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COMMUNICATION

Bipolar electrode depletion: membraneless filtration of charged species using an electrogenerated electric field gradient†

Eoin Sheridan, Kyle N. Knust and Richard M. Crooks*

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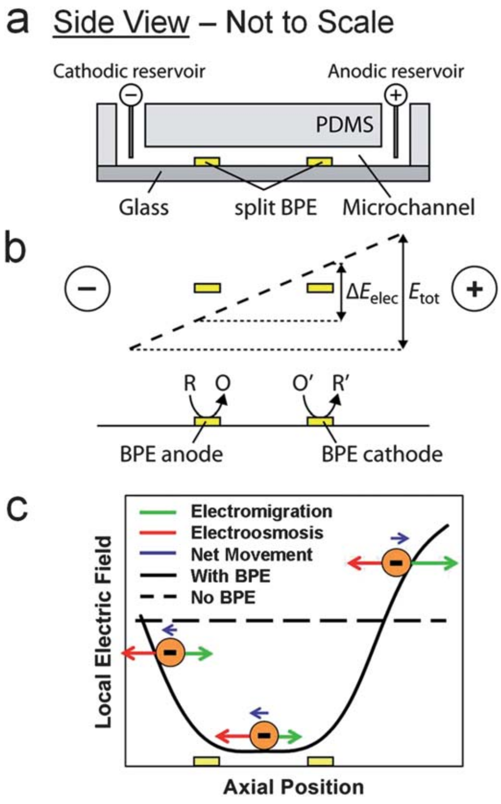
We report a method for removing ions from aqueous solutions without the use of a membrane. The approach, which we call bipolar electrode depletion (BED), is based on the formation of an asymmetric electric field profile in a microchannel containing a bipolar electrode (BPE). The asymmetric field arises from local increases in conductivity caused by faradaic reactions at the BPE. We show how the asymmetric field can be used to deplete anions from a microchannel *via* a combination of electrophoresis and electroosmosis. We also apply this approach to filter an anionic species from a mixture of charged and neutral species being transported through a microchannel *via* electroosmosis. This technique could be utilized for desalination or filtration of any species possessing a net charge (*e.g.* heavy-metals, bacteria, proteins, or functionalized-nanoparticles).

Here we report a method for removing ions from aqueous solutions that does not require a membrane. The approach, which we call bipolar electrode depletion (BED), is based on formation of an asymmetric electric field profile in a microchannel containing a bipolar electrode (BPE, Scheme 1). The asymmetric field arises from local increases in conductivity in the microchannel caused by faradaic reactions at the BPE when a voltage is applied across the channel (E_{tot}, Scheme 1b). The presence of the asymmetric electric field changes the relative magnitudes of the electrophoretic (EP) and electroosmotic flow (EOF) velocities of ions. In this paper we show how the asymmetric field can be used to deplete anions (Scheme 1c), but the approach can also be adapted for cation depletion. Specifically, we demonstrate two functions of this system. First, selective removal of tracer anions from a microchannel containing a mixture of cations, anions, and neutral compounds and, second, filtering of an anionic species from a mixture of charged and neutral species initially present in a reservoir. BED could also be used for desalination or membraneless filtration of any species possessing a net charge (*e.g.* heavy-metals, bacteria, proteins, or functionalized-nanoparticles).

Electric field gradient techniques are frequently used for separation and enrichment of charged analytes in microfluidic systems.[1–5] For example, Han and co-workers have recently shown that the electric field can also be used for filtration in applications such as water desalination.[6] Other approaches to membraneless filtration include capacitive deionization,[7,8] electrochemical precipitation,[9] laminar flow diffusion (H-filtering)[10] and asymmetric inertial migration.[11]

Bipolar electrochemistry is similar to the more familiar three-electrode approach for making electrochemical measurements, except in the former case the potential difference at the electrode/solution interface is controlled by applying a voltage to the solution (Scheme 1b).[12] BPEs have been the subject of a number of interesting analytical studies[12–26] and, most relevant to the present study, have proven to be useful for electric field gradient formation.[4,12,16,17] For



Scheme 1

Department of Chemistry and Biochemistry, Center for Electrochemistry, and the Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, 1 University Station, A5300, Austin, Texas, 78712-0165, U.S.A. E-mail: crooks@cm.utexas.edu

