Finite Element Analysis of a Closed-Cell Bipolar Electrochemistry Water Sensor

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Abstract: This work computationally characterizes a new bipolar electrochemical sensing scheme recently developed for the detection of heavy metals in water. The sensing scheme relies on a two-step protocol that couples a closed bipolar electrochemical cell with an electrochemiluminescent reporter for quantitation. Device operation is simple, but the specific chemical, physical, and electrochemical parameters that instruct device function are yet to be determined. This study employees COMSOL Multiphysics® to construct a finite element model of the device for more systematic study. Current density at both BPE and electrolytes were determined, as well as the potential drop (versus adjacent reference) across the whole system and across the BPE. Additionally, electrode surface change (given the deposition of a species of interest) and some of its effects were modelled. Chemical processes of dilute species were also incorporated into the model and its impact on the design and functioning was assessed. Some factors that affect the position of the line of zero potential (LZP) were determined, such as relative conductivity of electrolytes and relative exposed area of the bipolar electrode. The model, although limited, sheds light to the main aspects that must be considering when designing and working with closed-cell bipolar electrodes as electrochemical sensors.

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Events such as the ongoing Flint, MI[1] and Newark, NJ[2] water crises highlight the need for reliable water quality assurance. Currently available water tests include laboratory analysis and commercial test strips. Both fail to adequately provide a description of potential water issues as they can be expensive, time consuming and rely on technical expertise. As such, current techniques can be inaccessible to the general populace.

Bipolar Electrochemistry is a relatively new field of electrochemistry that has great potential to tackle many of the issues with conventional electrochemical techniques[1]. In this format, an electrically isolated electrode is induced to polarize in solution against an externally applied electric field. The two ends of the same electrode then ser as both cathode and anode. Like in conventional electrochemical systems, redox reactions can then occur at each pole of the electrode if sufficient potential is applied. In contrast to conventional electrochemistry, however, current is constrained to the single solid electrode. Bipolar electrochemistry has shown great promise for a vast array of new applications [3]. Particularly, studies have shown the ease for this format to be useful for multiple simultaneous interactions even at the micro scale, with experimentally successful micro-BPE arrays.[4] .Recent work from this group and others has shown this format also provides an affordable way of performing traditionally cost prohibitive electrochemical experiments. Finally, portability and deployability seem to be areas in which bipolar electrochemistry could improve the current state of electrochemistry.

There are two general classes of bipolar electrochemical cells: open-cell and closed cell. In open-cell systems, the cell geometry allows current to flow through the bipolar electrode or through solution. However, in the closed-cell format, the reactions at each end of the bipolar electrode are physically isolated. As such, the behavior of the bipolar electrode and of the isolated solutions is different. In certain

manifestations, completely different electrolytes are exposed to the anode and cathode poles of the same bipolar electrode. This can have significant impact on the overall electrochemical kinetics and downstream device performance. Little work has been done to elucidate the specific impacts of electrode geometry, electrochemical kinetics, and electrolyte composition on the overall closed-cell bipolar electrode performance.

However, for all these technical advancements to occur, fundamental understanding of the physical phenomena underlying the mechanisms of bipolar electrochemistry must be fully understood and characterized. Several groups have in recent years produced meaningful work toward this goal [4] but closed-cell bipolar electrochemistry remains largely unexplored. Despite the commonalities with all general bipolar-electrochemistry based systems, a closed-cell system presents the technical challenge of isolating the half-reactions that may be at play and their transfer of electrons. Therefore, the understanding of electrode/electrolyte interphases is, to date, incomplete at best.

Physical Description of the Sensor used in the Finite Element Analysis

In this particular example, a two-step anodic protocol is implemented where lead (as aqueous Pb^{+2}) in ultrapure water is the system in one of the isolated wells and a system consisting of 24mM $K_{3/4}[Fe(CN)_6]$, 10μM of $Ru(bpy)_3$, 10mM of $(S_2O_8^{2-})$ and 0.1M NH_4CL. Both wells are filled up with 90μL of the indicated solutions. The electrodes are made by laser engraving of Fluorine doped Tin Oxide (FTO) glass. The operation of the sensor requires a two-step protocol modelled on traditional anodic stripping voltammetry.

