

A MATLAB-Based Teaching Approach to Dilute and Concentrated Solution Theories of Electrochemical Cells*

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Students at high school as well as at early college level are sometimes confused, when studying electrochemical cells, over the mass transfer in the electrolyte and conduction within the cells, which results in the completion of the electrical circuit. Dilute and concentrated solution theories are two of the predominant concepts for understanding the mass transfer within the electrolyte. A MATLAB® based program has been developed to help in teaching and to aid the understanding of the dilute and concentrated solution theories of electrochemical systems. The MATLAB® based code that has been developed can be used to supplement a lecture on electrochemical cells as part of an electrochemistry course for early undergraduate students. The objective is to help in the understanding of the migration and diffusion of ions in electrochemical systems and how they affect the current, concentration distributions and potentials within a cell. The role of a 'supporting electrolyte' and its function, as seen in case studies for dilute solution electrolytes, is reported. In addition, basic chemistry and early engineering college students can be given assignments to manipulate a variety of parameters as part of a larger assignment and to observe the effects of these parameters on the working of a simple electrochemical system, draw inferences and modify or extend the software to a number of different cases.

Keywords: electrochemistry; electrolytic/galvanic cells; electrochemical potentials; transport phenomena; corrosion; energy storage, computer-based learning.

INTRODUCTION

THE MOST IMPORTANT PART of an electrochemical cell are the working and counter electrodes. This is where the electrochemical reaction takes place and to give the results for the desired application. For electroplating cells, this can be the electrochemical deposition reaction or it can be the reactions in the battery during discharge. From a layman's point of view, the electrodes can be viewed as the post-offices where all mail transactions take place. The mass transfer in the electrolyte (analogous to the postman), a very important function for the efficient operation of the electrochemical cell, is—according to a literature survey—where much of the students' confusion lies, as will be shown below. The transport in electrolytes is a complicated phenomenon that describes the movement of the ions with the electrolyte. This transport results in the movement of ions within the electrolyte and the completion of the circuit within the cell. A common misconception among students is that the conduction in the electrolyte is caused by the movement of electrons, contradicting Faraday's law of electrolysis. Morikawa et al. [1] discuss this in detail on their theory on teaching electroneutrality in electrolyte cells. Yang et al. [2] also describe the misconceptions of

students about conduction in electrolytes in batteries. Ozakya et al. [3], Bojczuk et al. [4], Finley et al. [5] and Butts et al. [6] also state that electrochemistry is one of the most difficult subjects for new college students to master. In addition, Ozakya et al. [3], as recently as 2006, show that one of the most common difficulties that students face in understanding galvanic cells is over the conduction in the electrolyte, with a large percentage thinking that electronic conduction in the electrolyte is the reason for the completion of the circuit. While electronic conduction is plausible in certain electrolytes, it is not the main conduction mechanism. Birss et al. [7] also draw attention to the necessity of improving the teaching of electrochemical cells by providing a better explanation of the current flow in the cells. Here we aim to provide a tool for understanding the conduction in electrolytes.

There are two dominant theories to describe the behavior of electrolytes: the dilute solution theory and the concentrated solution theory. The dilute solution theory is frequently used by electrochemists in many problems where an infinitely dilute electrolyte is used. Normally aqueous solutions of salts (such as $MgCl_2$, KCl , etc.) can be considered to be dilute solutions. In particular, Equations (1), (2) and (3) of Newman et al. [8, 9] are those that have been programmed into MATLAB. These equations can be found in many other texts on

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electrochemistry, for example that of Bard and Faulkner [10]. These are the equations for the flux of each of the dissolved species in the electrolyte as given in Equation (1):

$$N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i \mathbf{v} \quad (1)$$

and the equation for the current in the electrolyte due to the movement of the charges species (ions) as given by Equation (2):

$$\mathbf{i} = F \sum_i z_i N_i \quad (2)$$

and the electro-neutrality condition as given by Equation (3):

$$0 = \sum_i c_i z_i \quad (3)$$

where N_i is the flux of ion i ; z_i is the charge on ion i (negative for anions); u_i is the mobility of ion i (defined differently by Newman than in some texts); F is Faraday's constant; c_i is the concentration of ion i (moles per unit volume); ϕ is the potential in the electrolyte; D_i is the diffusivity of ion i ; \mathbf{v} is the electrolyte velocity (zero in what follows on the assumption of a stagnant electrolyte); and \mathbf{i} is the current density.

