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# Pressure-Driven Bipolar Electrochemistry

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S *Supporting Information*

**ABSTRACT:** Here we report that pressure-driven flow alone (no external electrical energy) can be used to drive faradaic electrochemical reactions in microchannels with charged walls. Specifically, we show that solution flow can generate streaming potentials on the order of volts and that this is sufficient to carry out reactions on the anodic and cathodic poles of a bipolar electrode (BPE). The existence of faradaic reactions is proven by electrodissolution of Ag from the anodic end of the BPE.

Here we report that pressure-driven flow alone can be used to drive electrochemical reactions in microchannels having charged walls. Specifically, we show that a solution flowing through a microchannel can generate a streaming potential[1] of up to ~8 V and that this is sufficient to carry out faradaic electrochemical reactions at bipolar electrodes (BPEs).[2] These results are significant, because they demonstrate that electrochemical reactions can be carried out in the absence of external electrical power. Accordingly, low-current devices, such as some electrochemical sensors, may be self-powered and hence used in emergency situations or regions of the world that do not have ready access to electricity.

The principles of bipolar electrochemistry have been described extensively,[2] and several interesting applications have been reported.[3−7] Briefly, a driving voltage applied across a microchannel containing an electrolyte solution results in a nearly linear potential drop within the solution. If a BPE is present within the channel, and if the potential differences between the solution and the two ends of the BPE ($\Delta E_{\text{elec}}$) are sufficiently high, then faradaic reactions occur at the poles of the BPE. A significant advantage of bipolar electrochemistry over conventional three-electrode electrochemistry is that no direct electrical connection to the sensing electrode is required.[2] Importantly, the current flowing through many BPEs can be indirectly measured simultaneously using electrogenerated chemiluminescence[5,6] or Ag electrodissolution.[7]

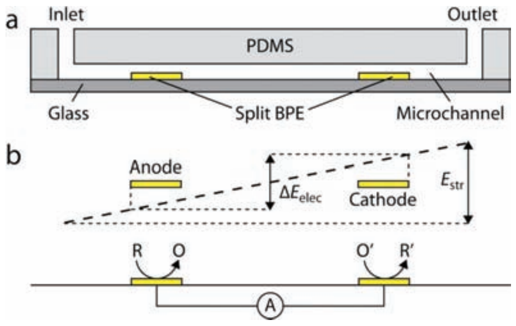
The streaming potential is essentially the opposite of electroosmosis. That is, pressure-driven flow in a microfluidic channel with charged walls induces a flow of counterions in the electrical double layer at the interface between the electrolyte solution and the channel walls. This motion of ions is an electrical current, and at open circuit it leads to a streaming potential difference ($E_{\text{str}}$) across the length of the microchannel.[1] The properties of $E_{\text{str}}$ are embodied by the Smoluchowski equation.[1]

$$E_{\text{str}} = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta K_L} \Delta P \qquad (1)$$

Here, $\varepsilon_0$ is the electrical permittivity of vacuum, $\varepsilon_r$ is the relative permittivity of the solution, $\Delta P$ is the pressure drop across the microchannel (Pa), which is proportional to the average volumetric flow rate ($\upsilon$) inside the microchannel (see Supporting Information), $\zeta$ is the zeta-potential of the channel walls (V), $\eta$ is the solution viscosity (Pa·s), and $K_L$ is the solution conductivity ($\Omega^{-1}\cdot\text{m}^{-1}$).[1] Note that eq 1 represents a simplified expression that does not take into consideration the $\zeta$ of composite surfaces or the conductance of the Au surface. The latter term was shown to be important in electrokinetic cells composed of parallel metal plates used for $\zeta$ measurements.[8]

If a BPE and redox-active species are present in a microchannel, and if $E_{\text{str}}$ is sufficiently high, then faradaic reactions may be induced at the poles of the BPE. This concept is illustrated in Scheme 1, where $\Delta E_{\text{elec}}$ is the portion of $E_{\text{str}}$ dropped across the BPE. Note that a split BPE is used in these experiments, which simply means that the anodic and cathodic poles of the BPE are connected external to the microchannel by a jumper wire.[9] We previously showed that this configuration is analogous to a continuous BPE having the same length.[9]

**Scheme 1**



Duval et al. observed that a streaming potential generated in a thin-layer electrokinetic cell can collapse under certain conditions.[8] Specifically, the streaming potential was found to be significantly lower when the cell contained a reversible redox couple, compared to the potential in its absence. They attributed this observation to faradaic depolarization of the electrode/

