is accomplished by fabricating a miniaturized, dual-barrel ultramicroelectrode (each electrode is ~ 650 nm radius). Aerosols, which are solid or liquid particles in a gas, range from 2 nanometers to over 100 µm[25]. By targeting a nebulized solution of hexacyanoferrate(II/III) at the electrode surface (**Figure 1**), aerosols (~20 µm diameters) hitting the micron-sized surface of the electrode can be resolved as discrete, stochastic events when measuring current as a function of time. We characterize the dual-barrel electrode with microscopy and cyclic voltammetry and show amperometric evidence of single aerosol collisions. The signal is achieved when an aerosol is large enough to cover both electrodes.

The dual-barrel electrode was fabricated as follows. Both channels of a quartz theta capillary were threaded with a 25 micrometer, platinum wire. The platinum wires were pushed into the middle of the capillary. The capillary was then inserted into a Sutter P-2000 laser puller. Four cycles (30s ON/30s OFF) of the following heat-sealing program were run: Heat = 765; Filament = 5; Velocity = 100; Delay = 200; Pull = 1. Once the capillary appeared sealed under microscope, a pull program was initiated: Heat = 715; Filament = 3; Velocity = 120; Delay = 128; Pull = 250. One of the dual-barrel electrodes that resulted was polished with the micropipette beveler and characterized with a Hamamatsu Digital Camera C13440 Orca-Flash using Leica Software (**Figure 2A**). The electrode was also characterized via cyclic voltammetry in 300mM hexacyanoferrate (II/III) (**Figure 2B**).

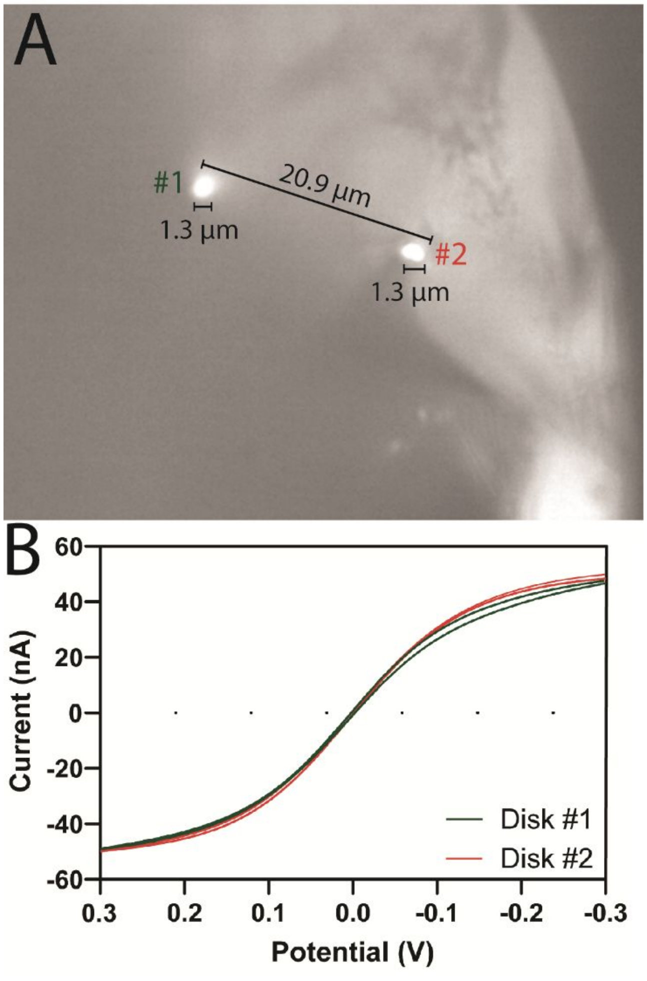

**Figure 2.** Optical Microscopy and Electrochemical Characterization of Electrodes. **A)** Pt disk dimensions and the inter-electrode distance that an aerosol must span to produce an amperometric response. **B)** cyclic voltammograms of the two platinum disks when one acts as the working electrode while the other acts as the quasi-counter/reference electrode. The voltammograms were taken in 300mM ferrocyanide/ferricyanide solution. The radius obtained from limiting current of the voltammogram closely matches the radius measured under microscopy.