Equation (1) fails when there are two or more concentration gradients present that are independent of each other. This necessitates a modification of the flux equation. A multicomponent diffusion equation is appropriate for such a case of a concentrated solution. An example of a concentrated electrolyte would be a mixture of solutions of NaCl and LiCl. For the concentrated solution theory, Equation (4) [8] is the most widely used and has been programmed in MATLAB.

$$c_i \nabla \mu_i = \sum_j K_{ij} (v_j - v_i) = RT \sum_j \frac{c_i c_j}{c_T D_{ij}} (v_j - v_i) \quad (4)$$

where: μ_i is the chemical potential of the species i ; K_{ij} are the friction coefficients or interaction coefficients of species i and j ; v_j , v_i are average velocities of species j and i ; R is the universal gas constant (8.3143 J/mol K); T is the temperature in K; c_T is the total concentration of the salt and solvent; D_{ij} are the diffusion coefficients for the interaction of species i and j ; and c_i is the concentration of species i .

CASE STUDIES USING THE DEVELOPED MATLAB CODE

The calculations presented by the program are all unit independent as long as one uses a consistent set of units but it is probably best to think of the results in c.g.s units. The results shown are the distributions of potential and concentration across a cell where the cathode (on the left) and anode are

separated by 2 cm. The case studies show how diffusivity, mobility and charge of ions influence the operating variables of the electrochemical cell.

With the above background on the theory of dilution and concentrated electrolyte solutions, and setting up the equations in MATLAB, a number of case studies are shown that can be discussed in class and extensions can be given as an exercise to students to incorporate and infer the consequent results. The parameters in the program that are important in carrying out the case study exercises are shown below.

Diffusion coefficients of ions

- Diffusion coefficient of cation 1 of supporting electrolyte = D1
- Diffusion coefficient of anion 1 of supporting electrolyte = D2
- Diffusion coefficient of electrochemically active cation = D3

Mobilities of ions

- Mobility of cation 1 of supporting electrolyte = u1
- Mobility of anion 1 of supporting electrolyte = u2
- Mobility of electrochemically active cation = u3

Charge of ions

- Charge on cation 1 of supporting electrolyte = z1
- Charge on anion 1 of supporting electrolyte = z2 (negative)
- Charge on electrochemically active cation = z3

A number of cases based on the values of the above mentioned parameters are shown below.

Case 1

Parameter values

$$\begin{aligned} D1 = D2 = D3 &= 10^{-5}, \\ u1 = u2 = u3 &= 100/F^2 \text{abs}(z_i); \\ z1 = 1, z2 &= -1, z3 = 1 \end{aligned}$$

Inference

For the first set of calculations, the diffusivities and mobilities of all the ions are the same. All ions have unit charge. 'Pot' in the figures is ϕ while 'Ref. pot.' is the potential sensed by a reference electrode responding to the anion. Note that some of the potentials are in mV while others are in dV (= 100 mV) in order for them to fit conveniently on the same plots. All concentrations are in millimole/cm³. The concentrations are sufficiently high that the limits of dilute solution theory are pushed; however, the purpose here is to be illustrative, rather than precise. The result using the above scheme is as shown in Fig. 1. The upper figures are for the steady state (constant current) and lower figures for the instant following current interruption. The figures on the left are with the supporting electrolyte. The profiles in the upper left of Fig. 1 are as expected. Anion concentrations rise as we move away from the cathode (resulting

in a tendency to diffuse towards the cathode, which exactly balances the migration towards the anode) while the inert cation concentration drops (for analogous reasons). The concentration gradient of the active cation results in a diffusion that assists its migration towards the cathode (where it is discharged). The potential (ϕ) is as expected and the potential of the sensing reference electrode drops, moving away from the cathode, because of the variation of the anion concentration across the cell.