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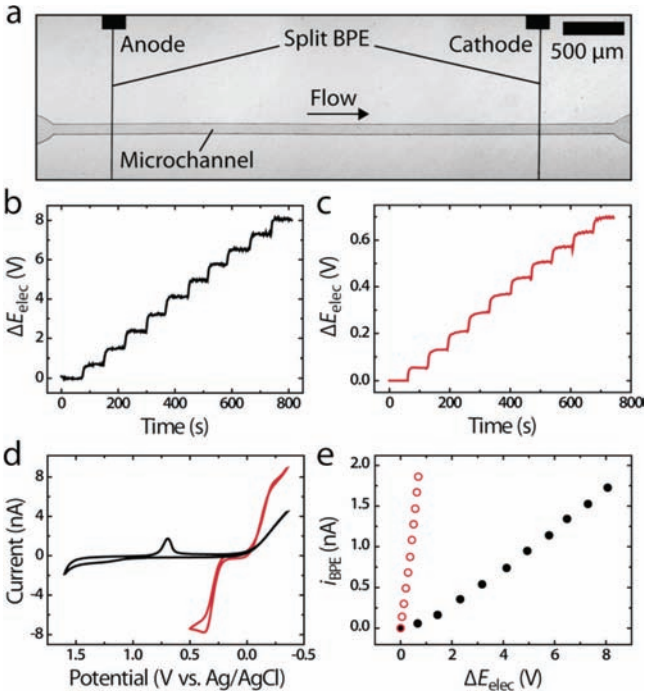

**Figure 1.** (a) Optical micrograph of a Type 1 microdevice. The microchannel was 6.0 mm long, 100 μm wide, and 25 μm high. The split BPE microbands were 10 μm wide and 100 μm long and had an outer edge-to-edge length of 4.5 mm. (b and c) Plots of $\Delta E_{elec}$ vs time, obtained using a Type 1 microdevice and measured while varying $v$ from 10 to 100 μL min$^{-1}$ in increments of 10 μL min$^{-1}$. The microchannel contained (b) DI $H_2O$ and (c) DI $H_2O$ plus 1.0 mM BQ/HQ. (d) CVs obtained in a two-electrode cell incorporating a 20 μm-diameter Au working electrode and a Ag/AgCl reference/counter electrode: black line, DI $H_2O$; red line, DI $H_2O$ plus 1.0 mM BQ/HQ. (e) Plots of $i_{BPE}$ vs $\Delta E_{elec}$ obtained using a Type 1 microdevice at different $v$, ranging from 10 to 100 μL min$^{-1}$ in increments of 10 μL min$^{-1}$: black circles, DI $H_2O$; empty red circles, DI $H_2O$ plus 1.0 mM BQ/HQ.

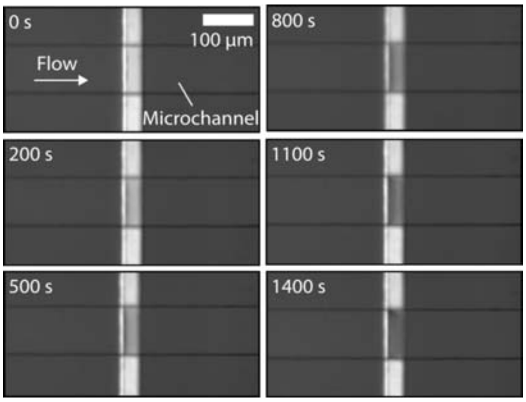

**Figure 2.** Time-resolved optical micrographs of the BPE Ag anodic pole of a Type 2 microdevice. The channel contained DI $H_2O$ plus 1.0 mM BQ and $v$ = 25 μL min$^{-1}$. The Ag layer was positioned at a slight offset to the underlying Au to provide improved contrast. The ends of the split BPE were connected externally with an ammeter, and $i_{BPE}$ was measured simultaneously (Figure S3).

solution interface and subsequently developed a rigorous theoretical framework for calculating ζ when the extent of faradaic depolarization is governed by mass transport[10] or by the kinetics of an interfacial electron transfer reaction.[11] However, no experimental measurements of the faradaic current were reported in this set of studies.

Figure 1a is an optical micrograph of the poly(dimethylsiloxane) (PDMS) microfluidic device used in the experiments reported here. Fabrication of this device is routine, and the details are provided in the Supporting Information. Note that the Au microbands extend beyond the PDMS microchannel so that a voltmeter or an ammeter can be connected between them. This makes it possible to measure the potential between the ends of the BPE, $\Delta E_{elec}$, or the current flowing through it, $i_{BPE}$. Two types of split BPEs were used for these experiments. Both consisted of Au, had an outer edge-to-edge length of 4.5 mm, and spanned the width of the microchannel. The wires comprising the BPEs used for potential and current measurements, which we refer to as Type 1, were 10 μm wide, while Type 2 BPEs, which were used for Ag electrodissolution, were 50 μm wide. The anode of the Type 2 BPEs was overcoated with 5 nm of Cr and 20 nm of Ag.

