Electron-Transfer Reactions at the Plasma−Liquid Interface

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S *Supporting Information*

ABSTRACT: Electrochemical reactions are normally initiated in solution by metal electrodes such as Pt, which are expensive and limited in supply. In this Communication, we demonstrate that an atmospheric-pressure microplasma can act as a gaseous, metal-free electrode to mediate electron-transfer reactions in aqueous solutions. Ferricyanide is reduced to ferrocyanide by plasma electrons, and the reduction rate is found to depend on discharge current. The ability to initiate and control electrochemical reactions at the plasma−liquid interface opens a new direction for electrochemistry based on interactions between gas-phase electrons and ionic solutions.

Electrochemical systems are characterized by charge-transfer reactions across dissimilar phases, most commonly solid−liquid interfaces.[1] In a typical electrochemical cell, two metal electrodes are separated by an aqueous ion-conducting electrolyte, and electric potential differences lead to charge-transfer reactions at the metal electrode/ionic electrolyte interfaces. However, electrochemical reactions are not limited to those that occur at the interface of solid metals and liquids. Insulators have been charged by contact electrification and used as stand-alone electrodes to induce a variety of charge-transfer reactions in solution, including hydrogen gas formation and metal deposition.[2] Alternatively, a small number of studies exist, dating back to Gubkin,[3] with gaseous electrodes where charge is transferred to an electrolyte via an electrical discharge (i.e., plasma).[4−6] Despite a long history, remarkably little is known about the nature of charge-transfer reactions at a plasma−liquid interface. Plasmas are usually operated at sub-atmospheric pressure, limiting previous studies to solvents with very low vapor pressures, e.g., ionic liquids and polymeric species.[7,8] In addition, the complex conditions present in a plasma, consisting of ultraviolet radiation, radicals, electrons, and ions, result in non-Faradaic processes that do not allow charge-transfer reactions to be clearly identified.[9,10]

We are interested in understanding charge-transfer reactions at the plasma−liquid interface. The initiation of electrochemical reactions by a gaseous electrode is of technological interest because metals such as Pt, which are commonly used as electrodes, are expensive and limited in supply, and there has been growing interest to eliminate them.[11−13] There are potential materials applications, as well, of plasma-assisted electrochemistry such as the synthesis of nanostructured materials.[14,15] However, it is not clear how gas-phase electrons interact with ions in solutions in comparison to electrochemical systems involving metal electrodes.
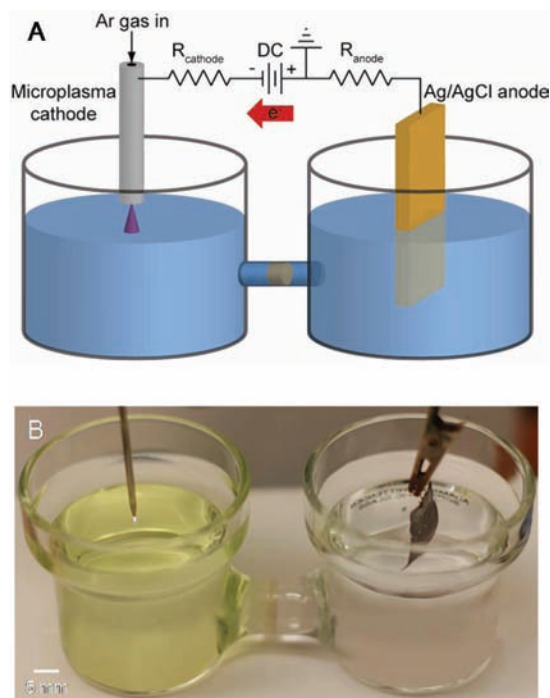

Figure 1. Schematic (A) and photograph (B) of electrochemical cell with a gaseous cathode electrode. An atmospheric-pressure microplasma was formed in an Ar gas flow between a stainless-steel capillary tube and the electrolyte surface. The anode electrode was Ag/AgCl.

