Modeling inadequacy in supercapacitors

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1 Introduction

2 Methodology

2.1 Upscaling

Our 2D computational domain consists of 5 contacting regions: two current collectors sandwiching a porous anode, a separator, and a porous cathode. The porous electrodes contain both, a solid matrix and a liquid electrolyte that fully occupies the voids within the solid matrix. The separator is considered to be a perfect electronic insulator, thus it only allows liquid ions to pass through.

For the simplest scenario of an ideally polarizable electrode, i.e. one where no Faradaic processes occur, a current transferred from the solid matrix to the solution phase goes towards only charging the double-layer at the electrode/electrolyte interface. This implies that:

$$\nabla \cdot \mathbf{i_l} = \frac{\partial aq}{\partial t} \tag{1}$$

where $\mathbf{i}_l$ is the current density in the liquid electrolyte phase, a is the interfacial area per unit volume, and q is the surface charge density of the double layer. Since $q = C\Delta\Phi = C(\Phi_l - \Phi_s) = C\eta$, where η is the surface overpotential, C is the double-layer capacitance, and Φ_l and Φ_s are the liquid and solid potentials respectively, Eq. (1) becomes:

$$\nabla \cdot \mathbf{i_l} = aC\frac{\partial \eta}{\partial t} \tag{2}$$

Due to the *overall* (considering that the length scale of the charged double layer $\ll$ the

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length scale of the electrodes) electroneutrality of the porous electrodes, we also have as a consequence of conservation of charge that:

$$\nabla \cdot \mathbf{i_s} + \nabla \cdot \mathbf{i_l} = 0 \tag{3}$$

where $\mathbf{i}_s$ is the current density in the solid matrix phase.

In the solid phase, the current density is the result of migration of electrons, which is goverened by Ohm's law according to:

$$\mathbf{i_s} = -\sigma \nabla \Phi_s \tag{4}$$

where σ is the solid matrix electronic conductivitiy.

Similarly in the liquid phase, assuming that there are no concentration gradients or convection due to bulk fluid motion, the current density is solely a result of ion migration:

$$\mathbf{i_l} = -\kappa \nabla \Phi_l \tag{5}$$

where κ is the liquid ionic conductivity.

We are going to assume that (i) the current collectors are sufficiently thin, such that they could essentially be considered as homogeneous in the x-direction, (ii) property variations in the y-direction are negligible, such that our 2D domain could be reduced to a quasi-1D domain along x, and (iii) material properties are constants, independent of space and time.

Using the above set of equations and assumptions, the governing equations of our "high-fidelity" supercapacitor system reduce to:

$$aC\frac{\partial \eta}{\partial t} = -\kappa \frac{\partial^2 \Phi_l}{\partial x^2} \tag{6}$$

$$aC\frac{\partial \eta}{\partial t} = \sigma \frac{\partial^2 \Phi_s}{\partial x^2} \tag{7}$$

$$\kappa \frac{\partial^2 \Phi_l}{\partial x^2} = 0 \tag{8}$$

Note that Eqs. (6)–(7) hold in the interior of the porous electrodes, while Eq. (8) holds in

the interior of the separator. Eq. (8) is a result of the fact that the current density in the separator is carried entirely by the liquid current density, $\mathbf{i_l}$ (in other words, $\mathbf{i_s} = 0$).

Let the anode current collector be at $x = 0$, the negative electrode be at $0 < x < L$, the separator be at $L < x < L + s$, the positive electrode be at $L + s < x < 2L + s$, and the cathode current collector be at $x = 2L + s$. Insert an illustrative schematic later...

The associated boundary and interface conditions for our domain are given by:

$$
\begin{cases}
\mathbf{i_l} = -\kappa \partial \Phi_l / \partial x = 0 \; ; \; \Phi_s = 0 & x = 0 \\[4pt]
\mathbf{i_s} = -\sigma \partial \Phi_s / \partial x = 0 & x = L \\[4pt]
\mathbf{i_s} = -\sigma \partial \Phi_s / \partial x = 0 & x = L + s \\[4pt]
\mathbf{i_l} = -\kappa \partial \Phi_l / \partial x = 0 \; ; \; \mathbf{i_s} = -\sigma \partial \Phi_s / \partial x = -I & x = 2L + s \\[4pt]
\left. -\kappa \frac{\partial \Phi_l}{\partial x} \right|_{x=L} = \left. -\kappa \frac{\partial \Phi_l}{\partial x} \right|_{x=L+s} &
\end{cases}
\tag{9}
$$

I is the total current density at the current collector during charging or discharging. It is assumed that a constant current is applied at one of the current collectors during charging/discharging, while the other current collector is grounded (a different boundary condition could be chosen, but for the current analysis, we will adopt this one). There are no fluxes in or out of the computational domain, except for the input/output flux at the current collectors. Note that the last interface condition is actually a direct result of Eq. (8), so including it as an interface condition is in some sense redundant.

