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Special Issue

Principles of Bipolar Electrochemistry

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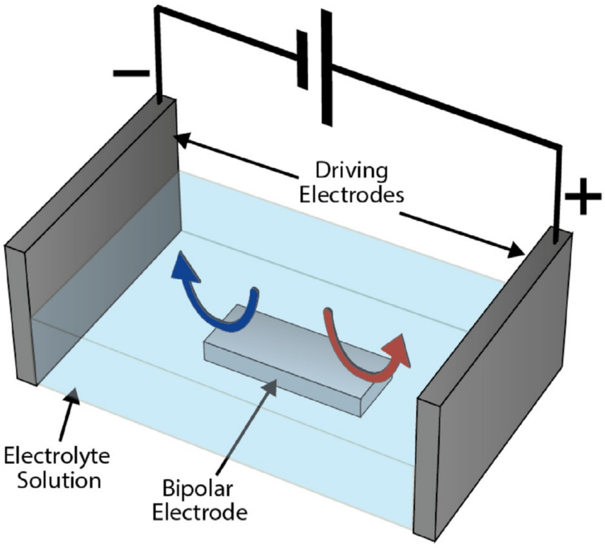
This is a tutorial on the basic concepts underlying bipolar electrochemistry. It is intended as an accompaniment to *ChemElectroChem*'s special issue on this topic. The guest editors of this special issue think it is worthwhile to introduce bipolar electrochemistry to a broader (electrochemistry) audience by explaining the similarities and differences between bipolar electrochemistry and normal electrochemical methods. The work presented herein has been adapted from: S. E. Fosdick, K. N. Knust; K. Scida; R. M. Crooks "Bipolar Electrochemistry" *Angew. Chem. Int. Ed.* **2013**, *52*, 10438–10456 (DOI: 10.1002/anie.201300947); "Bipolare Elektrochemie" *Angew. Chem.* **2013**, *125*, 10632–10651 (DOI: 10.1002/ange.201300947).

The objective of this tutorial is to provide readers with a short overview of the basic concepts underlying bipolar electrochemistry. Bipolar electrochemistry appears, at first glance, quite different from normal electrochemical methods. Just a little understanding, however, reveals that the two approaches are more similar than they are different. Specifically, in both bipolar and normal electrochemistry, it is the interfacial potential difference that drives electrochemical reactions. The difference between the two is simply which side of the interface is being controlled: the solution or the electrode.

Scheme 1 shows a typical experimental configuration used for carrying out bipolar electrochemistry. Here, the driving electrodes apply a uniform electric field across the electrolyte solution, and the resulting faradaic electrochemical reactions at the bipolar electrode (BPE) are shown occurring at the anodic (blue arrow) and cathodic (red arrow) poles of the BPE. As discussed later, the interfacial potential difference between the solution and BPE is highest at the ends of the electrode, so faradaic processes are always observed there first.

The essential difference between normal electrochemistry and bipolar electrochemistry can be illustrated by the following simple thought experiment. Consider the electrochemical cell shown in Scheme 1, wherein the BPE is platinum and the aqueous solution contains a dilute, inert electrolyte. When the power supply is turned on to, for example, 1.0 V, no faradaic reactions are observed at either the driving electrodes or the BPE. However, at a critical voltage that depends on a number of experimental factors, bubbles are observed at the two ends of the BPE. Analysis would show that those at the cathodic pole are hydrogen and those at the anodic pole are oxygen. In other words, even though the BPE itself is an equipotential surface (or nearly so) and even though there is no ohmic contract to the BPE, the electrolysis of water is occurring at its two poles. The remainder of this short tutorial explains how we can rationalize this observation.



Scheme 1.

Cells for carrying out bipolar electrochemistry can be configured to accommodate a range of applications from preparative-scale electrosynthesis to microanalysis. For example, Scheme 2a is an illustration showing a simple microscale cell design used by our group.[1] In this case, a BPE, or an array consisting of multiple BPEs,[2] is embedded within a microfluidic channel that has a height of tens of microns, a width of hundreds of microns, and a length of perhaps a centimeter. Potential contaminants electrogenerated at the driving electrodes do not interfere with the BPE in this design, because of the macroscale length of the channel.

