Final Report - DOE-UTAUSTIN-FE15758
Project Title: Continuous Ion Separations by Insertion Processes
Date: January 11, 2023
Grant No. DE-FG02-06ER15758
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Abstract

Humanity is reliant on many important chemical separations which are performed daily at the industrial scale. With a historical dependence on thermal distillation techniques, which require large amounts of energy, chemical separations account for 10-15% of energy consumption worldwide. Membrane-based alternatives mitigate separation energy demand, yet prove challenging to scale-up and possess intrinsic limitations. Membranes usually separate species based on size and charge exclusion mechanisms. Importantly, however, improvements in the selectivity of membranes almost always leads to lower permeability. Much of the fundamental research in the field of membrane separations is focused on breaking the scaling relationship between selectivity and permeance, and improving membrane lifetime and stability. As discussed next, our group is developing electrochemically active membranes that can be actuated by application of an electric field. The long-term goal is to control selectivity and permeance.

The specific goal of this project was to investigate the exploitation of ion insertion processes for the continuous and potential-controlled separation of ions. We proposed that an intercalation material operated as a bipolar electrode (BPE) would insert ions at one pole while simultaneously deinserting ions at the other pole. This results in the continuous transport of ions through the electrochemically-actuated and ionically-conductive material. This is significant because selective ion transport through the material can be toggled "on" and "off" by controlling the electrochemical state(s) of the material. In addition, we propose that insertion of ions into an intercalation material will result in a local ion depletion zone (IDZ) and a corresponding electric field gradient, which could be utilized for the redirection of secondary ions (defined as ions that are redirected as a consequence of their interaction with a local electric field gradient). Success in this approach would enable electrochemical control over separation, continuous ion transport, improved transport specificity compared to conventional membranes, and the elimination of undesirable faradaic side products like H^+ which have proved problematic for previously reported systems.

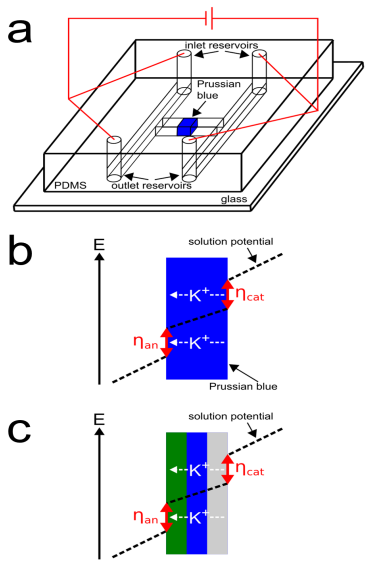
This aspect of our project has had three main focuses. The first focus is the design and fabrication of a microfluidic system containing a Prussian blue (PB) deposit to be actuated as a BPE. The second focus explores the quantitative study of ion transport through the PB BPE within the microfluidic system and characterization of local IDZ formation and the corresponding electric field gradient. The third focus seeks to confirm the actuation of PB as a BPE by use of simple macroscale systems.

A second key aspect of our research has related to removal of microplastics from water. For this part of the project, we used experiments and finite element simulations to investigate electrokinetics within straight microchannels that contain a BPE and an unbuffered electrolyte solution. Our findings indicated that in the presence of a sufficiently high electric field, water electrolysis proceeds at the bipolar electrode and leads to variations in both solution conductivity and ionic current density along the length of the microchannel. The significance of this finding is twofold. First, the results indicate that both solution conductivity and ionic current density variations significantly contribute to yield sharp electric field gradients near the BPE poles. The key point is that ionic current density variations constitute a fundamentally new mechanism for

forming electric field gradients in solution. Second, we showed that the electric field gradients that form near the bipolar electrode poles in unbuffered solution are useful for continuously separating microplastics from water in a bifurcated microchannel. This result expands the potential scope of membrane-free separations using bipolar electrodes.

Use of polymer films to control ion motion

Work described herein utilizes the well-characterized intercalation material ferric hexacyanoferrate, an organic framework coordination polymer commonly referred to as PB ($KFe^{III}Fe^{II}(CN)_6$), which inserts and deinserts small alkali metal cations during redox processes. Specifically, upon reduction of PB to Prussian white (PW) ($K_2Fe^{II}Fe^{II}(CN)_6$) K^+ is simultaneously inserted to maintain electroneutrality. Likewise, oxidation of PB to Berlin green (BG) ($Fe^{III}Fe^{III}(CN)_6$) results in simultaneous deinsertion of K^+. In addition, PB can be synthesized by simple procedures and electrochemically cycled many times without significant performance degradation. For these reasons, we selected PB as the model intercalation material of study.