† Electronic supplementary information (ESI) available: Experimental details, a movie showing the entire experiment in Fig. 1a, depletion of BODIPY^{2-} from the microchannel, and a movie of a 15 s microchannel depletion experiment by applying E_{tot} = 120.0 V. See DOI: 10.1039/c1an15510e

example, we have previously shown that charged analytes can be enriched in a microchannel using a technique called bipolar electrode focusing (BEF).[16,17] In BEF, a sufficiently high value of E_{tot} (Scheme 1b) is applied across a microchannel to induce faradaic reactions at a BPE. As normally configured, the products of the reactions are OH^- (at the cathodic pole of the BPE) and H^+ (at the anodic pole); that is, the products of water electrolysis. If the electrolyte in the channel is a pH-sensitive buffer, such as Tris/$TrisH^+$, then $TrisH^+$ will react with OH^- near the cathodic pole to yield neutral Tris. This homogeneous reaction removes charge carriers from solution and leads to a region of low solution conductivity in the reaction zone. This in turn results in the formation of an electric field gradient at which enrichment occurs *via* an electric field gradient focusing mechanism.[16]

The situation for BED is similar to that of BEF, with one important difference: the supporting electrolyte used in the experiment is not sensitive to the products formed at the BPE. That is, OH^- and H^+ formed at the cathodic and anodic poles of the BPE, respectively, do not neutralize the electrolyte. In fact, OH^- and H^+ add to the local conductivity of the solution rather than subtracting from it. Except for this important but subtle difference, the experimental configuration used for BED is similar to that of BEF (Scheme 1a). As illustrated in Scheme 1c, the increase in solution conductivity near the poles of the BPE changes the electric field profile within the microchannel. In regions of high electric field strength, the movement of anions is dominated by EP toward the anodic reservoir. Conversely, in regions of low electric field strength, EP is locally slower so EOF (which is nearly constant throughout the channel)[27] dominates, transporting anions toward the cathode. Note that the absence of a buffer in the channel means it is likely that a pH gradient forms close to the BPE, but this is not expected to have a substantial effect on the BED mechanism.

Fig. 1a shows fluorescence micrographs of a depletion experiment. This experiment was carried out as follows. First, a PDMS/glass hybrid microfluidic device (microchannel dimensions: 6 mm × 100 µm × 21 µm, $l \times w \times h$)[16] was filled with an aqueous solution containing 100 µM $BODIPY^{2-}$. Equal volumes of solution were added to the reservoirs situated at either end of the microchannel so that there was no pressure driven flow (PDF). A 2.0 mm-long BPE was created in the microchannel by connecting a pair of Au microbands separated by the desired distance. Second, $E_{tot} = 20.0$ V was applied to the electrodes in the reservoirs at either end of the microchannel. As shown in Fig. 1a, this immediately results in movement of $BODIPY^{2-}$ away from the channel center and toward the reservoirs. Within 60 s, the concentration of $BODIPY^{2-}$ within the channel is below the detection limit of our fluorescence microscope.

Electric field profiles measured during this experiment are shown in Fig. 1b. These types of measurements have been described previously,[16] but, briefly, a series of Au microbands located in the channel (visible as white vertical lines in Fig. 1a) were used to measure the potential profile of the solution in the microchannel using a scanning digital multimeter (SDMM, Model 2700, Keithley Instruments, Inc., Cleveland, OH). As discussed earlier, H^+ and OH^- produced by water oxidation and reduction at the BPE anode and cathode, respectively (Fig. 1c), account for the non-linear electric field in the microchannel (Fig. 1b). That is, formation of H^+ and OH^- at the BPE poles increases the local conductivity in the vicinity of the BPE. Due to the corresponding lowering of the electric field in this region, transport is dominated by the cathodic EOF rather than by EP. Consequently, the anodic compartment of the microchannel (the region between the BPE and the anodic reservoir) is not populated significantly by ions formed at the BPE (Fig. 1c). Moreover, the majority of H^+ formed at the BPE anode is neutralized by OH^- (Fig. 1c) so that the cathodic compartment does not become significantly enriched in H^+ or OH^-. However, the small contribution to transport of H^+ by EP ensures that there is some excess electrogenerated H^+ present in the cathodic compartment. The electric field profile (Fig. 1b) measured in the channel reflects these local changes in ionic distribution.

