Supporting Information for:

Determining nanocapillary geometry from electrochemical impedance spectroscopy using a variable topology network circuit model.

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Developing and explaining the Variable Topology Model

Developing the differential equation

To begin we use a network of resistors and capacitors to model a nanopore or nanocapillary.



Next transform the circuit elements into discrete elements.

Let

$$\frac{\mathrm{dR}}{\mathrm{dx}} = R' = \frac{1}{\pi r^2(x) \kappa_c}$$

And

$$\frac{\mathrm{d}C}{\mathrm{d}x} = C' = 2\,\pi\,r(x)\,\tilde{C}_{0}$$

Where \tilde{C}_c is the capacitance per unit area.

Next, let each element in the network be a discrete element and transform the transmission line into a differential equation. Consider adding an infinitesimal amount of impedance ΔZ to the total impedance that is $Z + \Delta Z$. Let this be one side of the differential equation. On the other side also add Z to ΔZ , however, partition ΔZ into resistive and capacitive elements and add the capacitive element in parallel to the total impedance

$$Z + \Delta Z = \Delta x R' + \frac{1}{\frac{1}{z} + \Delta x i\omega C'} = \Delta x R' + \frac{Z}{Z \Delta x i\omega C' + 1}$$

Next expand the right side of the differential equation into a Taylor series in terms of Δx .

$$Z(x) + \Delta Z = Z(x) - i \Delta x \omega Z(x)^2 C'(x) - \Delta x^2 \omega^2 Z(x)^3 C'(x)^2 + O(\Delta x^3)$$

 $Z(x) + \Delta Z = Z(x) - i \Delta x \omega Z(x)^2 C'(x) + O(\Delta x^2)$

$$Z + \Delta Z = \Delta x R' + Z \left(1 - Z \Delta x i \omega C' + \left(Z \Delta x i \omega C' \right)^2 + \dots \right)$$

Subtract off the total impedance from both sides

$$\Delta Z = \Delta x R' + Z \left(-Z \Delta x i \omega C' + \left(Z \Delta x i \omega C' \right)^2 - \dots \right)$$

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Dividing by Δx and taking the limit that Δx going to zero we have

 $Z' = R' - Z^2 \, i\omega C'$

The higher ordered terms in the differential equation will have at least one Δx , thus these terms are zero when we take the limit as Δx goes to zero.

Rearranging

$$\mathbf{Z}' + \mathbf{Z}^2 i\omega \mathbf{C}' - \mathbf{R}' = 0 \tag{S 1}$$

Note that Z, C, and R are functions of x where x is the coordinate along the length of the nanopore. Notice this is a first order differential equation.

We use a zero impedance boundary condition, that is, a nanopore of zero length will have zero impedance: Z(0) = 0 along with the above definitions of C' and R'.

Constant Radius

For $r(x)=r_1$, equation (S 1) gives a solution, Z, as a function of x. Where again, x is the coordinate along the length of the nanopore. For a nanopore of length L, one would think to simply set x equal to L. However, this will produce an asymmetric solution. For the general case, to symmetrize this function one solves equation (S 1) with r(x) from 0 to L/2. Then adds to this the mirror image of r(x), shifted back to the origin. The linear example of this will be demonstrated below. This, however, is simple for a constant radius function. Since, the mirror of r_1 shifted back to the origin, is a again, r_1 . For a constant radius function solve equation (S 1) with $r(x) = r_1$, then let x = L/2, half of the nanopore. Then multiply the total impedance by 2, this is equivalent to solving the differential equation twice, with $r(x) = r_1$ and $r(x) = r_1$, then adding the solutions. The solution below is for a constant radius cylinder.

$$Z_{r(x)=r_1}(\omega) = \frac{L \tanh\left(L\sqrt{\frac{i\,\omega\,\tilde{C}_c}{2\,r_1\,\kappa_c}}\right)}{\left(\pi\,r_1^2\,\kappa_c\right)\left(L\sqrt{\frac{i\,\omega\,\tilde{C}_c}{2\,r_1\,\kappa_c}}\right)}$$

This can be converted into lifetimes

$$Z_{r(x)=r_1}(\omega) = \frac{Z_{\text{cyl}} \tanh\left(\sqrt{i \,\tau_{\text{cyl}} \,\omega/4}\right)}{\sqrt{i \,\tau_{\text{cyl}} \,\omega/4}}$$
(S 2)