Another interesting fact to be noted is that without the supporting electrolyte (upper right plot) the potential drop across the electrolyte is large (about 45 mV) compared with the case (3 mV) for when the supporting electrolyte is present. We have a clear illustration of the virtue of a supporting electrolyte in reducing cell voltage (or increasing cell current if the potential drop across the cell is maintained). The potential distribution is distinctly nonlinear without a supporting electrolyte. Without such an electrolyte, Equation (1) for ion 3 is more significant in determining the potential and the large change in concentration (relative to its value at the cathode) for this ion results in non-linearity in ϕ (first term on the right of Equation (1)). [In this plot the concentration line for ion 2 is obscured by that for ion 3, but this can be observed by using the zoom in tool in the

MATLAB[®] figure window generated by the software.] For the case of the supporting electrolyte, the movement of the secondary ions is due to diffusion and convection, while the ions of the supporting electrolyte participate in migration. There are numerous examples of the use of supporting electrolytes in industry but recently it has been shown that silver nanowire arrays could be grown by adding a supporting electrolyte [11].

Case 2: Effect of increasing diffusivities

Parameter values

$$D1 = D2 = D3 = 10^{-4};$$

$$u1 = u2 = u3 = 100/F^2 \text{abs}(z_i);$$

$$z1 = 1, z2 = -1, z3 = 1$$

Inference

For the second set of calculations, all the parameters are kept the same as in Case 1 but all the diffusivities were increased by an order of magnitude. The results are shown in Fig. 2. Now the supporting ions require only modest concentration gradients in order to balance their tendency to migrate, since diffusivities are higher by an order of magnitude. Consequently the reference electrode potential lies much closer to ϕ . Note that ϕ is almost unchanged, from Case 1, for the