The supercapacitor is considered to be initially fully discharged, thus:

$$\Phi_s(x; t = 0) = \Phi_l(x; t = 0) = 0 \tag{10}$$

An anlytical solution for the spatio-temproal evolution of η could be obtained through applying a change of variables, which transforms Eqs. (6)–(7) into the familiar diffusion equation. The variable transformation technique will be outlined in what follows.

Let $\eta' = (\mathbf{i_s}/\sigma) - (\mathbf{i_l}/\kappa)$. We first notice that:

$$
\begin{aligned}
\eta' &= -\frac{\partial \Phi_s}{\partial x} + \frac{\partial \Phi_l}{\partial x} \\[4pt]
&= \frac{\partial (\Phi_l - \Phi_s)}{\partial x} \\[4pt]
&= \frac{\partial \eta}{\partial x}
\end{aligned}
\tag{11}
$$

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We also have that:

$$aC\frac{\partial\eta}{\partial t} = \frac{\partial \mathbf{i_l}}{\partial x} = -\frac{\partial \mathbf{i_s}}{\partial x}$$

Thus:

$$\frac{\partial}{\partial x}\left(\frac{\mathbf{i_s}}{\sigma} - \frac{\mathbf{i_l}}{\kappa}\right) = -\left(\frac{aC}{\sigma} + \frac{aC}{\kappa}\right)\frac{\partial\eta}{\partial t}$$

$$\implies \frac{\partial\eta}{\partial t} = \left[\frac{\kappa\sigma}{aC(\kappa+\sigma)}\right]\frac{\partial\eta'}{\partial x}$$

$$= -\left[\frac{\kappa\sigma}{aC(\kappa+\sigma)}\right]\frac{\partial^2\eta}{\partial x^2}$$

$$= -\alpha\frac{\partial^2\eta}{\partial x^2} \tag{12}$$

where $\alpha = \kappa\sigma/[aC(\kappa+\sigma)]$. Consequently, an analytic solution for $\eta(x,t)$ and $\eta'(x,t)$ can be obtained using either Fourier series or Laplace transform. By the conservation of charge, we have that $I = \mathbf{i_s} + \mathbf{i_l} \implies \mathbf{i_l} = I - \mathbf{i_s}$. Therefore, to obtain the current density in the solid or liquid phase:

$$\eta' = \frac{\mathbf{i_s}}{\sigma} - \frac{\mathbf{i_l}}{\kappa} = \frac{\mathbf{i_s}}{\sigma} - \frac{I}{\kappa} + \frac{\mathbf{i_s}}{\kappa}$$

$$= \frac{(\kappa+\sigma)}{\sigma\kappa}\mathbf{i_s} - \frac{I}{\kappa}$$

$$\implies \mathbf{i_s} = \left(\eta' + \frac{I}{\kappa}\right)\frac{\sigma\kappa}{\kappa+\sigma} \tag{13}$$

Using Eqs. (4)&(13), we can obtain the potential in the soild matrix:

$$\Phi_s = -\int \frac{\mathbf{i_s}}{\sigma}\, dx \quad + \text{cst} \tag{14}$$

In our system's domain, the constant in Eq. (14) is zero for the left electrode (since the left current collector is grounded), while the constant is inferred indirectly from the the liquid potential, Φ_l, and the overpotential, η, for the right electrode.