Here, we report for the first time evidence of electron-transfer reactions at the plasma−liquid interface. Our study is enabled by the recent development of a nonthermal, atmospheric-pressure microplasma source[16] which can be stably formed on a solution surface at ambient conditions. Using the ferricyanide/ferrocyanide redox couple as a model system, we show that charge transfer depends on the properties of the discharge; for example, the reduction rate of ferricyanide is found to increase with discharge current, which in turn is related to the flux of plasma electrons to the solution surface. These findings open a new direction for electrochemistry where gas-phase electrons with tunable fluxes or energies are used to initiate and control electrochemical reactions in solution.

Plasma-assisted electrochemical reactions were carried out in a glass cell (Adams & Chittenden), schematically depicted in Figure 1a. The electrolytes in the anodic and cathodic sides were

prevented from mixing by a fritted glass plug. Separate compartments for the cathode and anode permitted isolation of the half-cell reaction occurring at the plasma—liquid interface. In the anode side, an Ag/AgCl mesh was partly immersed in the electrolyte and served as the counter electrode. A stainless steel capillary tube (180 μm i.d. $\times$ 5 cm length, Varian, Inc.) was positioned 2 mm away from and normal to the surface of the electrolyte in the cathode side using a micrometer-controlled linear stage and fed with argon gas flow. A microplasma was ignited in the exit argon flow and sustained by a negatively biased DC power supply (Figure 1b). During experiments, the microplasma impinged on the surface of the electrolyte, over a surface area of $\sim$1 mm^2. The discharge current, i_d, was kept constant and found to vary by <5% (Supporting Information (SI)). Over the course of an experiment, the temperature of the bath increased by no more than 5 °C. No stirring was applied in order to avoid disturbing the solution surface and minimize fluctuations in the discharge current.

We chose to study a well-known and well-characterized reaction, the reduction of ferricyanide $[Fe(CN)_6^{3-}]$ to ferrocyanide $[Fe(CN)_6^{4-}]$. The catholyte bath consisted of 15 mL of 0.2 mM potassium ferricyanide $[K_3Fe(CN)_6]$ and 0.1 M potassium chloride (KCl) dissolved in deionized water; the anolyte bath contained only 0.1 M KCl. The conversion of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ was monitored by ultraviolet—visible (UV—vis) spectrophotometry (Shimadzu UV-1800). Representative UV—vis spectra of solutions exposed to a plasma (i_d = 6 mA) for 0, 5 and, 15 min are shown in Figure 2a. The intensity of the absorbance peak at $\sim$420 nm is directly proportional to the concentration of $Fe(CN)_6^{3-}$ in solution,[17] and the decrease over time suggests that $Fe(CN)_6^{3-}$ is reduced to $Fe(CN)_6^{4-}$ by the plasma (see Figure 2a). Through a calibration procedure (SI), we obtained the percentage of $Fe(CN)_6^{3-}$ species reduced by the plasma (Figure 2b). The results show that $Fe(CN)_6^{3-}$ is progressively reduced over time, and the rate of reduction is proportional to the discharge current. For a given discharge current, the electron flux (number of electrons per unit area per unit time) delivered to the surface of the solution by the plasma remains constant; thus, the $Fe(CN)_6^{3-}$ contained in the solution is reduced at a relatively constant rate. When the discharge current is raised, the electron density in the plasma increases,[18] a higher flux of electrons reaches the solution surface, and the rate of reduction increases.

