

Supporting Information:

Reverse current pulse method to restore uniform concentration profiles in ion-selective membranes. Part II: Comparison of the efficiency of the different protocols

Justin M. Zook and Ernő Lindner

Department of Biomedical Engineering, The University of Memphis, Memphis, TN, 38152, USA

Abstract

This supporting information includes several sections that enhance the understanding of the material presented in the paper: (1) A novel analytic solution of the concentration profiles during alternating applied current and controlled voltage is derived to verify the FEM simulations. (2) The FEM simulation parameters are provided for alternating applied current and controlled voltage. (3) The equations for the calculation of the breakpoint during the reverse current step are presented both for the normal pulse and “triple pulse” methods. (4) Table S1 presents the values of t_{relax} needed to achieve 1% relative boundary concentration errors for each of the restoration methods. (5) Table S2 presents the number of pretreatment cycles needed to achieve less than 1% relative boundary concentration errors for each of the restoration methods

Analytic solution for alternating applied current and voltage

We have derived an analytic solution for a single cycle of applied current and controlled voltage. In order to derive this solution, we neglected the resistive voltage drop inside the membrane, as was done previously in the models for pulsed amperometry.^{21, 22} Note that with the assumption of zero resistance, the concentrations return immediately to their original values at the membrane-solution interfaces, requiring an infinite initial current. The first part of the solution is for a simple current step, for which we described the solution in a previous paper:⁶

$$C_{L,1}(x,t) = C_L^o + \frac{2kI_1}{nAF} \frac{d}{D_L} \sum_{m=0}^{\infty} (-1)^m \frac{1}{\pi^2 (m+1/2)^2} \sin \left[(2m+1) \frac{\pi x}{2d} \right] \left(1 - e^{-\frac{\pi^2 D_L t (m+1/2)^2}{d^2}} \right) \quad (\text{S1})$$

From Fourier series theory, we can get a solution for the voltage step with the initial value $C_{L,1}(x,t_1)$, where t_1 is the time of the initial current pulse:

$$C_{L,2}(x,t) = \sum_{l=1}^{\infty} b_l \sin\left[\frac{l\pi x}{d}\right] e^{\frac{-\pi^2 D_L (t-t_1) l^2}{d^2}} \quad (S2)$$

where

$$b_l = \frac{2}{d} \int_0^d C_{L,1}(x,t_1) \sin\left[\frac{l\pi x}{d}\right] dx \quad (S3)$$

Finally, after substituting Eq. S1 into Eq. S3 and integrating, we get the solution after the controlled voltage step ($t > t_1$):

$$C_{L,2}(x,t) = C_L^o + \frac{4kI_1}{nAF} \frac{d}{\pi^3 D_L} \sum_{l=1}^{\infty} \sum_{m=0}^{\infty} \left[\frac{(-1)^l l}{(m+1/2)^2 \left[(m+1/2)^2 - l^2 \right]} \sin\left[\frac{l\pi x}{d}\right] e^{\frac{-\pi^2 D_L (t-t_1) l^2}{d^2}} \left(1 - e^{\frac{-\pi^2 D_L t_1 (m+1/2)^2}{d^2}} \right) \right] \quad (S4)$$

It is possible to derive the solutions for additional cycles of current and voltage pulses, but each cycle adds an additional two nested summations, so that the computational time increases exponentially and is impractical for more than several cycles. Therefore, we have used the analytic solution only to verify the results of the finite element method for a single current/voltage cycle.

FEM simulation parameters:

In order to eliminate discontinuities in the boundary concentrations when neglecting r_{ohm} , instead of specifying a step in concentration at the boundary, Eq. 3 or 6 was used with a negligible $r_{ohm} = 5.4 \times 10^{-4}$ ($R_{ohm}=0.2 \Omega\text{cm}^2$). Parameters used in the equations, unless otherwise specified, were $k=1$, $n=1$, $d=0.01$ cm, $D=2 \times 10^{-8}$ cm²/s, $C^o=10$ mM, and $I_1=600$ nA/cm². Time steps were controlled automatically by Comsol Multiphysics, although to minimize errors when changing from applied current to controlled voltage, time steps were forced to occur every $R_{ohm} \times t_1 \times 10^{-6}$ seconds for $R_{ohm} \times t_1 \times 10^{-6} < t_1 < R_{ohm} \times t_1 \times 10^{-4}$. In addition, time steps were forced to occur at least every $0.005 \times t_1$ seconds during the applied current step. The 96 spatial elements were chosen to be more closely spaced near the boundaries of the membrane, with a spacing of 5×10^{-5} cm at the boundaries and a maximum spacing of 10^{-3} cm in the center. With these parameters, concentration change errors were less than 0.1%.