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In order to obtain the upscaled (averaged) equations, we are simply going to spatially average the governing Eqs. (6)–(8) over the entire domain length in the x-direction. Averaging Eq. (6) over $0 \leq x \leq L$ and $L + s \leq x \leq 2L + s$, we obtain:

$$aC\frac{\partial \overline{\eta^L}}{\partial t} = -\frac{\kappa}{L}\left(\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L} - \frac{\partial \Phi_l}{\partial x}\bigg|_{x=0}\right)$$

$$aC\frac{\partial \overline{\eta^R}}{\partial t} = -\frac{\kappa}{L}\left(\frac{\partial \Phi_l}{\partial x}\bigg|_{x=2L+s} - \frac{\partial \Phi_l}{\partial x}\bigg|_{x=L+s}\right) \tag{15}$$

where $\overline{\eta} = \overline{\Phi}_l - \overline{\Phi}_s$, and the superscripts L and R refer to the left and right electrodes respectively. From the boundary conditions in (9), we have that $\mathbf{i}_l(x = 0) = \mathbf{i}_l(x = 2L+s) = 0$. Thus, the above averaged equations reduce to:

$$aC\frac{\partial \overline{\eta^L}}{\partial t} = -\frac{\kappa}{L}\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L}$$

$$aC\frac{\partial \overline{\eta^R}}{\partial t} = \frac{\kappa}{L}\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L+s} \tag{16}$$

Similarly, averaging Eq. (7) and using the boundary conditions, we obtain:

$$aC\frac{\partial \overline{\eta^L}}{\partial t} = -\frac{\sigma}{L}\frac{\partial \Phi_s}{\partial x}\bigg|_{x=0}$$

$$aC\frac{\partial \overline{\eta^R}}{\partial t} = \frac{\sigma}{L}\frac{\partial \Phi_s}{\partial x}\bigg|_{x=2L+s} \tag{17}$$

Averaging Eq. (8) along $L \leq x \leq L + s$, we simply get back the electode/separator interface condition:

$$\kappa\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L} = \kappa\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L+s} \tag{18}$$

From the averaged Eqs. (16)–(18) above and the boundary conditions in (9), we get that:

$$\frac{\partial \overline{\eta^L}}{\partial t} = -\frac{\partial \overline{\eta^R}}{\partial t} = \frac{-I}{aCL} \tag{19}$$

$$\kappa\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L} = \kappa\frac{\partial \Phi_l}{\partial x}\bigg|_{x=L+s} = I \tag{20}$$

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$$\sigma \frac{\partial \Phi_s}{\partial x}\bigg|_{x=0} = I \tag{21}$$

Our goal is to compute the voltage or potential drop, $\Delta\Phi_{\text{cell}} = \Phi_c^R - \Phi_c^L$ across the entire electrochemical cell, where Φ_c is the potential of the current collector and the superscripts refer to the left and right collectors as before. Note that $\Phi_c = \overline{\Phi}_c$, due to our earlier assumption of spatially homogeneous current collectors. The discrepancy between the computed cell voltage using the upscaled model and the computed cell voltage using the high-fidelity equations, provides us with a measure to quantify the inadequacy of the upscaled model.

Another measure of interest to us consists of the response of the solid and liquid potentials inside the electrodes to the imposed boundary condition at the current collector. The upscaled equations provide us with only the values of the currents at the interfaces, but not in the interior of the electrodes. Thus, one approach is to try to approximate the behavior of the current, and consequently that of the potential, by assuming a spatio-temporal current profile within the electrodes. The discrepancy between the high-fidelity potential response and that of the assumed upscaled response, provides us with another measure to quantify the inadequacy of the upscaled model.

We know that $\mathbf{i_s} = I$ at the boundaries and $\mathbf{i_s} = 0$ at the interfaces, which precludes the solid current density being uniform in the electrodes. The simplest non-uniform profile we can assume for $\mathbf{i_s}$ in the interior of the electrodes is a linear profile. Thus, $\mathbf{i_s^L} = -I(x-L)/L$ and $\mathbf{i_s^R} = I(x-L-s)/L$. (Direction of the current is given by the flux vector). Consequently, since $\mathbf{i_s} = -\sigma\partial\Phi_s/\partial x$, we have that

$$\Phi_s^L = \frac{I}{\sigma L}\left(\frac{x^2}{2} - Lx\right) \tag{22}$$

$$\Phi_s^R = \frac{-I}{\sigma L}\left(\frac{x^2}{2} - Lx - sx\right) + \text{cst} \tag{23}$$

Note that the constant in Eq. (22) is zero, since $\Phi_s^L(x = 0) = 0$, while the constant in Eq. (23) can indirectly be inferred as before. The above formulation could be generalized to higher order polynomial expansions, which could also include temporal variations as well

according to the following:

$$\mathbf{i_s} = \sum_{n=0}^{p} c_n(t)\, x^n \tag{24}$$

$$\Phi_s = \sum_{n=0}^{p} \frac{c_n(t)\, x^{n+1}}{n+1} + c_0{}'(t) \tag{25}$$

The polynomial coefficients are determined through an optimization procedure, such as a least-squares minimization of the difference between the high-fidelity and upscaled observations. Boundary and interface conditions are then imposed as constraints during the optimization process. Another route would be to formulate time evolution equations for the coefficients themselves (I don't know how we could do this in a physically meaningful manner...I'm still thinking about it. What we know is that the solid current changes from being non-linear to linear as time evolves during the charging process.). The above basis expansion could be further generalized through the use of PC expansions for example.