During the first step, a positive working electrode polarized the BPE end in the lead containing well resulting on the plating of solid led onto the BPE. During this first step, it is assumed that the oxidation of ferrocyanide is the main reaction. On the second step, stripping occurs and the bipolar electrode (BPE) acts then as a bridge through where only electrons can flow from one system to the other. An electrochemiluminescence reaction with the $Ru(bpy)_3$ then occurs at the now negative end (cathode) of the BPE in the reporter reservoir.
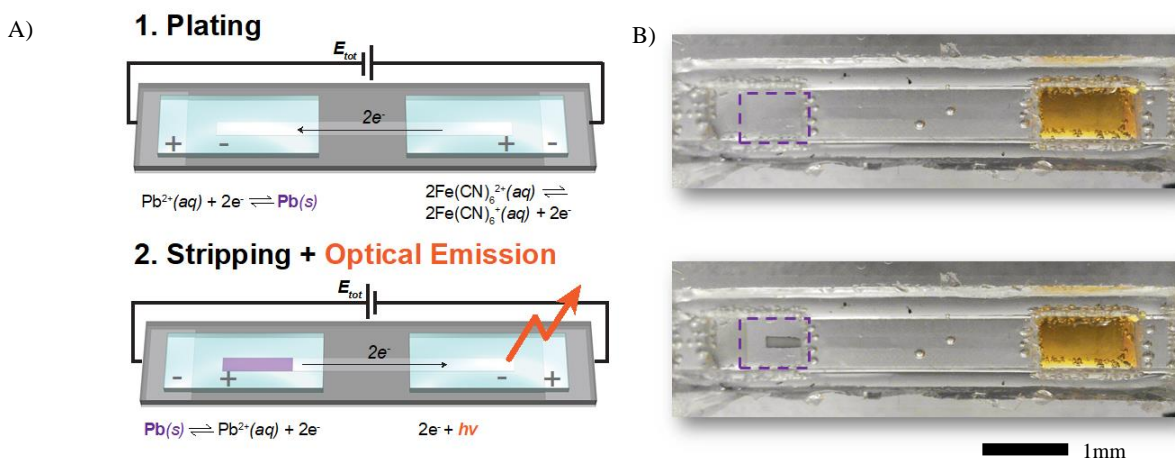

Figure 1. Two-step protocol for optical anodic stripping voltammetry experiments in closed-cell bipolar electrode format. (A) Experimental design and schematics of sensor. (B) Picture of lead deposition on bipolar electrode corresponding to the end of the first step.

Finite Element Analysis

A finite element analysis is the modelling of a physical system to predict the behavior of the system under different circumstances. In particular, it is useful for finite areas of interest where a set of known or approximate differential equations reign. The present finite element analysis was performed with COMSOL Multiphysics 5.2, with the Electrochemistry module, utilizing the secondary current distribution and transport of diluted species physics for a time-dependent study. A triangular, small-sized with higher node concentration at the electrode-electrolyte interphases was selected for the analysis, given the small scale in which surface changes occur in the device and for computational efficiency.

A 2D approximation of the sensor geometry was implemented, focusing on the stripping step given the potential electrode changes that could occur during the plating of the analyte. The 2D approximation is considered adequate in this model since a primary factor to consider is the ratio of electrolyte to electrode surface, which in this model is a simplified linear interphase. Figure 2 shows the exact geometry in which the working electrodes, approximated as linear, are highlighted in black and red and the BPE is shown in yellow. The modelled composition in each well is the same as indicated for the physical model and conductivities for solutions and material are indicated as per experimental measurements.

The secondary current distribution model separately performs a Nernstian adjustment for concentration changes effected during device operation. Respective conductivities (measured for electrolytes, calculated for FTO) were defined to best represent the real device. Four Electrode-Electrolyte Interfaces (Electrode Surface) nodes were added, one for each area in which either the working electrodes or the BPE ends are in contact with the solutions. Additionally, to account for the deposition of the analyte, two Transport of Diluted Species (TDS) nodes were added, one per each well.

Transport in solution was evaluated in several ways. First, experimental data indicated that virtually no ohmic heating would occur. Specifically, the glass sheet was put under the operating conditions (5V) for 5 minutes and only a small increase, >.1%, +0.21C (or ~500J) was observed. Therefore, convection is omitted as mechanism of transport. Particularly, as water is the solvent for all experiments, small temperature changes are not expected to have an impact on species transport, particularly given water's large heat capacity. This assumption may not hold in other solvents and with other electrode materials and/or currents. Therefore, electromigration is assumed to be not only the main, but also the only **method of transport of species**.

