Modeling Inadequacy in Simplified Models of Supercapacitors

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1 Model Description

Figure (1) shows an schematic illustration of a supercapacitor cell which consists of

- Anode current collector

- Porous anode (-) electrode: solid matrix and liquid electrolyte

- Separator : electronic insulator that allows ion to pass through (ion permeable)

- Porous cathode (+) electrode: solid matrix and liquid electrolyte
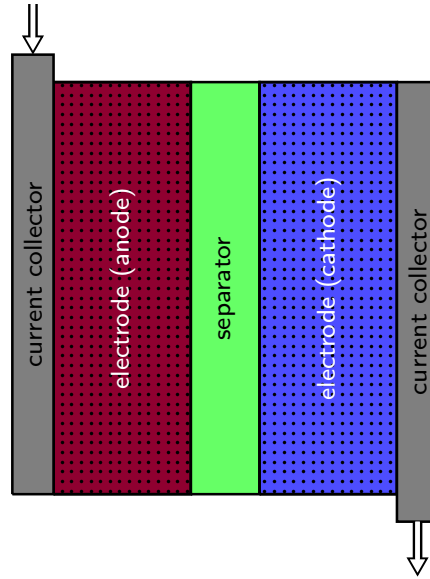
- Cathode current collector.

Figure 1: Schematic diagram of supercapacitors.

The current density in the matrix and solution phases can be expressed by Ohm's law as

$$\mathbf{i}_1 = -\sigma \nabla \phi_1 \tag{1}$$
$$\mathbf{i}_2 = -\kappa \nabla \phi_2 \tag{2}$$

where $\mathbf{i}_1$ is the current density in solid matrix phase due to migration of electrons, $\mathbf{i}_2$ is the current density in the liquid electrolyte phase due to ion migration (assuming no concentration gradient and no convection due to bulk fluid motion), ϕ_s and ϕ_2 are potentials, and σ is solid matrix electronic conductivity and κ is liquid ionic conductivity.

Conservation of charge dictates that

$$I = \mathbf{i}_1 + \mathbf{i}_2 \tag{3}$$

and

$$-\nabla \cdot \mathbf{i}_1 = \nabla \cdot \mathbf{i}_2 = ai_n \tag{4}$$

where I is the total current density, a is the interfacial area per unit volume and the current transferred from the matrix phase to the electrolyte is the sum of the double-layer and the faradaic currents

$$i_n = C\frac{\partial}{\partial t}(\phi_1 - \phi_2) + i_0 \left(\exp(\frac{\alpha_a F}{RT}\eta) - \exp(-\frac{\alpha_a F}{RT}\eta) \right) \tag{5}$$

where C is the double-layer capacitance, i_0 is the exchange current density, α_a and α_a the anodic and cathodic charge transfer coefficients, respectively. F, R, and T stand for Faradays constant, the universal gas constant and temperature. In the above relation, η is the overpotential, defined as the difference between solid and liquid potentials with the equilibrium potential U_{eq} as reference,

$$\eta = \Delta\phi - U_{eq} = \phi_1 - \phi_2 - U_{eq}.$$

For the simplest scenario of an ideally polarizable electrode, i.e. no Faradaic processes, 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:

$$\nabla \cdot \mathbf{i}_2 = \frac{\partial aq}{\partial t} = aC\frac{\partial \eta}{\partial t} \tag{6}$$

where q is the surface charge density of the double layer such as

$$q = C\Delta\phi = C(\phi_1 - \phi_2) = C\eta \tag{7}$$

1.1 Governing equation

Assuming:

i. The electrical resistivity of the current collector is low (or it is sufficiently thin) that one can assume uniform distribution of ϕ_1 over the collector domain: *homogeneous in the x-direction*,

ii. There is no electron/ion fluxes cross the top and bottom boundaries (zero Neumann). Also due to high conductivity of collectors, the voltage over the whole interface on the collector side is negligible (similar to case that tab on the left collector is grounded): *2D domain could be reduced to a quasi-1D domain*,

iii. The material properties are constant within a layer,

the governing equations of the supercapacitor system reduce to

$$aC\frac{\partial \eta}{\partial t} = -\kappa\frac{\partial^2 \phi_2}{\partial x^2} \tag{8}$$

$$aC\frac{\partial \eta}{\partial t} = \sigma\frac{\partial^2 \phi_1}{\partial x^2} \tag{9}$$

$$\kappa\frac{\partial^2 \phi_2}{\partial x^2} = 0 \tag{10}$$

where the first two relations hold in the interior of the porous electrodes and the last one holds in interior of the separator ($\mathbf{i}_1 = 0$).