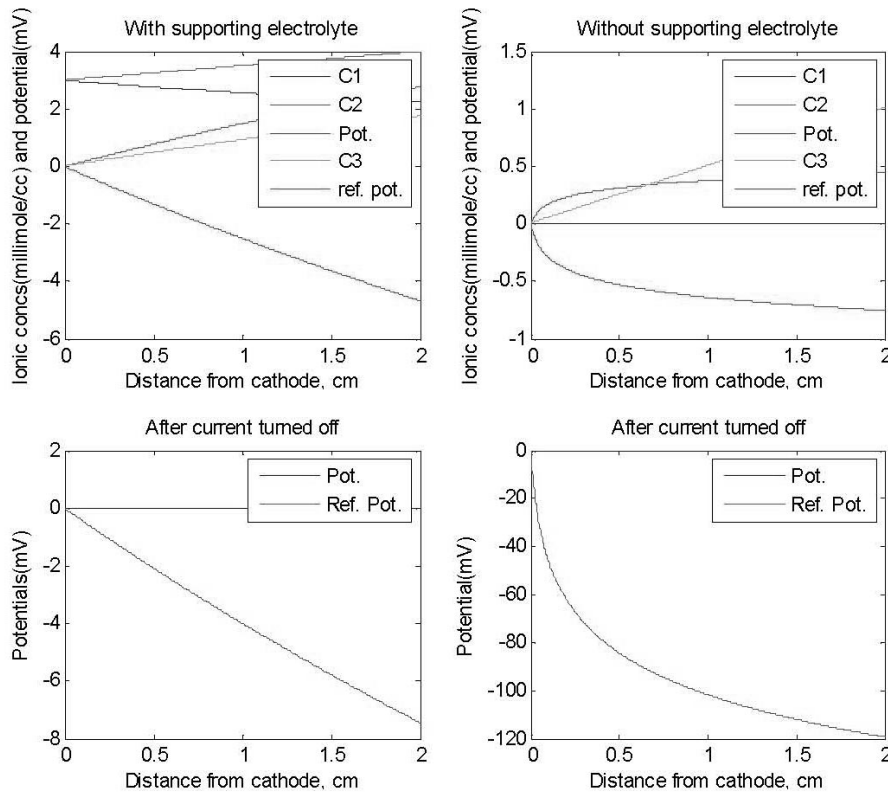


Fig. 1. Potential and concentration distributions for $D_1 = D_2 = D_3 = 10^{-5} \text{ cm}^2/\text{s}$, $u_1 = u_2 = u_3 = 100/F^2 \text{ abs}(z_i) \text{ mol cm}^2/(\text{J s})$ and $z_1 = 1, z_2 = -1, z_3 = 1$.

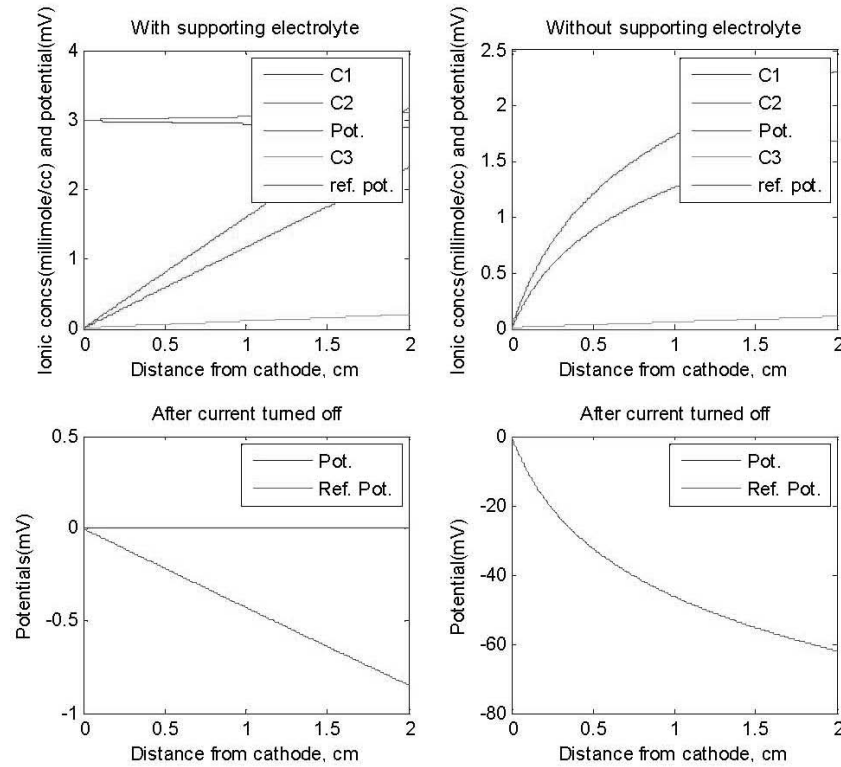


Fig. 2. Potential and concentration distributions for $D_1 = D_2 = D_3 = 10^{-4} \text{ cm}^2/\text{s}$ and $u_1 = u_2 = u_3 = 100/F^2 \text{ abs}(z_i) \text{ mol cm}^2/(\text{J s})$ and $z_1 = 1, z_2 = -1, z_3 = 1$.

supported electrolyte case but is almost halved for the unsupported case. Clearly diffusion is an important phenomenon in the movement of ions in this cell as shown in the second term on the right hand side of Equation (1). A higher diffusion component can be added to the electrolyte to obtain a more uniform thickness in an electroplating application.