To verify that $Fe(CN)_6^{3-}$ was indeed reduced to $Fe(CN)_6^{4-}$ and not destroyed by the plasma, we performed cyclic voltammetry with a three-electrode system comprised of a glassy carbon rotating-disk working electrode controlled by a potentiostat (CH Instruments electrochemical workstation model 660B), an Ag/AgCl reference electrode, and a Pt mesh auxiliary electrode. Representative cyclic voltammograms of solutions of ferricyanide exposed to a plasma (i_d = 6 mA) for 0, 5, and 15 min are shown in Figure 2c. A steady-state cathodic current plateau proportional to the $Fe(CN)_6^{3-}$ concentration is observed for the initial solution. After plasma exposure, this current plateau decreases and a new anodic current plateau appears, indicating the presence of $Fe(CN)_6^{4-}$ in solution and clearly showing that $Fe(CN)_6^{3-}$ was reduced to $Fe(CN)_6^{4-}$ by the plasma. The current plateaus for $Fe(CN)_6^{3-}$ reduction and $Fe(CN)_6^{4-}$ oxidation decrease and increase, respectively, by the same magnitude, which confirms that $Fe(CN)_6^{3-}$ was not destroyed. The current plateau for $Fe(CN)_6^{4-}$ oxidation increases with time as more and more $Fe(CN)_6^{4-}$ is generated in solution, consistent with UV—vis absorbance results. For samples analyzed by both spectrophotometric
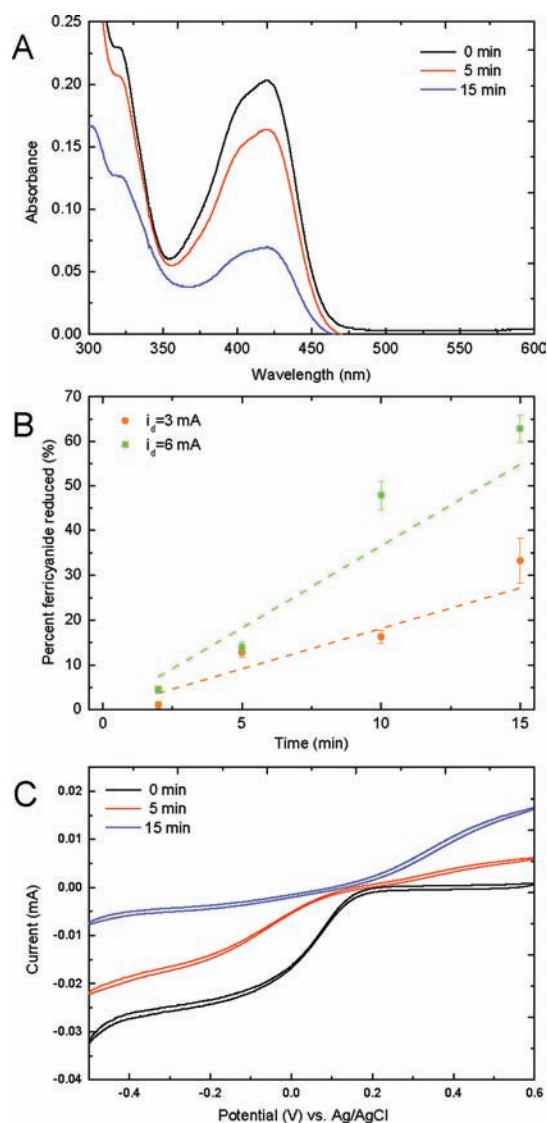

Figure 2. (A) UV—vis absorbance spectra of solutions of ferricyanide after exposure to the plasma for 0, 5, and 15 min (discharge current, i_d = 6 mA), (B) percent of ferricyanide reduced in solution as a function of time at discharge currents (i_d) of 3 and 6 mA, and (C) cyclic voltammograms of solutions of ferricyanide after exposure to the plasma for 0, 5, and 15 min.

and cyclic voltammetric methods, the estimated amounts of $Fe(CN)_6^{3-}$ reduced by the plasma correspond well (SI).