Boundary conditions: Assuming that a constant current is applied at one of the current collectors during charging/discharging, while the other current collector is grounded (Figure 2), the boundary condition for a domain with electrode width of L and separator width of s can be written as

$$
\begin{cases}
\mathbf{i}_2 = 0; \mathbf{i}_1 = -I & ; & x = 0 \\
\mathbf{i}_1 = 0 & ; & x = L \\
\mathbf{i}_1 = 0 & ; & x = L + s \\
\mathbf{i}_2 = 0; \phi_1 = 0 & ; & x = 2L + s \\
-\kappa \frac{\partial \phi_2}{\partial x}\big|_{x=L} = -\kappa \frac{\partial \phi_2}{\partial x}\big|_{x=L+s}
\end{cases}
\tag{11}
$$

where I is the total current density at the current collector during charging or discharging.

Initial conditions:

$$
\phi_1(x; t = 0) = \phi_1^0; \phi_2(x; t = 0) = \phi_2^0;
\tag{12}
$$

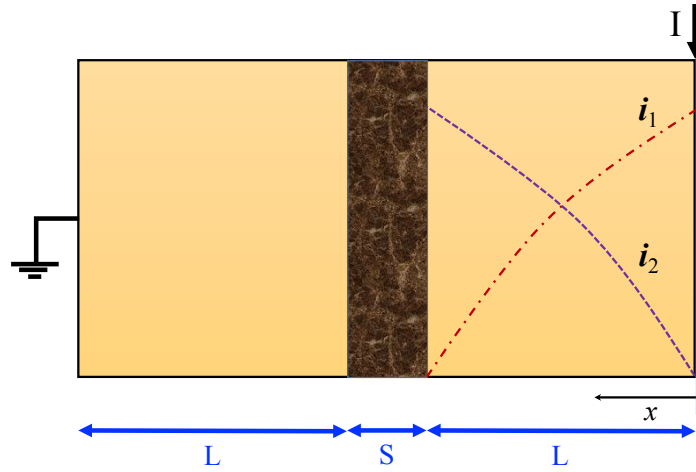where $\phi_1^0 = \phi_2^0$ for the case that the supercapacitor is initially fully discharged.

Figure 2: Schematic diagram of the supercapacitor considered here.

One can consider the cell voltage as a QoI in supercapcitors, which is defined as the potential drop across the system, $V_{cell} = \Delta\phi_{cell} = \phi_{collector}^L - \phi_{collector}^R$. The voltage of a cell consisting of two (identical) electrodes with a separator between them can be evaluated using

$$
V_{cell} = 2V_0 - 2V_{electrode} - V_{seperator}
\tag{13}
$$

where V_0 accounts for the initial voltage of the cell, and $V_{seperator}$ and $V_{electrode}$ accounts for the potential drop across seperator and each of the electrodes respectively and they can be written as

$$
V_{seperator} = I \frac{S}{\kappa_s}
\tag{14}
$$

$$
V_{electrode} = \phi_1\big|_{x=0} - \phi_2\big|_{x=L}
\tag{15}
$$

2   Overpotential Through Electrodes

Following dimensionless variables are taken into account,

$$\xi \;=\; \frac{x}{L} \tag{16}$$

$$\gamma \;=\; \frac{\kappa}{\sigma} \tag{17}$$

$$\tau \;=\; \frac{\kappa\sigma}{\kappa+\sigma}\frac{t}{aCL^2} \tag{18}$$

$$\beta \;=\; \frac{S}{\kappa_s}\frac{\kappa\sigma}{L(\kappa+\sigma)} \tag{19}$$

$$I^* \;=\; I\frac{L}{V_0}\frac{\kappa+\sigma}{\kappa\sigma} \tag{20}$$

2.1   High Fidelity model

The non-dimensional governing equation for the 1D model can be written as follow:

$$\boxed{\text{High Fidelity model}: \quad \frac{\partial \eta_{HF}}{\partial \tau} = \frac{\partial^2 \eta_{HF}}{\partial \xi^2}} \tag{21}$$