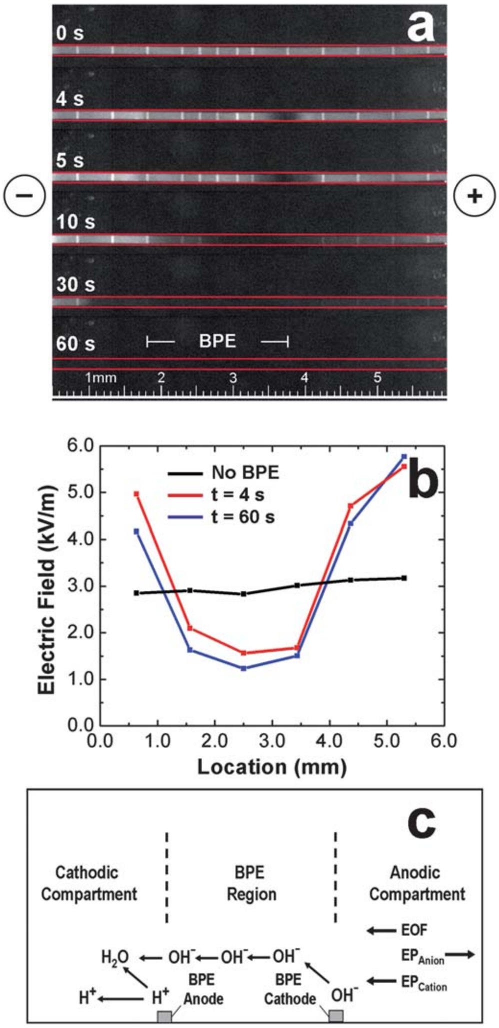


Fig. 1 (a) A series of fluorescence micrographs showing depletion of $BODIPY^{2-}$ from a microchannel during the first 60 s after application of $E_{tot} = 20.0$ V. A 2.0 mm-long BPE was situated near the center of the microchannel, and the initial $BODIPY^{2-}$ concentration was 100 µM. The bright vertical stripes apparent in the channel are Au microbands, which could be connected to form a BPE or used to measure the electric field. The scale indicates the axial location, where the cathodic and anodic reservoirs (not pictured) are located at 0.0 mm and 6.0 mm, respectively. The complete movie from which these images were extracted is provided in the Electronic Supplementary Information. (b) Electric field profiles measured during the experiment shown in 1a, and during a control experiment with no BPE present in the microchannel. (c) Representation of the movement of ions in the microchannel during a depletion experiment. The movement of H^+ and OH^- is dominated by EOF, and they combine near the anodic pole of the BPE to form water.

The key point is that the formation and redistribution of ions in the microchannel results in the development of an asymmetric electric field profile (Fig. 1b), and this leads to depletion of tracer anions in the microchannel (Fig. 1a). The degree of electric field asymmetry increases slightly between the initiation of depletion (Fig. 1b, red line) and complete channel depletion (Fig. 1b, blue line). In the absence of a BPE (Fig. 1b, black line) the electric field is nearly flat so depletion does not occur.

The rate of channel depletion can be modulated by selecting different values of E_{tot}. For example, the channel could be depleted in just 15 s by applying $E_{tot} = 120.0$ V (see Electronic Supplementary Information). A greater E_{tot} increases the rate of depletion due to an increased rate of EOF and EP.

Fig. 2 shows that the same type of device used to generate the data in Fig. 1 can also be used to membranelessly filter ions from a mixture. This type of experiment is carried out as follows. First, the cathodic reservoir and channel were filled with water. Second, the anodic reservoir was filled with an aqueous mixture of 100 μM BODIPY^{2-} and 100 μM Rhodamine B (RhB). The initial reservoir volumes were equal (no PDF), so the tracers remained in the anodic reservoir in the absence of an applied voltage (E_{tot}). RhB is a net-neutral zwitterion, so it does not undergo EP. Instead, RhB moves with the bulk flow of solution (EOF). Finally, a 2.0 mm-long BPE was created within the microchannel by connecting a pair of Au microbands. In this experiment, the BPE was located in the left side of the microchannel so that BODIPY^{2-} could enter the channel during the experiment and be more easily viewed during the course of the experiment. A BPE in the center of the microchannel would act in the same manner, but filtration would occur within the reservoir so it would not be possible to visualize it. The membraneless filtration process was observed by capturing fluorescence micrographs using RhB and BODIPY^{2-} fluorescence filters to independently observe the movement of the two tracers during a 40 s experiment.