Scheme 1

Scheme 1 illustrates the idea underpinning our results. It shows a PB deposit between two parallel microfluidic channels (Scheme 1a). Upon application of a driving voltage using Pt wire electrodes, an electric field develops across the PB and this induces anodic and cathodic poles, which experience overpotentials η_{an} and η_{cat}, respectively, on either side of the PB (Scheme 1b). This in turn leads to electrochemical reduction of PB to PW at the cathodic pole and simultaneous insertion of K^+. The opposite process occurs at the induced anode of the BPE: oxidation of PB to BG and simultaneous release of K^+. Thus the PB is referred to as a BPE. Accordingly, K^+ is taken up at the cathodic pole of the PB BPE, transported across it, and then discharged at the anodic pole (Scheme 1c).

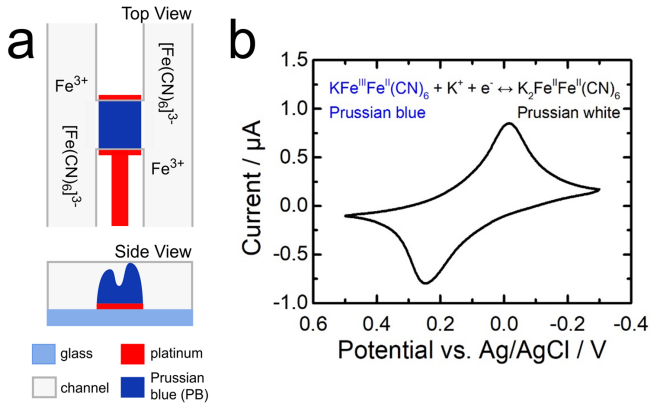


Figure 1. (a) Schematic illustration of the microfluidic channel configuration. Solution used for electrodeposition of PB contains 2.0 mM $FeCl_3$, 2.0 mM $K_3[Fe(CN)_6]$, 0.10 M KCl, and 0.10 M HCl. Electrodeposition is performed by cyclic voltammetry with a Pt wire counter electrode and a Ag/AgCl reference electrode. (b) Cyclic voltammogram of PB electrodeposited onto the Pt electrode situated in the cross channel shown in (a). The solution used to obtain the cyclic voltammogram contained 0.10 M HCl and 0.10 M KCl, and the scan rate was 50 mV/s.

Most ions diffuse through insertion materials at rates between 10^{-8} and 10^{-14} cm^2/s, and therefore it is essential to fabricate PB of appropriate dimensions to accommodate these reported rates. To this end, we electrochemically deposit PB atop a 100 µm x 100 µm Pt microelectrode located on the floor of the connecting cross channel (as shown in Figure 1a). Simply cycling the potential of the Pt microelectrode by cyclic

voltammetry in the presence of Fe^{3+} and $[Fe(CN)_6]^{3+}$ produces a PB deposit atop the Pt microelectrode. This is confirmed by the emergence of distinct redox peaks as the PB is reduced to PW and then oxidized back to PB (Figure 1b). Key to electrochemical deposition is synthesis of a relatively thick PB monolith atop the Pt microelectrode with regions extending to the ceiling of the microchannel but not significantly impeding solution flow through the connecting cross channel. Upon application of a driving voltage across the microchannel (Scheme 1a), a fraction of the total current passes through the PB BPE, while the remaining current passes through solution. Therefore, electrochemically deposited PB operates as an open BPE.

Figure 2a shows the configuration of the microfluidic system used to study K^+ transport through the PB BPE. When operated as a BPE, K^+ insertion at the cathodic pole of the PB leads to a local decrease in ion concentration, which is termed the ion depletion zone (IDZ). Simultaneously, K^+ deinsertion at the anodic edge of the PB leads to a local increase in ion concentration: the ion enrichment zone (IEZ). Formation of the IDZ enhances the local electric field gradient, and within this gradient charged species undergo faster electromigration. Moreover, if convection and electromigration are equal in magnitude but opposite in direction, then charged species experience a net velocity of zero and are concentrated at a particular point on the electric field gradient. This phenomenon, which is referred to as electric field gradient focusing, is used here with $BODIPY^{2-}$ fluorophore to validate the continuous transport of K^+ through the PB BPE.