Case 3: Effect of doubling mobilities of ions

Parameter values

$$\begin{aligned} D_1 = D_2 = D_3 &= 10^{-5}; \\ u_1 = u_2 = u_3 &= 200/F^2 \text{ abs}(z_i); \\ z_1 = 1, z_2 = -1, z_3 &= 1 \end{aligned}$$

Inference

For the next set of calculations, we revert the diffusivities to the values they had for Case 1 while doubling the mobilities of all the ions. In reality the diffusivities and the mobilities are related (by the Nernst–Einstein equation) and it is not correct to set them separately. However, this is one advantage of the program in that it allows the adjustment of any parameters at the whim of the student. It can be seen from Fig. 3 that the drop in ϕ across the cell is less than in Case 1, for both supported and unsupported electrolytes, as is expected due to increased mobilities.

A couple of example case studies are shown that

vary the parameters influencing the electrochemical phenomena in concentrated solutions.

Case 4

Parameters

$$\begin{aligned} D_1 = D_2 = D_3 &= 10^{-5} \text{ cm}^2/\text{s}, \\ \text{and } z_1 = 1, z_2 = -1, z_3 &= 1 \end{aligned}$$

Inference

For the first set of calculations, the parameters are the same as in Case 1. The result using the above scheme is as shown in Fig. 4. The upper figures are for the steady state (constant current) case. The figures on the left are with the supporting electrolyte. The profiles in the upper left of Fig. 4 are as expected and are almost the same as the dilute solution case. Anion concentrations rise as we move away from the cathode (resulting in a tendency to diffuse towards the cathode that exactly balances the migration towards the anode), while the inert cation concentration drops (for analogous reasons). The concentration gradient of the active cation results in a diffusion that assists its migration towards the cathode (where it is discharged).

Without the supporting electrolyte (upper right plot) the potential drop across the electrolyte is large (about 120 mV) compared with the case (7 mV) for the supporting electrolyte present. As in the dilute solution case, this clearly illustrates the