The voltage applied between the driving electrodes (E_{tot}) results in an electric field in solution that causes the BPE to float to an equilibrium potential (E_{elec}) that depends on its position in the field and the composition of the electrolyte solution.[3] Because the electrode is a conductor, E_{elec} is, as mentioned earlier, the same (or nearly so) everywhere on its surface. However, the interfacial potential difference between the BPE and the solution varies along its length due to the presence of the electric field in solution. It is the corresponding anodic and

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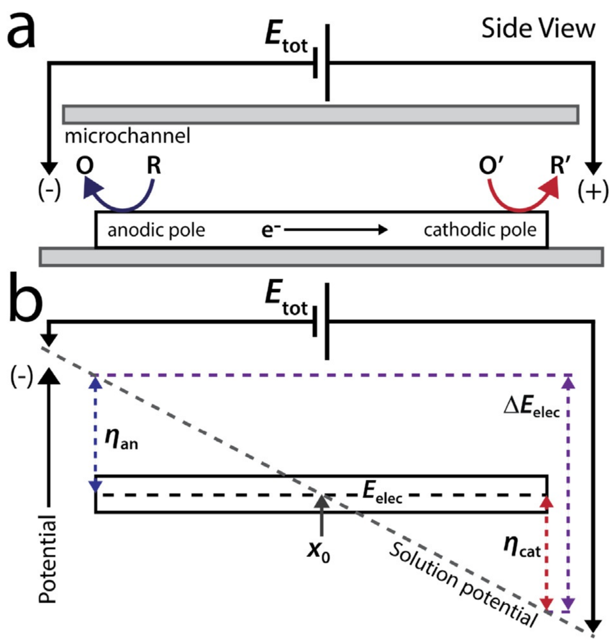
An invited contribution to a Special Issue on Bipolar Electrochemistry



Scheme 2.

cathodic overpotentials, η_{an} and η_{cat}, respectively, that drive electrochemical reactions at the poles. Scheme 2b shows that the magnitudes of these overpotentials depend mainly on just two experimental variables: the magnitude of E_{tot} and the length of the BPE. The location on the BPE that defines the boundary between the two poles, and which itself has zero overpotential with respect to the solution, is defined as x_0. Although x_0 is represented as being at the center of the BPE in Scheme 2b, its actual location depends on the nature of the faradaic processes occurring at the poles.[3]

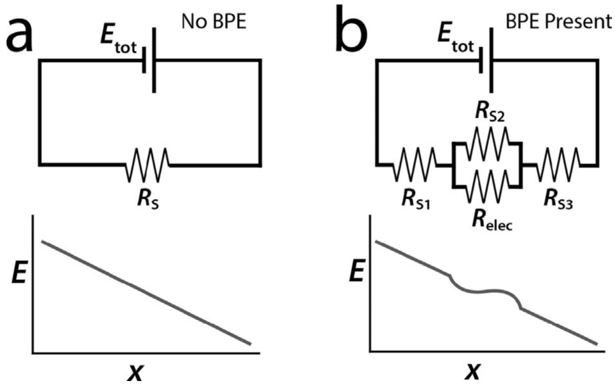
As mentioned earlier, the magnitudes of the overpotentials vary along the length of a BPE, with the highest overpotentials occurring at the extremities. This is in contrast to the working electrode in a traditional three-electrode cell configuration, wherein the interfacial potential difference is generally considered to be uniform. Importantly, the non-uniformity of the interfacial potential differences along the length of a BPE can be useful. For example, it can be used to simultaneously drive reactions at different rates or to synthesize materials and thin films having a graded composition or density (examples of which are provided in this issue).