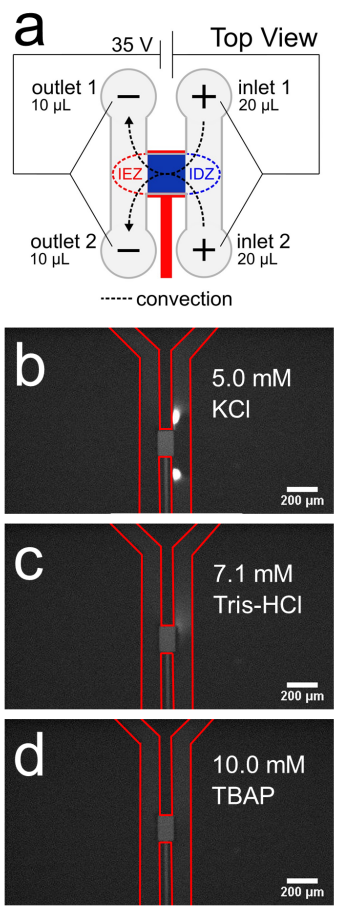


Figure 2. (a) Schematic illustration of the microfluidic channel configuration used to actuate the BPE. The solution volumes introduced into each reservoir to induce flow are indicated, as are the driving electrodes. (b-d) Fluorescence micrographs captured 70 s after applying a voltage of 35.0 V to the driving electrodes shown in (a). The fluidic channels are outlined in red. All three solutions contained 1.0 µM $BODIPY^{2-}$ and were at near neutral pH. In addition, the salts indicated in the individual frames were also present. The concentrations of the salts were adjusted to the values indicated in the figure to ensure that the conductivities of each of the three solutions were the same. As configured (Frame a), convection (electroosmotic and pressure-driven flow) is from right to left across the cross channel.

Figure 2b is a fluorescence micrograph captured during operation of the PB as a BPE with 5.0 mM KCl and 1.0 µM $BODIPY^{2-}$ present in the channels. The image was obtained 70 s after application of the driving voltage. The bright areas in the right channel near the cathodic pole of the BPE are regions of high concentration of $BODIPY^{2-}$. The maximum enrichment for this experiment was 170-fold, which occurred at the end of the experiment (t = 150 s). As discussed earlier, enrichment of $BODIPY^{2-}$ at this location confirms the presence of the IDZ and hence transport of K^+ across the PB BPE (Scheme 1). The distribution of $BODIPY^{2-}$ enrichment into two lobes is a consequence of the symmetry of both fluid flow and the electric field (Figure 2a).

To confirm that K^+ transport through the PB BPE is responsible for formation of the IDZ, we carried out two important control experiments. These involved replacing K^+ in the electrolyte with either $TrisH^+$ or tetrabutylammonium (TBA^+), which are both much larger cations than K^+ and known to be excluded from the PB lattice. Repeating the same experiment described for Figure 2b except with electrolyte containing TrisHCl or TBA perchlorate resulted in essentially no $BODIPY^{2-}$ enrichment (Figure 2c and 2d), because the larger cations are excluded from the PB lattice and hence no IDZ or IEZ forms. We have also confirmed that in the absence of PB atop the Pt microelectrode, processes occurring at the Pt microelectrode alone do not lead to formation of an IDZ or $BODIPY^{2-}$ enrichment. However, there are two key deficiencies to this system. First, it is unclear if the underlying Pt microelectrode assists in controlling the potential across the PB. Second, direct or indirect measurements of the current passing through the open PB BPE are not possible. To address these issues, a new approach to PB synthesis was conceived.

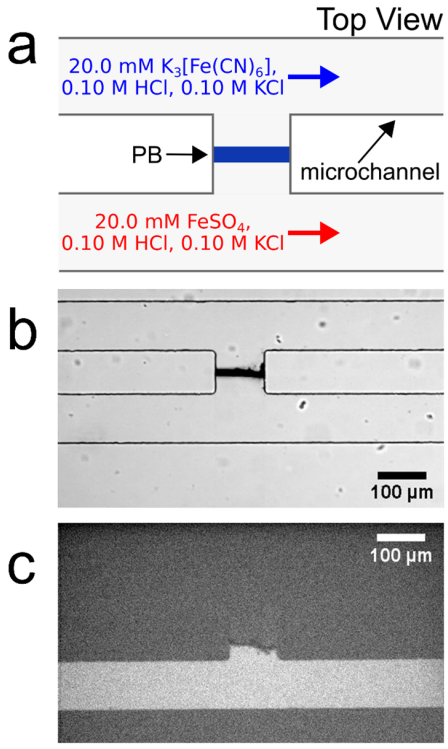


Figure 3. (a) Schematic illustration showing the microfluidic channel configuration and solutions used for co-flow chemical deposition of PB. (b) Micrograph of the PB following deposition for 50 s. (c) Fluorescence micrograph captured with 5.0 mM KCl in the top channel and 5.0 mM KCl and 1.0 µM $BODIPY^{2-}$ in the bottom channel. The flow rate in the bottom channel was ~50% higher than in the top channel.