Where

$$R_{\rm cyl} = \frac{L}{\pi r_1^2 \kappa_l}$$

And

$$\tau_{\rm cyl} = \frac{2 \, L^2 \, \tilde{C}_c}{r_1 \, \kappa_c}$$

Lastly, lets look at the limits of the function. For the constant radius cylindrical model, in either the DC limit (i.e. $\omega=0$) or that of no surface charge density the model predicts that the nanopore will act as a pure electrolytic resistor.

$$\operatorname{Limit}_{\omega \to 0} Z_{r(x)=r_1}(\omega) = Z_{r(x)=r_1}(\omega) = \operatorname{Limit}_{\tilde{C}_c \to 0} = \frac{L}{\pi r_1^2 \kappa_c}$$

In the limit of high frequency, the impedance of a capacitor is zero, and the current path will follow that path of least resistance, that of the capacitor, and thus give and overall impedance of zero

$$\underset{\omega \to \infty}{\text{Limit } Z_{r(x)=r_1}(\omega) = 0}$$

Lozenge

Next we solve equation (S 1) for a linearly varying r(x). To begin with we solve half of the hour glass from x=0 to x=L/2, with r(x) being

$$r(x) = 2x(r_1 - r_0)/L + r_0$$
(S 3)

To symmetrize the impedance element solution, we interchange the capillary radii in equation (S 3):

$$r(L/2 - x) = r_0 - 2\left(x - \frac{L}{2}\right)(r_1 - r_0)/L$$
(S 4)

The solution of Equation (S 1) with Equation (S 3), integrating from x=0 to x=L/2 is

$$Z_{r(x)}(\omega) = \frac{\tau_0 R_{\text{loz}} \left(I_1(\xi_1) K_1(\xi_0) - I_1(\xi_0) K_1(\xi_1) \right)}{\xi_1 \left(\tau_1 - \tau_0 \right) \left(I_2(\xi_1) K_1(\xi_0) + I_1(\xi_0) K_2(\xi_1) \right)}.$$
(S 5)

The solution of equation (S 1) with equation (S 4) integrating from x = 0 to L/2,

$$Z_{r(L/2-x)}(\omega) = \frac{\tau_1 R_{\text{loz}} \left(I_1(\xi_1) K_1(\xi_0) - I_1(\xi_0) K_1(\xi_1) \right)}{(\tau_1 - \tau_0) \left(\xi_0 I_2(\xi_0) K_1(\xi_1) + \xi_0 I_1(\xi_1) K_2(\xi_0) \right)},$$
(S 6)

is added to equation (S 5) to give the symmetric lozenge impedance element:

$$\frac{Z_{\text{loz}}(\omega) = \frac{(R_{\text{loz}}(I_1(\xi_1) K_1(\xi_0) - I_1(\xi_0) K_1(\xi_1)))}{\tau_1 - \tau_0} \left(\frac{\tau_0}{\xi_1 (I_2(\xi_1) K_1(\xi_0) + I_1(\xi_0) K_2(\xi_1))} + \frac{\tau_1}{\xi_0 (I_2(\xi_0) K_1(\xi_1) + I_1(\xi_1) K_2(\xi_0))}\right)$$
(S 7)

where

$$\xi_0 = \sqrt{4\,i\,\tau_0\,\omega} \tag{S 8}$$

$$\xi_1 = \sqrt{4\,i\,\tau_1\,\omega} \tag{S 9}$$

$$R_{\rm loz} = \frac{L}{\kappa_c \,\pi \, r_0 \, r_1} \tag{S 10}$$

$$\tau_0 = \frac{L^2 r_0 \,\tilde{C}_c}{2 \, (r_1 - r_0)^2 \,\kappa_c} \tag{S 11}$$

$$\tau_1 = \frac{L^2 r_1 \tilde{C}_c}{2 (r_1 - r_0)^2 \kappa_c}$$
(S 12)