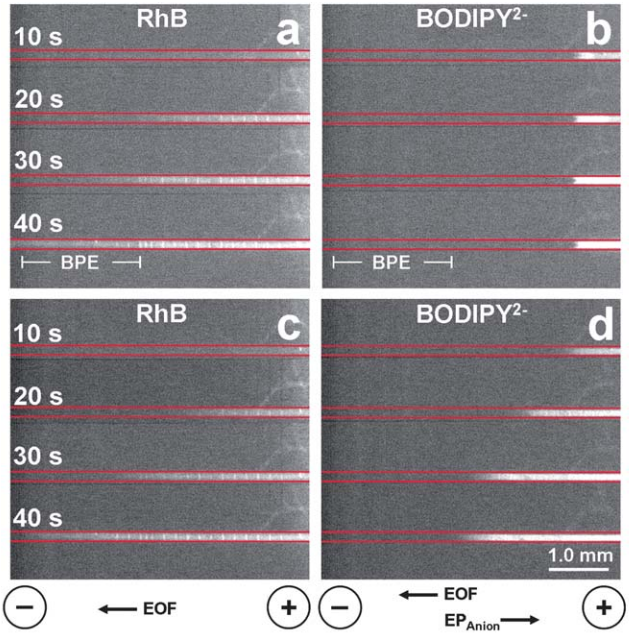


Fig. 2 (a) A series of micrographs captured using fluorescence filters selective for RhB and BODIPY^{2-}. The micrographs show RhB moving across the microchannel *via* EOF (a) while BODIPY^{2-} is filtered due to the presence of a 2.0-mm long BPE in the left side of the microchannel (b) upon application of $E_{tot} = 20.0$ V. A control experiment shows that the transport of RhB by EOF is not significantly changed by removing the BPE (c), but in the absence of a BPE, BODIPY^{2-} was not filtered (d). The light area evident on the right side of images 2a and 2c arises from the fluorescence of RhB in the anodic reservoir, which is just outside the field of view.

Fig. 2a shows that, in the presence of a 2.0 mm-long BPE and with $E_{tot} = 20.0$ V, the bulk solution (represented by RhB) moves through the microchannel by EOF and reaches the cathodic reservoir after 40 s. However, BODIPY^{2-} is prevented from penetrating very far into the channel (Fig. 2b) due to the elevated electric field near the anodic reservoir (Fig. 1b), which causes anions to migrate toward the anode by EP (counteracting the EOF). A control experiment (Fig. 2c and 2d) demonstrates that when the wire connecting the microbands that comprise the BPE is disconnected, but under otherwise identical conditions, both RhB and BODIPY^{2-} move across the channel simultaneously. Note that BODIPY^{2-} moves at a slower rate than RhB due to the combined influence of EP and EOF. The important point is that, in the presence of a BPE, the charged species (BODIPY^{2-}) is selectively filtered from the mixture moving across the microchannel due to the presence of an elevated electric field, which acts like a filter.

In summary, we have demonstrated a new technique for removing charged species from a microchannel and for separating charged species from a mixture containing neutrals (membraneless filtration). The method relies on the electrolysis of water at a BPE, and the corresponding local enhancement of conductivity and asymmetric electric field. A possible application of this method would be desalination of samples for mass spectrometric analysis. Additionally, BED could be used for other applications where filtration of a charged species is required, such as heavy-metal, bacterial, protein, or nanoparticle filtration. Importantly, the technique does not employ a membrane, so it does not suffer from fouling or clogging. Future work will seek to adapt this technique for cationic depletion, and to examine the behavior of counterions during the anionic depletion process. In particular, we plan to investigate the influence of depletion on electroneutrality within the microchannel.

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