A chemical deposition of PB is achieved by preparing two precursor solutions that upon mixing spontaneously form PB which rapidly precipitates out of solution (Figure 3a). In this manner, a free-standing and 10-20 µm wide PB deposit can be simply synthesized in the absence of an underlying Pt microelectrode (Figure 3b). Additionally, the synthesized PB is a solution-tight junction within the connecting cross channel (Figure 3c). In this case, upon application of a driving voltage across the microchannel (Scheme 1a) all current must pass through the PB BPE. For this reason, chemically deposited PB operates as a closed BPE and enables measurement of current passing through it. With the two key deficiencies of the system utilizing electrochemical deposition of PB addressed, a similar study of ion transport through the chemically deposited PB actuated as a BPE was performed.

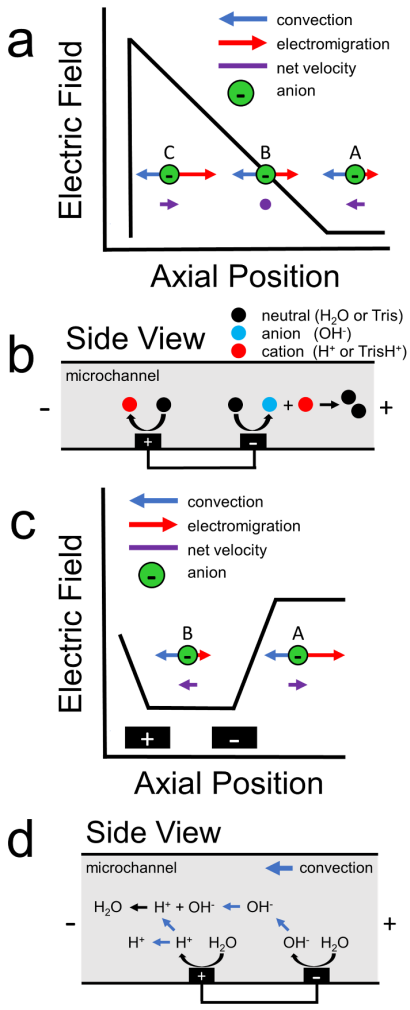
The key finding from this study is that the chemically deposited PB operates as a closed BPE results in the selective formation of an IDZ in the presence of K^+ as evidenced by $BODIPY^{2-}$ enrichment in the same manner as the previously discussed open BPE system.

Filtering and continuously separating microplastics from water using electric field gradients formed electrochemically in the absence of buffer

In this part of our project, we provided experimental results and finite element simulations aimed at understanding electrokinetics within microchannels that contain a bipolar electrode (BPE) and unbuffered electrolyte solution. This study is in contrast to earlier, related results from our group

that relied on buffered solutions to modulate the local electric field in microchannels. Our new findings reveal that faradaic water hydrolysis at a BPE modulates both the ionic conductivity and the ionic current passing through an unbuffered solution. This result is significant because ionic conductivity gradients and the variations in the ionic current yield sharp, local electric field gradients by a fundamentally new mechanism. That is, unlike previously reported methods, this approach does not rely on ion depletion zones or geometric factors to form electric field gradients. Finally, we showed that electric field gradients formed in unbuffered solutions are useful for both filtering and continuously separating microplastics from water. As we will discuss later, these results broaden the potential scope of membrane-free separations using BPEs.

Microplastics are usually defined as plastic particles having a diameter smaller than 5.0 mm. Over the past decade such particles have been detected in various media, including seawater, drinking water, air, and soil. As a result, there is a growing effort to understand the potential environmental and human health impacts of microplastics. As microplastic exposure and hazard studies are being performed, however, it is becoming clear that there are not appropriate analytical tools for sampling, separating, and detecting microplastics. In light of this, the development of appropriate analytical techniques is critical for the field.