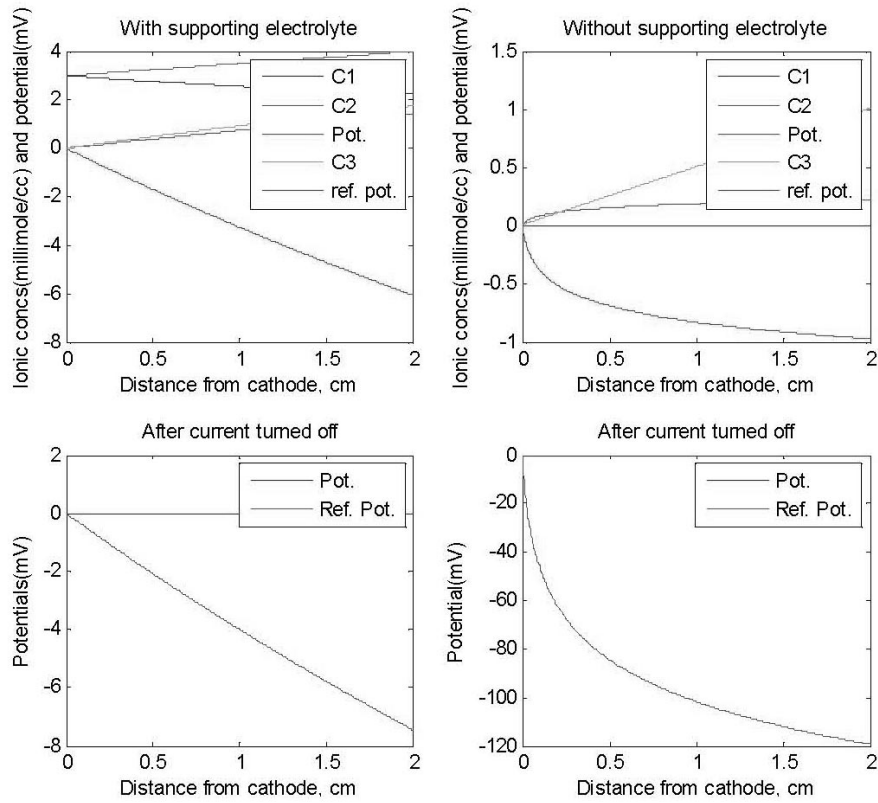


Fig. 3. Potential and concentration distributions for $D_1 = D_2 = D_3 = 10^{-5} \text{ cm}^2/\text{s}$ and $u_1 = u_2 = u_3 = 200/F^2 \text{ abs}(z_i) \text{ mol cm}^2/(\text{J s})$ and $z_1 = 1, z_2 = -1, z_3 = 1$

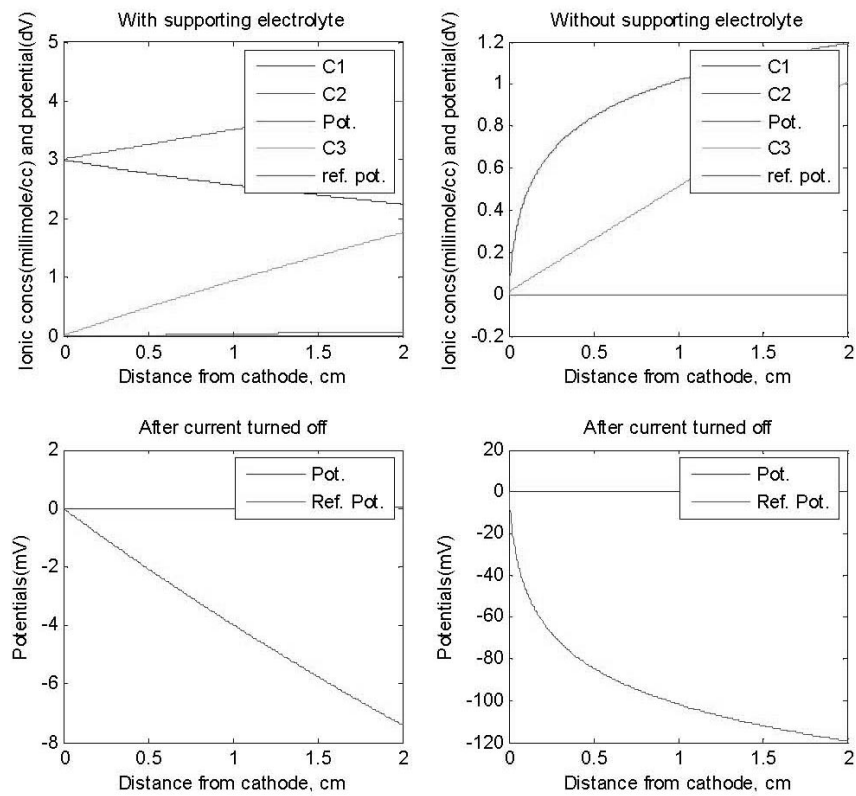


Fig. 4. Potential and concentration distributions for $D_1 = D_2 = D_3 = 10^{-5} \text{ cm}^2/\text{s}$, and $z_1 = 1, z_2 = -1, z_3 = 1$.