Note that since it is the plating step that is being modelled, an additional Dissolving/Depositing Species was added in the second Electrode Surface domain (which corresponds to the plating side of the BPE). Given the analyte concentration range of interest (μg/L according to EPA action limits[6], it was seen that no considerable electrode deformation could occur as there was not enough Pb^{2+} in the total volume utilized (~90μL) to considerably deform the electrode surface in any way.
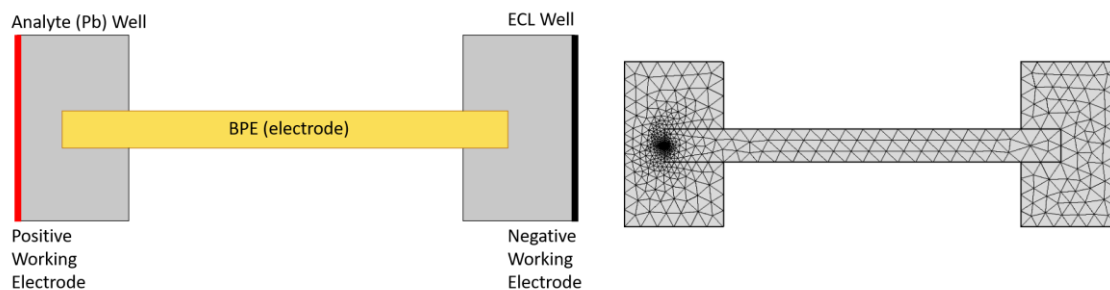

Figure 2. (L) 2D Approximation of the closed cell system with emphasis on the electrode-electrolyte interphases. (R) Triangular Mesh with higher node-density near the lead deposition area of BPE selected for this study.

Electroneutrality in Closed-Cell BPEs

A key question in BPE operation is how the deviation from electroneutrality impacts function. This is especially pertinent in closed-cell BPE systems where electrolyte half cells are physically isolated from ion transport. In this device geometry, as electros were striped from one well and put into another, a charge imbalance could be produced (much like in a capacitor). The role of supporting electrolytes in each of the wells was thus evaluated. This was of particular interest in the case of the ECL (reporting) side, in which the presence of high highly concentrated NH_4Cl and a very reactive peroxysulfate complicate the chemical and physical understanding of the process.

Heterogeneous Electrochemical Kinetics

Electrode kinetics are understood as drastically different at each electrolyte-electrode interface, with a general notion that at each negative site (in either step) water (or hydrogen in case of acidic mediums) seems to be the reactive species for which fast Linearized Butler-Volmer Kinetics (also known as Tafel kinetics) are assumed. In the case of the opposite polarity (positive in the plating step), the present species do not allow for such simplifications and Concertation-Dependent (Butler-Volmer) Kinetics are deemed as more appropriate, particularly given the small analyte concentration and small volumes. For other cases where concentrations and or volumes (thus ratios of solution to electrode surface) are large it is likely that different kinetics would be at play. This is in line with the short (5 minutes) experimentally determined time needed for plating.

Previous experimental determination suggested five minutes was an adequate duration for the initial plating step for Pb^{2+} at the analyte reservoir. Despite the flow of electrons across the BPE being virtually immediate upon the change of polarity (i.e. the change from plating to stripping), the deposition of species of interest is time sensitive (in as much that there is such thing as too little time depending on the working concentrations