Table 1 summarizes our experimental results for reduction of $Fe(CN)_6^{3-}$ by the plasma at different discharge currents and times. We infer that the percent or number of $Fe(CN)_6^{3-}$ molecules reduced increases linearly with time because of the constant flux of electrons to the solution surface. Similarly, the number of $Fe(CN)_6^{3-}$ molecules reduced increases with discharge current because the electron density (or flux) increases, as given by the following expression:

$$n_e = j/\mu E e \qquad (1)$$

where n_e is the electron density, j is the discharge current density (current per unit area), E is the electric field, and μ is the electron mobility. Despite the evidence for electron transfer, our

Table 1. Summary of Results Showing Reduction of Ferricyanide by the Plasma at Different Currents and Times of Exposure[a]

current (mA)	exposure time (min)	absorbance intensity @ 420 nm	percent reduction of $Fe(CN)_6^{3-}$	no. $Fe(CN)_6^{3-}$ molecules reduced	no. electrons injected
3	2	0.195	1.0	1.8×10^{16}	2.3×10^{18}
3	5	0.172	12.8	2.3×10^{17}	5.6×10^{18}
3	10	0.165	16.3	3.0×10^{17}	1.1×10^{19}
3	15	0.133	33.3	6.0×10^{17}	1.7×10^{19}
6	2	0.188	4.3	7.8×10^{16}	4.5×10^{18}
6	5	0.170	14.0	2.5×10^{17}	1.1×10^{19}
6	10	0.104	48.0	8.7×10^{17}	2.3×10^{19}
6	15	0.076	62.8	1.1×10^{18}	3.4×10^{19}

[a] The number of $Fe(CN)_6^{3-}$ molecules reduced is obtained from absorbance measurements, and the number of electrons injected is calculated from the cell (i.e., discharge) current.

calculations for the number of electrons injected by the plasma using Faraday's law indicate that a large number of electrons are not involved in ferricyanide reduction. To verify that there are no current losses at the plasma—liquid interface, we measured the current at both the plasma cathode and the Ag/AgCl anode and confirmed that the current at the cathode and anode sides was the same (SI). We also evaluated the current through the cell by replacing the Ag/AgCl electrode with Ag or Cu and studying anodic dissolution (SI). As shown in Figure 3, the weight losses measured at the anode are in excellent agreement with Faraday's law for both $Ag \rightarrow Ag^+ + e^-$ and $Cu \rightarrow Cu^{2+} + 2e^-$, suggesting that charge is transferred with 100% efficiency from the plasma to the liquid.

To further address the transfer of electrons from the plasma to the liquid, we measured the solution potential, with respect to an Ag/AgCl reference electrode (Accumet standard high temperature Ag/AgCl reference electrode, Fisher Scientific), by placing a Pt wire in contact with the solution at the plasma—liquid interface. We note that the voltage applied at the plasma electrode by our external power supply is not the conventional electrode potential, since there is a large voltage drop across the plasma (SI). The potential that actually controls the ferricyanide reduction is the solution potential, induced by the plasma at the surface of the catholyte bath. Before igniting the plasma, we measured a surface potential of ~0.43 V, as predicted by the Nernst equation for a nearly pure solution of ferricyanide (SI). This potential was found to rapidly decrease when the plasma was ignited and eventually reached a quasi steady-state value; higher discharge currents produced a larger potential drop (Figure 4). The decrease in the solution potential confirms that $Fe(CN)_6^{3-}$ is reduced to $Fe(CN)_6^{4-}$, and the steady-state potential suggests that the reduction occurs at a constant rate that is higher for higher discharge currents, which is in agreement with our UV—vis absorbance results. The interfacial region where the plasma contacts a liquid is fundamentally different than a metal—solution interface in a typical electrochemical system. In addition to the absence of surface sites for reactant species and reduction products to adsorb and accumulate, the edge of a plasma is characterized by a sheath with large electric field gradients that accelerate electrons to a surface.[19] This sheath potential should cause electrons to flow from the gas to the solution, analogous to the effect of the electrode potential at a metal—solution interface.
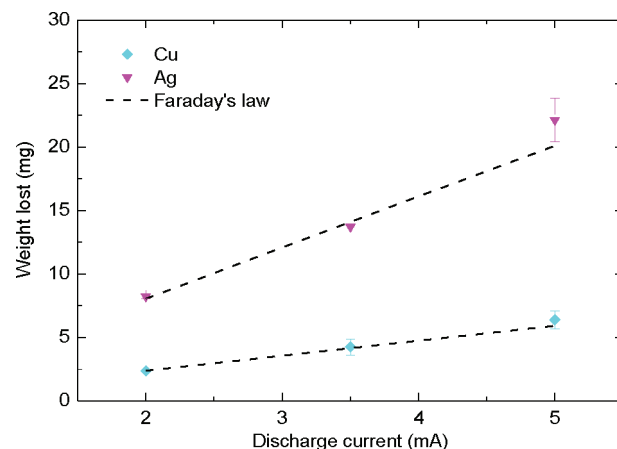