2.2 Modeling Assumptions

As noted in the pervious section, we are interested in solving the low-fidelity 0-D model, which consists of the spatially averaged high-fidelity equations over the electrode's entire length. One of the quantities of interest is the cell voltage, $V_{cell} = \Delta\Phi_{\text{cell}} = \Phi_c^R - \Phi_c^L$. However, integrating the 0-D equations by themselves do not provide us with sufficient information in order to compute the cell voltage. Consequently, we are going to assume a certain profile for the overpotential, η, inside the electrodes. The simplest spatial profile that we can assume, which is consistent with the boundary conditions, is that of a quadratically varying one.

Note that in what follows, I have switched the signs for the definition of η. So now we have, $\eta = \Phi_s - \Phi_l$, $\eta' = -\partial\eta/\partial x = i_s/\sigma - i_l/\kappa$.

Moreover, for non-dimensionalizing the equations, we are going to define the following variables:

$$\xi = \frac{x}{L}$$

$$\gamma = \frac{\kappa}{\sigma}$$

$$I' \equiv I_{unscaled}$$

$$I \equiv I_{scaled} = \frac{I'L}{V_0}\frac{\kappa + \sigma}{\kappa\sigma}$$

$$\tau = \frac{\kappa\sigma}{\kappa + \sigma}\frac{t}{aCL^2}$$

From the initial and boundary conditions, our quadratic modeled profile for the surface overpotential turns out to be:

$$\tilde{\eta} = \frac{I}{2}\xi^2 - \frac{I\gamma}{1+\gamma}\xi + I\tau - \frac{I}{6} + \frac{I\gamma}{2(1+\gamma)} \tag{26}$$

Since

$$\bar{\eta}(\tau) = \frac{a}{3} + \frac{b}{2} + c$$

where a,b,and c are the coefficients of the quadratic polynomial in Eq.(26), we can write the coefficient c as:

$$c = \overline{\eta} - \frac{I}{6} + \frac{I\gamma}{2(1+\gamma)}$$

Thus, we can express an explicit dependance on $\overline{\eta}$ in Eq.(26) as :

$$\tilde{\eta} = \frac{I}{2}\xi^2 - \frac{I\gamma}{1+\gamma}\xi + \overline{\eta} - \frac{I}{6} + \frac{I\gamma}{2(1+\gamma)} \tag{27}$$

Note that from now on in this section, I will simply refer to $\tilde{\eta}$ as η. This also applies to $\mathbf{i_s}, \mathbf{i_l}$, etc... However, it is to be implicitly understood that all of these refer to the modeled counterparts and not the actual "true" quantities. In the next section, I will start making the distinction again.

Thus, from Eq.(13), we get:

$$\mathbf{i_s} = \left(-\frac{1}{L}\frac{\partial\eta}{\partial\xi} + \frac{I'}{\kappa}\right)\frac{\sigma\kappa}{\kappa + \sigma} \tag{28}$$

and from charge continuity, we have that:

$$\mathbf{i_l} = I' - \mathbf{i_s} \tag{29}$$

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In order to be able to calculate the cell potential, we first need an expression for the potential drop in the liquid across an electrode. This is given by:

$$\Phi_l\big|_{\xi=0} - \Phi_l\big|_{\xi=1} = \int_{\xi=0}^{\xi=1} \frac{\mathbf{i_l}L}{\kappa}\, d\xi$$

$$= \frac{I'L}{\kappa} + \frac{\sigma I}{2(\kappa+\sigma)} - \frac{I\gamma}{\gamma+1}\frac{\sigma}{\kappa+\sigma} - \frac{I'\sigma L}{\kappa(\kappa+\sigma)} \tag{30}$$