The electric field that powers bipolar electrochemistry is typically applied by a pair (or more)[4] of driving electrodes (Scheme 1). The nature of the electric field formed between the driving electrodes depends on the cell geometry and the conductivity of the electrolyte solution. In some cases a linear electric field is generated by restricting the cross-sectional area of the solution between the driving electrodes, thereby increasing its resistance. This can be achieved by embedding the BPE in a microchannel having a small cross-sectional area (e.g., Scheme 2a) or by limiting the volume of electrolyte solution over a BPE in an open channel. We,[5] along with Duval and coworkers,[6–10] have discussed many of the parameters that control bipolar electrochemical processes. As alluded to earlier, these parameters include E_{tot}, the distance separating the driving electrodes, $l_{channel}$, and the length of the BPE, l_{elec}. The fraction of E_{tot} that is dropped over a BPE, which we refer to as ΔE_{elec}, can be estimated using Equation (1):[5,11,12]

$$\Delta E_{elec} = E_{tot}\left(\frac{l_{elec}}{l_{channel}}\right) \qquad (1)$$

The value of ΔE_{elec} is a critical parameter for analyzing electrochemical processes at BPEs. The simple relationship expressed in Equation (1) incorporates a number of assumptions that may be possible to ignore for some systems, but not others. For example, it assumes that an active BPE does not significantly affect the electric field in the solution, which is often not the case.

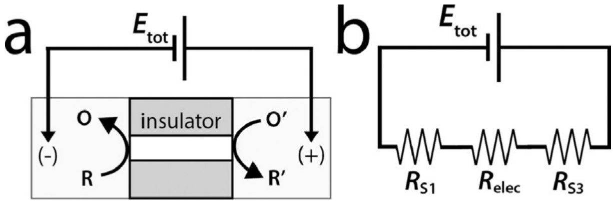
The foregoing point can be understood in terms of the equivalent circuits shown in Scheme 3, which are reasonably good approximations of the resistances present in the type of cell shown in Scheme 2a. In the absence of a BPE, the current flowing between the driving electrodes is entirely ionic (Scheme 3a). The magnitude of the ionic current moving through the electrolyte is then governed by the magnitude of the applied potential (E_{tot}) and the resistance of the solution (R_S). When faradaic reactions occur at a BPE, a second path for current, in the form of electrons moving through the BPE, is available (Scheme 3b).



Scheme 3.

We now define the parameter R_{elec}, which is the total resistance to electronic current posed by the BPE, hence, incorporating the charge transfer resistance (R_{ct})[13] and relevant aspects of mass transfer. If the resistance of the solution above the BPE (R_{S2}) is much lower than R_{elec}, then most of the current in the cell passes through the solution rather than the BPE. In this case, the electric field is not significantly perturbed by the BPE. However, when $R_{S2} > R_{elec}$, which can be achieved by lowering the concentration of the electrolyte, substantial current flows through the BPE. This alters the local electric field in solution, which is proportional to iR_{S2} (i is the total current flowing in the cell), thus resulting in a nonlinear electric field in the solution above the BPE. Duval and coworkers call this effect faradaic depolarization, and its magnitude depends on the strength of the electric field, the concentration of the supporting electrolyte, and the electrochemical properties of the electroactive species in the system.[6–10] It is also important to note that Equation (1) does not account for any potential dropped at the driving electrodes. The fractional loss of E_{tot} within the electrochemical double layers can, under some circumstances, be substantial.[3] Other electrochemical processes can also mitigate Equation (1), but these are far more minor than the two discussed here and are, therefore, beyond the scope of this short tutorial.

There is just one last nuance of bipolar electrochemistry that requires some discussion before diving into the more detailed articles that follow. Thus far this tutorial has focused exclusively on what are known as "open" BPEs. As discussed earlier (e.g., Scheme 3), these types of devices are defined by the existence of two possible current paths: electronic and ionic. However, several interesting reports describe the use of "closed" BPEs (Scheme 4 a).[14–15] In closed BPE configurations, the solutions contacting the BPE anode and cathode are physically separated from one another, and the only current path between the two half cells is through the BPE (Scheme 4 b). This has significant consequences, as described in ensuing articles.



Scheme 4.

Finally, it is right and proper to acknowledge two of the pioneers in the field of bipolar electrochemistry as applied to materials, synthesis, and analytical chemistry. Although neither are actively working in the field at this time, the guest editors recognize the importance of the early contributions of Fleischmann et al.[16] and Bradley et al.[17]

Acknowledgements

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