Figure 3. Weight loss measured for Cu and Ag foil anodes after operating a plasma-based electrochemical cell for various times and discharge currents (i_d). The electrolytes consisted of 1 mM HCl in deionized water for Cu and 1 mM HNO_3 in deionized water for Ag. The weight losses predicted by Faraday's law are also shown (dashed line).
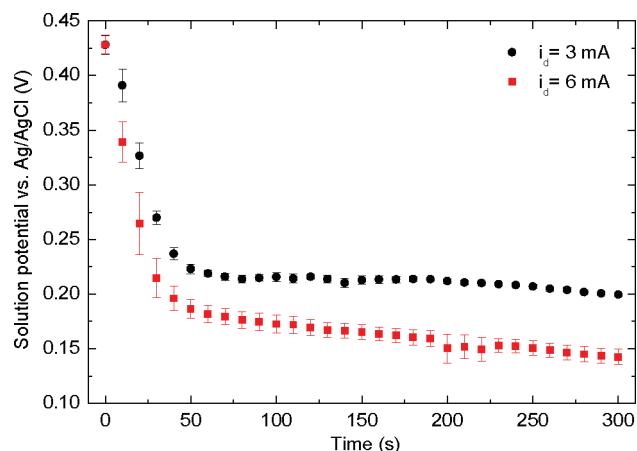

Figure 4. Solution potential measured as a function of time by a Pt probe placed at the plasma—liquid interface, with respect to an Ag/AgCl reference electrode. The solution potential was measured at two different discharge currents (i_d), 3 and 6 mA, every 10 s.

In order for reduction to occur, the donor and acceptor states in electron-transfer reactions such as this one must be of equal energy.[20] Since a plasma contains a complex distribution of electron energies, we propose that a fraction of the electrons with the appropriate energy reduce the $Fe(CN)_6^{3-}$ ions. The remaining electrons may be involved in other charge-transfer processes such as hydrogen formation $[2H^+ + 2e^- \rightarrow H_{2(g)}]$, as indicated by the pH change in the cathode bath (SI), leading to a lower than expected reduction of $Fe(CN)_6^{3-}$ molecules. Additional experiments are required to better understand and optimize electron transfer from the plasma to specific ionic species in the liquid.

While we have focused this study on a model reaction, there are other reactions where a plasma electrode would be more technologically useful. Elimination of expensive, precious metal electrodes is critical for large-scale electrochemical applications such as hydrogen generation[21]—our results suggest that the plasma could serve as the cathodic electrode to reduce H^+ to H_2. Similarly, plasmas could replace metal electrodes such as Cu

for CO_2 reduction to synthesize hydrocarbon fuels and potentially alter the product distribution.[22] Plasma reduction may offer advantages in materials synthesis, as previously mentioned for nanomaterials,[14,15] as well as polymeric materials,[23] where the absence of a solid electrode could enable homogeneous material synthesis. Broadly speaking, plasmas could also be used to deliver other excited species (in addition to electrons) such as atomic oxygen or hydrogen to access completely new chemical pathways.

In summary, we have demonstrated that a gaseous electrode is capable of transferring electrons and inducing electrochemical reactions in solution. The reaction rate is found to depend intimately on discharge parameters (e.g., discharge current) which control the electron density (or flux) and energy distribution of electrons in the plasma. The absence of a solid electrode and the ability to tune the electron density, electron energy, and solution potential open a new direction for electrochemistry based on reactions between gas-phase electrons and ionic electrolytes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Detailed experimental procedure and additional experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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