The cell potential can now be computed using:

$$V_{cell} = 2V_0 - 2\left(\Phi_l\big|_{\xi=0} - \Phi_l\big|_{\xi=1} + \eta\big|_{\xi=0}\right) - \frac{IL_s}{\kappa_s}$$

$$= 2V_0 - \frac{I'L_s}{\kappa_s} - \frac{2I'L}{\kappa} - \frac{2I}{3} - 2\overline{\eta} + \frac{2\kappa\sigma I}{(\kappa+\sigma)^2} + \frac{2I'\sigma L}{\kappa(\kappa+\sigma)} \tag{31}$$

2.3   Residual Information

Our system can now be described by solving either the high-fidelity (non-dimensionalized) equation for the surface overpotential:

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \xi^2} \tag{32}$$

or the spatially averaged low-fidelity equation:

$$\frac{\partial \overline{\eta}}{\partial \tau} = I \tag{33}$$

which is complemented with the modeled surface overpotential for the spatial variation inside the electrode:

$$\tilde{\eta} = \frac{I}{2}\xi^2 - \frac{I\gamma}{1+\gamma}\xi + \overline{\eta} - \frac{I}{6} + \frac{I\gamma}{2(1+\gamma)} \tag{34}$$

Accordingly, the residual produced by using the modeled surface overpotential, rather than the exact one to solve the high-fidelity PDE, is expressed as:

$$\mathcal{R}(\xi,\tau) = \frac{\partial \tilde{\eta}}{\partial \tau} - \frac{\partial^2 \tilde{\eta}}{\partial \xi^2} \tag{35}$$

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where,

$$\frac{\partial \tilde{\eta}}{\partial \tau} = \frac{\partial \tilde{\eta}}{\partial I}\frac{\partial I}{\partial \tau} + \frac{\partial \tilde{\eta}}{\partial \overline{\eta}}\frac{\partial \overline{\eta}}{\partial \tau}$$

$$= \frac{\partial I}{\partial \tau}\left(\frac{\xi^2}{2} - \frac{\gamma}{1+\gamma}\xi - \frac{1}{6} + \frac{\gamma}{2(1+\gamma)}\right) + I(\tau) \tag{36}$$

$$\frac{\partial^2 \tilde{\eta}}{\partial \xi^2} = I(\tau) \tag{37}$$

Thus:

$$\mathcal{R}(\xi,\tau) = \frac{\partial I}{\partial \tau}\left(\frac{\xi^2}{2} - \frac{\gamma}{1+\gamma}\xi - \frac{1}{6} + \frac{\gamma}{2(1+\gamma)}\right) \tag{38}$$

On the other hand, the error produced by using the inexact overpotential is defined as:

$$\varepsilon(\xi,\tau) = \eta - \tilde{\eta} \tag{39}$$

Accordingly, the evolution of the error in space and time could be expressed as:

$$\frac{\partial \varepsilon}{\partial \tau} = \frac{\partial(\eta - \tilde{\eta})}{\partial \tau} = \frac{\partial^2(\eta - \tilde{\eta})}{\partial \xi^2} - \mathcal{R}(\xi,\tau)$$

$$= \frac{\partial^2 \varepsilon}{\partial \xi^2} - \mathcal{R}(\xi,\tau) \tag{40}$$

We notice from Eq. (40) that the evolution of the error has a direct relationship with the residual. Consequently, through using "physics-derived" information about the evolution of the error and information from the residual, it might be possible to correct for the error in our predictions incurred from solving the low-fidelity equation without having to solve the high-fidelity system of equations. One possible route towards with could be to solve Eq. (33) along with a stochastic version of Eq. (34):

$$\tilde{\eta} = \frac{I}{2}\xi^2 - \frac{I\gamma}{1+\gamma}\xi + \overline{\eta} - \frac{I}{6} + \frac{I\gamma}{2(1+\gamma)} + \mathcal{P}_\varepsilon(\xi,\tau) \tag{41}$$

where $\mathcal{P}_\varepsilon(\xi,\tau)$ represents a suitable probability distribution for the error $\varepsilon(\xi,\tau)$.

The above problems simplifies a bit, if we are only aim for quantifying the error (or inadequacy) in our quantity of interest (QoI), which in our case is the cell potential V_{cell}. The error introduced by solving the low-fidelity equation appears only in the second term of the expression for V_{cell}. Thus, propagating the stochastic overpotential through the relevant Eqs. (28)–(30), we notice that only the error at the electrode/separator boundary, $\varepsilon(\xi = 1, \tau)$ affects the outcome of the QoI. In other words, quantifying the time evolution of the error at $\xi = 1$ is sufficient for quantifying the error in the QoI.

3 Problem formulation

4 Results

5 Discussion