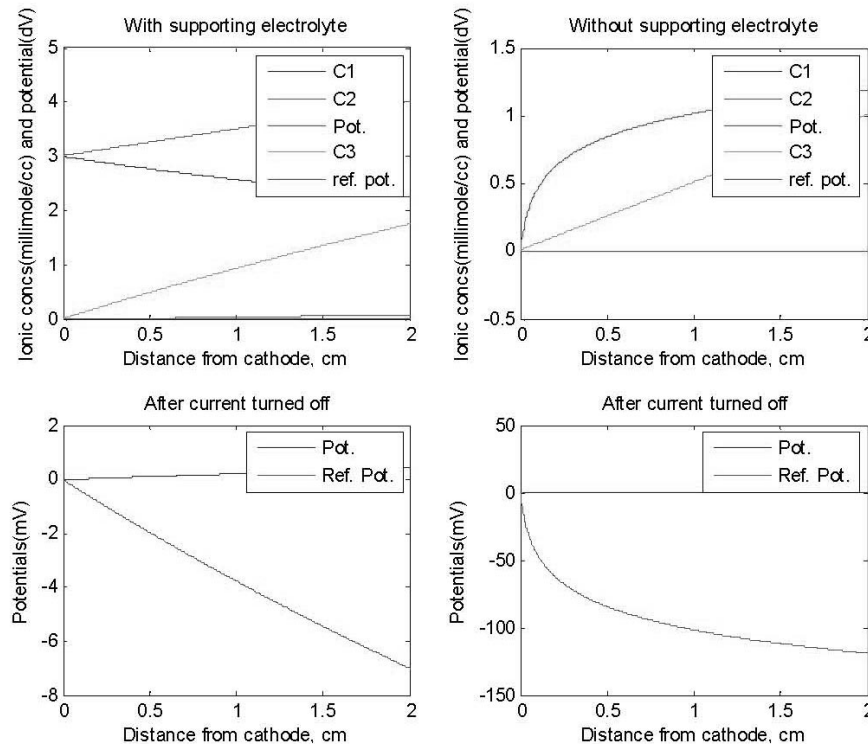


Fig. 5. Potential and concentration distributions for $D_1 = D_3 = 10^{-5} \text{ cm}^2/\text{s}$, $D_2 = 10^{-3} \text{ cm}^2/\text{s}$ and $z_1 = 1$, $z_2 = -1$, $z_3 = 1$.

advantage of a supporting electrolyte in reducing cell voltage.

Case 5

Parameters

$$D_1 = D_3 = 10^{-5} \text{ cm}^2/\text{s},$$

$$D_2 = 10^{-3} \text{ cm}^2/\text{s} \text{ and } z_1 = 1, z_2 = -1, z_3 = 1$$

Inference

For the next set of calculations, the diffusivities of all the ions are same as those of Case 4, except that the diffusivity of the anion is increased by two orders of magnitude. The potential is no longer uniform and zero after current interruption, but rather there is a diffusion potential which results in a net potential after current interruption as can be seen in Fig. 5.

CONCLUSIONS

The importance of assigning students case studies using the MATLAB program is to encourage them to carry out 'thought experiments' based on parameter values that can either be imaginary or extracted from tables or papers as part of class assignments and/or projects. Students can be assigned a number of case studies to see the effect of the various parameters on the concentra-

tion and potential distributions. Some other possible case studies that instructors can assign to students are:

- Drastically increasing the mobility of the electroactive cation.
- Drastically increasing the diffusivity of the electroactive cation.
- Changing the concentration of the supporting electrolyte.
- Changing the current through the cell to several different values to determine whether the cell resistance is Ohmic (potential difference across the cell proportional to current).
- Changing the separation between the electrodes to determine whether the potential drop across the cell changes proportionately.
- Determining when the potential in the electrolyte obeys Laplace's equation (in this case potential varies linearly with position) as with conduction in a metal.
- Effects of varying the concentrations, diffusivities and mobilities of each ion over a broad range.
- The current through the cell can be altered to determine whether or not the cell behaves like an Ohmic resistor with current proportional to applied voltage difference.
- The electrode separation can be varied to determine if, as in electronic conduction, the potential difference, at a specified current, is proportional to this difference.

In summary, the MATLAB program embodying calculations based on the dilute and concentrated solution theories can be a useful tool for students learning electrochemistry at the grade level or in early college level. The student/teacher can change

any of the important parameters governing the distribution of potential and concentration and he/she can recreate the figures of this paper or generate a host of other different results for dilute and concentrated electrolytes for any application.

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