Critical to the detection of discrete aerosol events is the dual-barrel electrode. Typically, aerosols are detected using a liquid collector volume to capture the aerosols and provide a cell for electrochemical measurements, such as in microfluidic devices[26] or PILSNER[27]. While this is necessary to maintain electrical connection for measurements, this requirement could be circumvented if the platinum disks and inter-electrode distance was small enough, and/or the aerosol landing on the electrode face was large enough to span both electrodes and the inter-electrode distance. For this observation, we characterized the dual-barrel electrode with microscopy and cyclic voltammetry and measured the particle distribution of the hexacyanoferrate (II/III) aerosol particles. From the microscopy results presented in Figure 2A, droplets with pL volumes can be probed, and the system is easily miniaturizable.

Cyclic voltammetry with the dual-barrel electrode in 300mM hexacyanoferrate (II/III) shows the expected sigmoidal shape (**Figure 2B**), regardless of which barrel is the working electrode and which is the quasi-reference/counter electrode. The radius of the electrode can be determined by using the analytical solution

$$i_{ss}=4nFDCa \qquad \textbf{Equation 1}$$

where $i_{ss}$ is the steady state current, $n$ is the number of electrons involved in the reaction, $F$ is Faraday's constant, $D$ is the diffusion coefficient, $C$ is the concentration of the redox species, and $a$ is the radius of the working electrode. The steady state current of the voltammograms were 49.0 nA for disk #1 and 49.9 nA for disk #2. **Equation 1** indicates the radii are 0.63 µm for disk #1 and 0.64 µm for disk #2 (**Equation S1**). Optical microscopy measurements agree well with the voltammetry, showing two platinum disks with diameters of 1.3 µm each (**Figure 2A**). The opposite edges of these disks are separated by 20.9 µm, indicating that an aerosol of sufficient size must impact and cover this distance to report an electrochemical signal. To see if the solution we nebulized produced large enough aerosols, we sampled aerosols with the Durag D-11 spectrometer. **Figure S1** shows a size distribution of hexacyanoferrate(II/III) aerosols, where a portion of particles have diameters of 20 µm or greater. It should be noted that the report of these relatively large aerosols will likely underestimate the actual count due to their collision against the inner walls of the instrumentation's sampling line. In addition, the aqueous droplets are likely to spread out across the hydrophilic surface of the glass upon impaction, suggesting that even aerosols with smaller diameters could bridge the distance between electrodes and produce a response.

Thus, our particle sampling and electrode characterization indicate that there are large enough aerosol particles to show stochastic collisions on our dual-barrel electrode. At present, we cannot differentiate one very large aerosol from several small aerosols between the electrodes that quickly coalesce to yield an electrochemical signal. We suggest based on the transience of our observed signals, rapid evaporation of aqueous droplets, and the constant flow of aerosol and gas over the electrode surface, that any transients observed are from single, micrometer-sized droplets. We investigated this by nebulizing a 300 mM, 1:1 solution of redox species, hexacyanoferrate (II/III) and recording the response with an amperometric *i*-t trace (**Figure 3**) at +0.3 V vs. the hexacyanoferrate (II/III) couple (this couple will poise the second electrode upon impact).

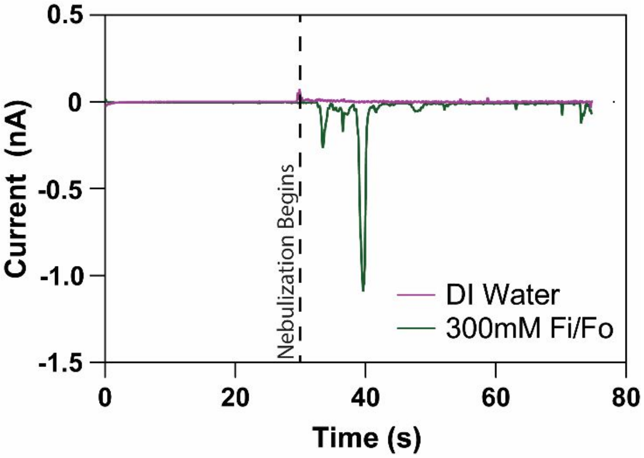

**Figure 3.** Amperometric *i*-t trace showing discrete aerosol impact events, most notably at 33 and 40s. The potential is held at +0.3 V for this experiment. When the solution of 300mM hexacyanoferrate(II/III) (Fi/Fo) is nebulized (beginning at 30s), the ferrocyanide in aerosols that impact the dual-barrel electrode will convert to ferricyanide, producing a spike in current. The distance from the nebulizer to the electrode tip was held at ~2.5 cm.