Reverse current breakpoint equations:

For relatively short times (less than ~60 min for typical membranes), the maximum time ($\tau_2 - t_1$) that a given reverse current can be applied was derived previously²⁴ as:

$$0 = C_L^o + \frac{kI_1}{nAF} \frac{2}{\sqrt{D_L \pi}} \tau_2^{1/2} + \frac{k(I_2 - I_1)}{nAF} \frac{2}{\sqrt{D_L \pi}} (\tau_2 - t_1)^{1/2} \quad (\text{S5a and b})$$
$$0 = \tau_1^{1/2} + \tau_2^{1/2} + \left(\frac{I_2}{I_1} - 1 \right) (\tau_2 - t_1)^{1/2}$$

Eq. S5b is expressed in terms of the ordinary chronopotentiometric breakpoint τ_1 for current I_1 , which is easily obtained experimentally by applying current I_1 until a breakpoint is observed.^{7,9} This equation was solved using Matlab for τ_2 , which is the optimal t_2 for $t_2 \geq \tau_2$. Next, to find the optimal combination of I_2 and t_2 , I_2 was varied and t_2 was calculated from Eq. S5.

From our simulations for short times ($t_1 \leq 10$ s), we found two limiting cases:

(1) For breakpoint measurements, where the initial current is applied until the breakpoint time (i.e., $t_1 = \tau_1$), the optimal program is with

$$f_{\text{charge}} = 1 - (a \times t_{\text{relax}} + b)^{-1} \text{ if } t_{\text{relax}} \leq 10 \quad (\text{S6})$$

where $a=14.9$ and $b=17.8$.

(2) For measurements when the initial current time is much less than the breakpoint ($t_1 < 60 \times \tau_1$ for $<0.5\%$ error in optimal f_{charge}), the optimal program is for Eq. S6 with $a=21.7$ and $b=26.0$.

When $\tau_1 < t_1 < 60 \times \tau_1$, the optimal value for f_{charge} will be between these two limiting cases. From the calculated value for f_{charge} , one can calculate I_2 and t_2 from Eqs. 7 and S6 for any given I_1 and t_1 . The values for a and b given above are optimal for minimizing the maximum error in the boundary concentrations at the end of each initial applied current pulse over 100 cycles.

In some cases, the experimenter may not want to determine first the breakpoint τ_1 or numerically solve Eq. S5. To simplify the calculations and experiments, one can solve Eq. S5b with $t_1 = \tau_1$ and $f_{\text{charge}} = 1$ to get a conservative estimate of I_2 as $I_2 = -2.383 \times I_1$, for use instead of Eq. S6.

For the triple pulse method, the optimal f_{charge} is given by Eq. S6 with $a = 5.988$ and $b = 9.992$ for $t_1 = \tau_1$, and $a = 7.148$ and $b = 12.391$ for $t_1 \ll \tau_1$. The breakpoint during the reverse current step can be calculated from Eq. S7:

$$0 = C_L^o + \frac{kI_1}{nAF} \frac{2}{\sqrt{D_L \pi}} \tau_2^{1/2} - \frac{kI_1}{nAF} \frac{2}{\sqrt{D_L \pi}} (\tau_2 - t_1)^{1/2} - \frac{kI_2}{nAF} \frac{2}{\sqrt{D_L \pi}} (\tau_2 - 2t_1)^{1/2} \quad (\text{S7a and b})$$

$$0 = \tau_1^{1/2} + \tau_2^{1/2} - (\tau_2 - t_1)^{1/2} - \left(\frac{I_2}{I_1} \right) (\tau_2 - 2t_1)^{1/2}$$

Again, to simplify the calculations and experiments, one can solve Eq. S7b with $t_1 = \tau_1$ and $f_{\text{charge}} = 1$ to get a conservative estimate of I_2 as $I_2 = -1.828 \times I_1$, for use instead of Eq. S7.

Table S1: Value of t_{relax} required to achieve a maximum $\pm 1\%$ error in boundary concentrations for 100 cycles

	Regular Pulse	Triple Pulse
Zero Current	2500	2500
Zero Current Differential Voltage	14	22
Reverse Current (optimal f_{charge})	6.7	12
Reverse Current Differential Voltage (optimal f_{charge})	3.3	6.0
Reverse Current ($f_{\text{charge}}=1$)	11	21
Reverse Current Differential Voltage ($f_{\text{charge}}=1$)	3.5	6.4
Controlled voltage ($r_{\text{ohm}} < 0.2$)	14	26

Table S2: Number of required pretreatment cycles necessary to make repeated pulsed potentiometric experiments with less than 1% error. Applied pulse width $t_1 = 1$ s

	t_{relax}			
	1	4	10	40
Reverse current ($f_{\text{charge}}=1$)	22	3	0	0
Reverse current with ΔV as analytical signal ($f_{\text{charge}}=1$)	2	0	0	0
Controlled Voltage ($r_{\text{ohm}}=5.4 \times 10^{-4}$)	51	9	1	0
Controlled Voltage ($r_{\text{ohm}}=0.054$)	53	10	1	0
Controlled Voltage ($r_{\text{ohm}}=0.54$)	68	18	3	0
Controlled Voltage ($r_{\text{ohm}}=5.4$)	96	78	42	3