Scheme 2

Charge-based separation processes are promising candidates for studying microplastics, because common plastics are often charged or develop a charge upon interacting with natural organic matter when in solution. Scheme 2a illustrates how an electric field gradient can be used to focus charged analytes such as proteins. In this scheme, consider the motion of anions within a variable electric field. We assume uniform convection and uniform electrophoretic mobility of the charged analyte. At position *A*, convection dominates electromigration and anions move from right-to-left. In contrast, at position *B*, convection and migration are equal and opposite, and therefore anions experience no net force at this location. Lastly, anions that diffuse downstream to position *C* encounter a high electric field. This enhanced electric field acts as a restorative force, redirecting anions back to position *B*. The net effect is continuous focusing of the anionic species along the electric field gradient. Sensibly, this method is termed electric field gradient focusing.

Scheme 2b illustrates a specific method for creating and controlling local electric fields: faradaic ion concentration polarization (fICP). Here, a BPE is patterned on the floor of a microfluidic channel containing a buffered electrolyte solution. When a sufficiently high voltage is applied across the length of the microfluidic channel, water electrolysis occurs at the ends of the BPE. For example, water reduction occurs at the BPE cathode to form OH^- (eq 1). If Tris buffer is present in solution, then OH^- reacts with $TrisH^+$ to yield neutral Tris (eq 2). To maintain charge neutrality across the BPE, water oxidation at the BPE anode produces H^+ (eq 3).

BPE cathode:

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (1)

$TrisH^+ + OH^- \rightarrow Tris + H_2O$ (2)

BPE anode:

$2H_2O \rightarrow 4H^+ + 4e^- + O_2$ (3)

During fICP, buffer neutralization (eq 2) in solution near the BPE cathode is important because it results in a lower local concentration of ions relative to the bulk solution. Accordingly, this region is termed an ion depletion zone (IDZ), and it is characterized by a relatively high solution resistance compared to the bulk. In the presence of an applied electric field, the solution conductivity gradient between the bulk solution and the IDZ forms a co-located electric field gradient.

We have shown that the electric field gradient formed during fICP is useful for enriching, separating, and controlling analyte motion in solution. One key limitation associated with the use of fICP for technological applications, however, is that fICP relies on the presence of a buffer in solution to facilitate the formation of the IDZ and concomitant electric field gradient. Therefore, it is desirable to consider methods that operate on the same principle as fICP but that do not require a buffer for practical uses like separating microplastics in seawater or fresh water.

In 2011, our group described an electrokinetic technique related to fICP that utilized BPEs in *unbuffered* solution to filter anions in microchannels. Due to the absence of a buffer in solution, we proposed that water electrolysis at the BPE locally increased solution conductivity between the BPE poles. As a result, the electric field between the BPE poles decreased relative to the electric field outside of the BPE poles. Scheme 2c is a schematic illustration for the proposed shape of the electric field during this experiment. As shown in this scheme, the elevated electric field upstream (to the right, at position *A*) of the BPE cathode results in increased electromigration. Under this set of conditions, electromigration of anions dominates convection (due to electroosmotic flow, EOF) and redirects anions upstream. Downstream of the BPE cathode (to the left, at position *B*), anions experience a decreased electric field. Here, anions flow downstream because convection dominates electromigration. The net effect is that low mobility anions are filtered from the vicinity of the BPE. Finally, it is important to note that, unlike fICP, this technique does not rely on the formation of an IDZ to alter the electric field. Rather, the increase in ion concentration between the BPE poles, relative to the bulk solution, accounts for the changes in the local electric field.

The present study used both experiments and finite element simulations to develop an understanding of how ion filtering works in unbuffered electrolyte solutions. The results indicate that sharp electric field gradients form in solution near the BPE poles for two reasons. First, ionic conductivity gradients form and alter the electric field as discussed above in the context of Scheme 2c. Second, the BPE provides an alternative pathway for current to flow through the system. As a result, the BPE shunts electrical current away from the microchannel, which leads to less *ionic* current flowing in solution between the BPE poles relative to outside of the BPE poles. These variations in ionic current contribute to the electric field gradients that form in solution. This latter point is important because, while it is widely understood that BPEs shunt current away from solution, the consequences on the local electric field have previously been overlooked.

Finally, we showed that by using a bifurcated microchannel, this new method for forming electric field gradients facilitates the continuous separation of microplastics in unbuffered electrolyte solutions. The key point is that electrokinetic separations using BPEs are no longer limited to buffered solutions, which will greatly increase the range of possible separations using BPEs.