The trace shows discrete events of stochastic aerosol collisions across the time scale of the experiment once nebulization begins at 30s. These collisions can be seen most notably at 33 and 40 seconds. One might suggest that these peaks are due to mechanical disturbance of droplets impacting the electrode disks. However, when compared to the control trace of nebulized ultrapure water, there are no anodic peaks like there are when 300mM hexacyanoferrate (II/III) is nebulized. Thus, the peaks in **Figure 3** seem to indicate the oxidation of ferrocyanide at the electrode surface. In addition, because aerosols contain each form of the redox couple, cathodic events can also be probed. By holding the potential sufficiently negative to reduce hexacyanoferrate(III) (-0.3V), the stochastic collisions can be seen as discrete events when ferricyanide is converted to ferrocyanide within an aerosol (**Figure S2**). Thus, the current response is dictated by whether species are being oxidized or reduced, depending on the potential that is being applied.

While many stochastic events in the literature result in a peak that decays to a new steady state level, these aerosol collisions always return to the original steady state current. The amperometric transients observed suggest that redox molecules in the droplet are rapidly consumed or are only momentarily in contact with the electrode surface. The small quantity of redox molecules present in an aerosol would not produce a steady state current for long. In some cases, an aerosol may survive long enough (i.e., not evaporate) to produce a brief steady state current before vanishing, like the event at 48 seconds. However, most stochastic events do not reach a new steady state, likely due to evaporation and the constant spray of aqueous particles across the surface of the electrode. Another important note on these transients is that they are not always equal in magnitude. We suggest that heterogeneity in transient size not only depends on the evaporation but the geometry of the droplet on the dual-barrel ultramicroelectrode. The contact angle of aqueous droplets on quartz is less than 90 degrees[28]. Thus, the closer the aerosol droplet boundary is to the working electrode, the more diffusion of redox species to the electrode will be hindered. This will in turn hinder the intensity of the current response. COMSOL Multiphysics simulations of an identical environment show that as the droplet boundary approaches the working electrode, the current response diminishes (**Supporting Information, Table S1**). The diffusion layer reaches the droplet boundary, consuming all the species at the boundary such that diffusion is limited to the other directions. With the diffusion of the redox species hindered, the current is diminished.

Many observations have supported the idea that the droplet|air interface is highly important in driving chemistry that does not occur in the bulk phase. New measurement science tools are necessary to probe chemical reactions at the single droplet level. As a measurement tool to study kinetics, electrochemistry can probe rates that span over 12 orders of magnitude. In this Communication, we have extended stochastic electrochemical methods to single aerosol droplets. We achieved this by developing dual-barrel ultramicroelectrodes, where ultramicroelectrodes are separated by only a few micrometers. When an aerosol that is large enough to traverse both electrodes irreversibly adsorbs, the electrochemistry of the single adsorbed droplet can be probed. These transient events are dependent on the redox species present, and on whether the potential is anodic or cathodic. The magnitude of these events is also affected by the geometry and location of the aerosol impact on the electrode. Our measurements represent a significant advance in measurement science and open the door to probe the droplet|air interface on a droplet-by-droplet basis.

## ASSOCIATED CONTENT

**Supporting Information**. Materials, Calculations of electrode radii, Histogram and raw count of 300mM hexacyanoferrate(II/III) aerosols, Amperometric response of 300mM hexacyanoferrate(II/III) at reductive potentials, Steady state current as a function of droplet-electrode distance, COMSOL Multiphysics simulation details (PDF).

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## Author Contributions

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## Notes

The authors declare no competing financial interest.

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