 $\operatorname{Limit}_{\omega \to \infty} Z_{\operatorname{loz}}(\omega) = \operatorname{Limit}_{\tilde{C}_c \to 0} Z_{\operatorname{loz}}(\omega) = \frac{L}{\kappa_c \, \pi \, r_1 \, r_0}$

where

$$\frac{L}{\kappa_c \pi r_1 r_0} = 2 \int_0^{\frac{L}{2}} \frac{1}{\kappa_c \pi r^2(x)} \, dx$$

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Each half of the nanopore will give the same impedance

And lastly, as with the constant radius nanopore

$$\begin{split} \underset{\omega \to \infty}{\text{Limit}} & Z_{\text{loz}}(\omega) = 0 \\ \underset{\omega \to \infty}{\text{Limit}} & \operatorname{Arg}(Z_{\text{loz}}(\omega)) = -\pi/4 \\ \underset{\omega \to 0}{\text{Limit}} & \operatorname{Arg}(Z_{\text{loz}}(\omega)) = 0 \end{split}$$

Cone

Equation (S 7) can be converted to a truncated cone geometry by substituting 2L for L in equations (S10-S12) and dividing equation (S 12) by 2. This produces a Z_{VTW} function that properly describes the impedance of a cone. That is, whether an r(x) is evaluated or the mirror image of r(x), translated back to the origin, the model will produce the same impedance, as would an experiment.

Quadratic Radius Dependence

Next we solve equation (S 1) for a quadratically varying r(x)

$$r(x) = r_1 + \frac{4r_0 x^2}{L^2}$$
(S 13)

To symmetrize the impedance element solution, we interchange the capillary radii in equation (S 13):

$$r(L/2 - x) = r_0 + \frac{4r_1 x^2}{L^2}$$
(S 14)

The solution of Equation (S 1) with Equation (S 13) and integrating from x=0 to x=L/2 is

$$Z_{\text{quad}/2}(\omega) = \frac{(3-2\gamma)^2 (2\gamma+3) \kappa \rho^3 \left(P_{\gamma_+}^2(0) \left(\rho Q_{\gamma_-}^2(i\rho) + i Q_{\gamma_+}^2(i\rho)\right) - Q_{\gamma_+}^2(0) \left(\rho P_{\gamma_-}^2(i\rho) + i P_{\gamma_+}^2(i\rho)\right)\right)}{4 \pi L^3 \left(\rho^2 + 1\right)^2 \omega^2 \tilde{C}^2 \left(P_{\gamma_+}^2(0) Q_{\gamma_-}^2(i\rho) - Q_{\gamma_+}^2(0) P_{\gamma_-}^2(i\rho)\right)}$$
(S 15)

where $P_n^m(x)$ is the associated Legendre polynomial and $Q_n^m(x)$ associated Legendre function of the second kind.

$$\rho = \sqrt{r_0/r_1} \tag{S16}$$

$$\gamma_{\pm} = \sqrt{\frac{9}{4} + \frac{iL^2 \,\omega \,\tilde{C}}{2 \, r_0 \,\kappa_c}} \,\pm \frac{1}{2} \tag{S 17}$$

$$\gamma = \frac{\gamma_+ + \gamma_-}{2} \tag{S 18}$$

Symmetrization is accomplished by the same process as in the linear case: r_0 and r_1 are interchanged in equation (S 15) and the result added to equation (S 15).

Active Set (AS) Fits

Below are the active set fits to the experimental data.



- Global model of the Instrument Response
- Fits to Local Parameters background component of the data



Background Resistance





	Estimate	Standard Error	t Statistic	P-Value
C _{Obk}	9.00	0.4	24	0.00014
C _{1bk}	46.0	0.6	72	5.9×10 ⁻⁶

Background Response Time



Direct fit of Global background functions to Background data

The background circuit element was globally modeled as a simple electrolyte solution resistor ($R_{bk} = R_{cell}/\kappa_b$) with a powerlaw conductivity-dependent capacitance constant ($C_{bk} = C_{Ibk} \kappa_b^{3/2} + C_{0bk}$). The time scale of the instrument response was nonmonotonic with conductivity. The 3/2 power law in the capacitance results in a combination power law $\left(\tau_{bk} = R_{cell} \left(C_{Ibk} \sqrt{\kappa_b} + \frac{C_{0bk}}{\kappa_b}\right)\right)$ for the time response. Since the response of the electrochemical cell and electrodes is faster than the highest frequency Fourier component measured by the EIS instrumentation, the details of the circuit response are in the high frequency region of the spectrum that is not measured. There are likely two contributions to the instrument response time that have different dependencies on the conductivity. The same power law functions were observed to fit the instrument response of both the background measurement and the NCAM measurement.