Figure 1b is a plot of $\Delta E_{elec}$ versus time measured in a Type 1 microdevice while varying $v$ from 10 to 100 μL min$^{-1}$ in increments of 10 μL min$^{-1}$. The solution in the channel was deionized (DI) $H_2O$ obtained from a Millipore system ($\rho$ = 18.2 MΩ·cm). The data in Figure 1c were obtained under identical conditions, except in this case the solution also contained 1.0 mM *p*-benzoquinone (BQ) and 1.0 mM hydroquinone (HQ). The results in Figure S1 (Supporting Information), which were obtained from these plots, show that there is a linear relationship between $\Delta E_{elec}$ and $v$ in both cases. The maximum measured $\Delta E_{elec}$ values were 8.1 V for DI $H_2O$ and 0.7 V for 1.0 mM BQ/HQ. Compared to previous reports, these are surprisingly high values.[8] We believe this is, in part, a consequence of the split BPE design. That is, in the split BPE configuration, the electrodes themselves contribute only 2% to the total area between their outer edges. The remainder is glass, and this minimizes the contribution of surface conductance to eq 1 (vide supra).

The results presented in Figure 1b and 1c can be understood best in terms of cyclic voltammograms (CVs) obtained using a classical two-electrode cell. Figure 1d shows CVs obtained in this type of cell for solutions of DI $H_2O$ containing no intentionally added electrolyte and DI $H_2O$ containing 1.0 mM BQ/HQ. In the former case, $O_2$ reduction is observed at 0.0 V and Au oxidation at 1.0 V, with the onset of $H_2O$ oxidation at ~1.5 V (vs Ag/AgCl). In the latter case, BQ reduction is observed at 0.0 V and HQ oxidation at 0.2 V (vs Ag/AgCl). Using the assumptions embodied in Scheme 1b and considering the CVs in Figure 1d, it follows that the minimum $\Delta E_{elec}$ required for the onset of faradaic reactions at the ends of a Au BPE is 1.0 V for $H_2O$ but only 0.2 V if 1.0 mM BQ/HQ is also present.[2] The observation of smaller $\Delta E_{elec}$ values in Figure 1c can then be ascribed to the presence of the BQ/HQ couple, which acts as a depolarizer of the Au/solution interface. This conclusion is in agreement with results reported by Duval et al.[8] and Ordeig et al.[4] However, if depolarization occurs, the conductance term in eq 1 acquires a bipolar faradaic contribution,[8] which results in a nonlinear dependence of $E_{str}$ on $\Delta P$. This phenomenon has been demonstrated both theoretically[8,10] and experimentally.[12] However, the limited pressure range used here (see Supporting Information) is not sufficient to observe this effect.

Plots of $i_{BPE}$ versus time corresponding to the data in Figure 1b and 1c are provided in Figure S2 and summarized in

Figure 1e. These results show that, for a given $\Delta E_{elec}$, much higher $i_{BPE}$ values are obtained when the BQ/HQ couple is present. This finding is consistent with the CVs shown in Figure 1d. However, the maximum measured current for 1.0 mM BQ/HQ obtained at $\upsilon$ = 100 $\mu$L min$^{-1}$ was 1.9 nA, which is 100 times smaller than the steady-state, mass-transport limited current predicted by the Levich equation for the reduction of 1.0 mM BQ at a 10 $\mu$m × 100 $\mu$m microband at the same flow rate.[13] This is because when current is allowed to flow through the BPE, faradaic depolarization becomes significant. As such, $\Delta E_{elec}$ is lower than the values shown in Figure 1c, which were obtained under open-circuit conditions. Accordingly, the maximum $i_{BPE}$ in Figure 1e has not reached its mass-transport limited value.

A Type 2 microdevice, having a Ag anode, was used to prove that faradaic processes account for $i_{BPE}$ in these experiments. Figure 2 shows optical micrographs of the Ag anodic pole of the BPE as a function of time at $\upsilon$ = 25 $\mu$L min$^{-1}$. In this case, the solution in the microchannel contained only 1.0 mM BQ, as Ag oxidation served as the anodic reaction. The micrographs reveal increased darkening of the BPE anode, which is indicative of Ag electrodissolution.[7] Complete Ag dissolution is apparent after 1400 s. When the number of equivalents of Ag present on the anode ($9.0 \times 10^{-12}$) and the average value of $i_{BPE}$ (0.63 nA, Figure S3) are taken into account, the calculated time for complete Ag dissolution is 1380 s. The close correspondence between experiment and expectation, coupled with the optical micrographs shown in Figure 2, confirm that the streaming potential leads to faradaic electrochemistry. Finally, it is important to note that, in a control experiment where the ends of the split BPE were not connected externally, Ag electrodissolution was not observed (Figure S4).

In summary, we have shown that bipolar electrochemistry may be achieved in the absence of an external electrical power source. Indeed, the pressures employed in the present study are sufficiently low that they can be easily generated using a manually operated syringe. Moreover, Ag electrodissolution can be visualized with a simple magnifying device,[7] which further simplifies this type of device for sensing applications that are coupled to a redox event at the cathodic pole of the BPE.[5]

## ASSOCIATED CONTENT

**Supporting Information.** Information about chemicals, materials, fabrication procedures, and instrumentation. Plots of $\Delta E_{elec}$ vs flow rate, $i_{BPE}$ vs time as a function of flow rate, $i_{BPE}$ vs flow rate, and $i_{BPE}$ vs time, measured while recording the optical micrographs in Figure 2. Control test for the silver electrodissolution experiment in Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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