Modelled Experiments

After the construction of the model, some of the parameters of interest where calculated, such as the potential drop which was determined at about 1.3V (Figure 3a) though much is to be said about this approximate result as water reduction and lead plating potentials are all well-known and do not particularly seem to correspond with the reported value. Reasons for this potential discrepancy are inherent to the model, particularly with a 2D geometry in which the ratio of electrolyte to electrode surface are largely different. Secondly, it was observed that the potential drop did not obey a linear change across the BPE. It is observed that at the BPE-electrolyte interphase there is a very sharp potential change. In contrast, the voltage drop across the unexposed BPE was modelled as largely linear and. In average, there is a change of about .1V/mm.
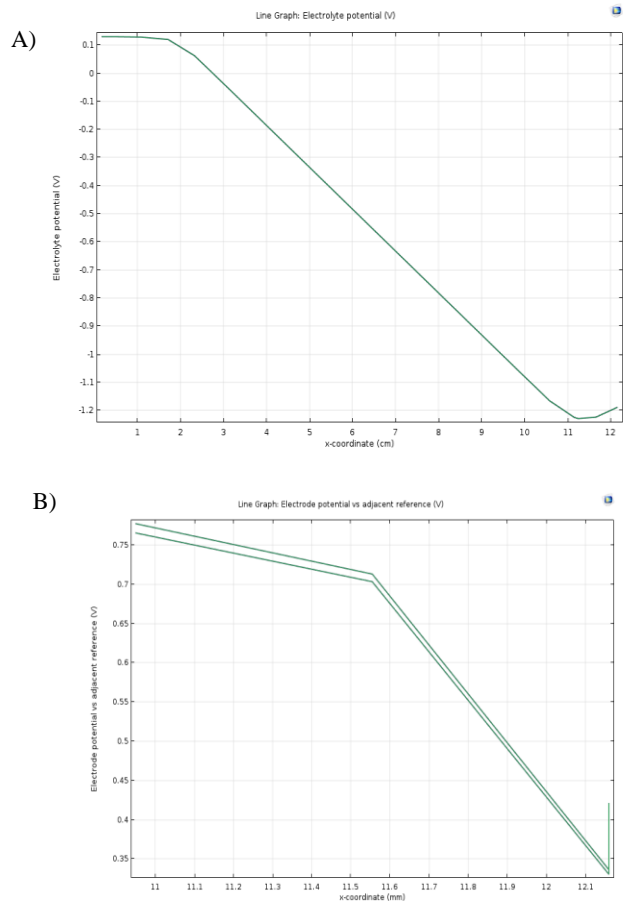
A)

B)

C)

Figure 3. A) Modelled Voltage Drop Across BPE B) Voltage Drop at BPE Analyte End. C) Effect of Conductivity Changes

D)

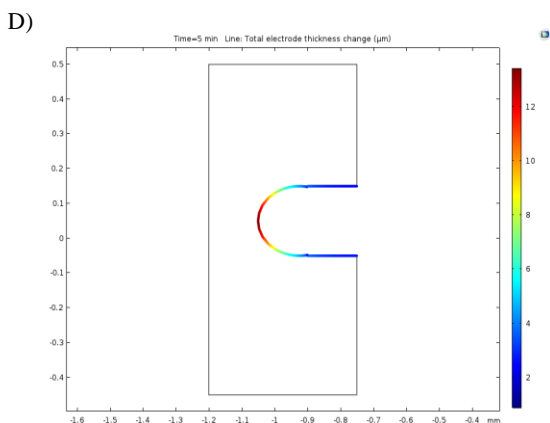Time=5 min Line: Total electrode thickness change (μm)

Figure 4. E-Field Density at Circular BPE End.

Line of zero Potential (LZP)

To identify a physical parameter of the sensor which could be used as a standard to observe the effect of various changes on the model, but that could also be experimentally validated, literature was searched and the line of zero potential was identified as the best option.

Initial results from the model indicated the point (or line in this geometry) at which the bipolar electrode was at 0V was not necessarily symmetric to the device, that is, not in the middle of the electrode. This position was subsequently evaluated as a possible metric for device performance or at least to assess the effect of particular changes on the system. One possible physical contribution to this asymmetry was the relative difference in electrolyte conductivities across the reservoirs. To test this effect, the LZP was noted as different conductivity ratios were input (by changing the conductivity of the solutions in each well). As shown in figure 3 the observed relationship is mostly linear. This result, even if not yet experimentally confirmed, sheds light into one of the largest challenges this device could face as drinking water

presents a widely varying range of conductivity depending on source or treatment prior to consumption. Analysis of changes in the position of the LZP based on the absence and varying amounts of supporting electrolyte where however not very conclusive.

Electrode Size and Shape

To assess the impact of the electrode shape and distance between working electrode and BPE, different shapes and sizes were explored.