Instrument Response changes with and without membrane present

The addition of the NCAM to the cell did not change the resistive contribution to the instrument response, $R_{cell} = (412\pm3 \text{ to } 410\pm2 \text{ m}^{-1})$, or the conductivity-dependent part of the capacitance, $C_{1bk} = (8.0 \text{ to } 7.8 \text{ pF } (\text{S/m})^{-3/2})$. With the membrane present, the conductivity-independent contribution to the capacitance increased from, $C_{0bk} = 16\text{pF}$ to 58pF.

Calibration of bulk solution conductivity

[NaCl]	$[\mathrm{Na}_{1+x}H_{2-x}\mathrm{PO}_4]$	κ from CRC	AS Blank Resistance
100 mM	10 mM	1.06	376.5
50 mM	10 mM	0.593	667.
20 mM	10 mM	0.305	1205
10 mM	10 mM	0.207	1728
0 mM	10 mM	0.109	3023

The cell constant was determined by fitting the observed blank cell resistivity values to conductivity values interpolated from the CRC using:



The corrected conductivity values fit to a simple $R \propto \kappa^{-1}$ law

	Estimate	Standard Error	t Statistic	P-Value	
Rcell	411.6	1.5	267	1.18×10^{-9}	

Calibrated bulk conductivity values:

Observed	Predicted	Standard Error	95% Confidence Interval
1.093	1.093	0.004	$\{1.082, 1.104\}$
0.627	0.617	0.002	$\{0.611, 0.624\}$
0.335	0.342	0.001	$\{0.338, 0.345\}$
0.237	0.238	0.001	$\{0.236, 0.241\}$
0.139	0.136	0.001	$\{0.135, 0.138\}$

Only RC Model

Here the simplest model and fit is shown. The capillary is modeled as a resistor with the membrane as a capacitor. As can be seen, the fits are poor with a reduced chi squared of about 4500.



Only Cylindrical Model with a capacitance membrane.

Next, the experimental data is fit with the capillary being modeled with Equation (S 2). This reduces the chi squared by almost 9 times. Below are the fits to the experimental data using Equation (S 2). Notice, however, that this model does not capture the degree of suppression of the peak in the Nyquist plot.



• *Z*_{loz} Model with a capacitance membrane.

Here the experimental data is fit with the capillary being modeled with Equation 7. This reduces the chi squared by over 8 times from Equation 2. Below are the fits to the experimental data using Equation 7 instead of Equation 2. Notice now these fits capture all the main features of the data.



Local Fit Parameters for Instrument Response and Membrane Surface

Table 1: Local fit parameters for instrument and membrane surface response. Note that the large error values for C_{bk} reflect the fact that the instrument response is faster than the highest frequency component measured in the EIS experiment.

NaCl	Buffer	$\kappa_{ m b}$	$C_{\rm mem}$	$R_{\rm ms}$	$C_{\rm ms}$	$R_{\rm bk}$	$C_{\rm bk}$
mM	mM	S/m	pF	Ω	mF	Ω	pF
100	10	$1.093 {\pm} 0.004$	$139{\pm}17$	26 ± 1	$0.068 {\pm} 0.008$	$360{\pm}7$	62 ± 266
50	10	$0.617 {\pm} 0.002$	$139{\pm}17$	45 ± 2	$0.040 {\pm} 0.004$	654 ± 10	$32{\pm}179$
20	10	$0.342 {\pm} 0.001$	$139{\pm}17$	68 ± 3	$0.029 {\pm} 0.003$	1158 ± 13	$19{\pm}133$
10	10	$0.238{\pm}0.001$	$139{\pm}17$	79 ± 3	$0.028 {\pm} 0.003$	$1716{\pm}14$	14 ± 96
0	10	$0.136{\pm}0.001$	$139{\pm}17$	76 ± 4	$0.038 {\pm} 0.005$	$3023{\pm}12$	11 ± 48

Global Fits

The global model fits were of nearly the same quality as the local fits. The data and fit lines appear below.



Experimental Setup

Below is a schematic of the experiment.