Following from the very sharp differences observed in the potential drops at each exposed BPE end, it was determined that some exploration of some physical and chemical considerations should be explored. The shape of the electrode (the BPE ends in this case) can have a significant impact on the current distribution.[7] The current rectangular design can be potentially problematic due to its larger electric field generation at the sharp corners. This can lead to analyte distribution issues within the reservoir. Circular shapes seem to offer a better distributed current density which in turn can translate into a more favorable deposition of the analyte of interest. This shape is expected to suffer fewer issues of electrode deformation or distorted electrode behavior, kinetics or simply transport of material. This however needs further experimental validation, particularly to determine if the effect predicted by this model is exaggerated or less significant than envisioned. But not only does shape seem to have an effect, the actual size of the electrode is also a parameter to consider. Under the same discussion of electrode shape, it was envisioned that a circular electrode end would behave better in a miniaturized setup. As it is envisioned that parallel testing can be done with arrays, the discussion of size becomes more relevant. Currently the size of the exposed BPE is about 2mm but work in the field has produced comparable effects in much smaller scale.
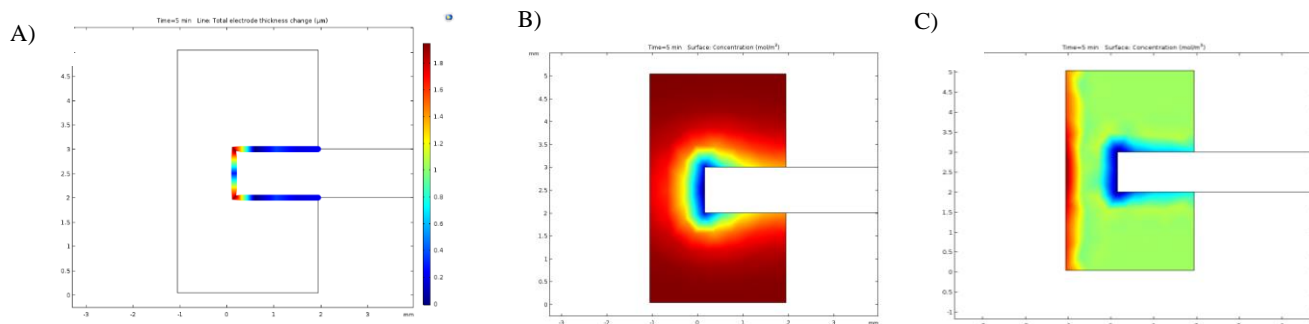
A)

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Figure 5. Experiments performed with the constructed model on effects of changes in selected physical and chemical parameters. A) E-field of a miniaturized model (1/5) with a circular BPE end. B) E-field of normal size BPE. C) Distribution of analyte at neutral pH. D) Distribution of analyte at measured pH (4.3).

Ratios of Exposed Electrode Area

Recalling the assumptions made of the ratio of solution to electrode area being small, with consequent fast kinetics, changes in total amount of BPE exposed to solution were performed to assess the impact on the overall performance of sensor, via the LZP proxy.

Additionally, the relative amount of BPE exposed (even at equal conductivity for both wells) did not seem to yield a large change in the position of the LZP. Another important consideration regarding the physical dimensions of the electrode is the distance between the BPE end and the working electrode. Particularly, if the distance between the BPE and the working electrode is too short, issues regarding diffusion were shown as possible, particularly if there is electrode growth. Much like the selection of shape, changes on distance, particularly if electrode growth happens in that direction for some high-concentration analyte, can lead to distorted behavior.

Conclusion

However, which experiments to even conduct and in general what issues to be thinking about are question that have largely been explored through the construction of this model. Most notoriously perhaps are questions surrounding charge imbalances and neutrality that are very particularly to the

Chemical Considerations

Following the understanding gained from exploring the relationship of conductivity and pH and water stability by constructing pourbaix diagrams, exploration of some chemical parameter of interest was done. Given that water is the solvent of interest and that in taps pH values can vary widely, pH was a main chemical parameter that was explored. Particularly, it was observed that at neutral pH (figure 4c) the analyte is much less localized than it is at the measured pH (a low 4.3) for the solution use experimentally. If experimentally true, this result highlights the importance of the electrode shape and of fine-tuning the method for most reliable deposition as more localized analyte with small areas of high current density could lead to issues of linearity and reporting.

closed-cell format. Furthermore, the determination of a useful parameter to use as metric for experiments, namely the LZP is largely valuable as it allows for both computational and (in possession of a three-point probe) experimental determination of impact of a large set of variables which is important given the widely varying character of the main driver of this research: drinking water.

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