Since the current is equal to the matrix phase and solution phase current at $x = 0$ and $x = L$, respectively, the following BCs hold for the PDE (21)

$$\xi = 0 \quad \rightarrow \quad \frac{\partial \eta_{HF}}{\partial \xi} = -I^*\frac{\gamma}{1+\gamma} \tag{22}$$

$$\xi = 1 \quad \rightarrow \quad \frac{\partial \eta_{HF}}{\partial \xi} = I^*\frac{1}{1+\gamma}$$

One can assume the general IC as

$$\eta(\xi, \tau = 0) = \eta_0(\xi) \tag{23}$$

Having the BCs and IC, one can write the exact solutions of the PDE (21) for $\eta_0(\xi) = 0$ as

$$\begin{aligned}
\eta_{HF} \;=\;& I^*\tau + \frac{I^*(3\xi^2 - 1)}{6(1+\gamma)} + \frac{I^*\gamma(3\xi^2 + 2 - 6\xi)}{6(1+\gamma)} \\
&- \frac{2I^*}{\pi^2(1+\gamma)}\sum_{n=1}^{\infty}\left[\frac{(-1)^n + \gamma}{n^2}\right]\cos(n\pi\xi)\exp(-n^2\pi^2\tau).
\end{aligned} \tag{24}$$

2.2   Low Fidelity model

The upscaled (averaged) model can be developed simply by spatially average the governing equation over the entire domain length in the x-direction. Therefore PDE of the HF model reduces to an ODE

$$\frac{\partial \eta_{LF}^{avg}}{\partial \tau} = I^* \tag{25}$$

One can assume a quadratically varying profile for overpotential inside the electrodes [?]

$$\eta_{LF}(\xi, \tau) = a(\tau)\xi^2 + b(\tau)\xi + c(\tau) \tag{26}$$

Using BCs in (22) one can obtain

$$a(\tau) = \frac{1}{2}I^* \quad ; \quad b(\tau) = -I^*\frac{\gamma}{1+\gamma} \tag{27}$$

4

An spatial averaged overpotential can be determined using (26):

$$\eta_{LF}^{avg}(\tau) = \int_0^1 \eta_{LF} \, d\xi = \frac{a(\tau)}{3} + \frac{b(\tau)}{2} + c(\tau) \tag{28}$$

Computing $c(\tau)$ from above equation, one can re-write (26) as

$$\boxed{\text{Low Fidelity model}: \quad \eta_{LF}(\xi,\tau) = \frac{1}{2}I^*(\tau)\xi^2 - I^*(\tau)\frac{\gamma}{1+\gamma}\xi + \eta_{LF}^{avg}(\tau) - \frac{I^*(\tau)}{6} + \frac{I^*(\tau)}{2}\frac{\gamma}{1+\gamma}} \tag{29}$$

where $\eta_{LF}^{avg}(\tau)$ is the solution of (25) given appropriate initial condition.

3 Cell Voltage

The QoI, cell voltage (13), needs to be computed from the overpotential values. The potential drop across the electrode can be derived by substituting of the dimensionless variables in (9)

$$\frac{\partial^2 \phi_1}{\partial \xi^2} = \frac{-\gamma}{1+\gamma}\frac{\partial \eta}{\partial \tau} = \frac{-\gamma}{1+\gamma}\frac{\partial^2 \eta}{\partial \xi^2} \tag{30}$$

along with the boundary conditions for ϕ_1 and η

$$\xi = 0 \quad \rightarrow \quad \frac{\partial \eta}{\partial \xi} = -I^*\frac{\gamma}{1+\gamma} \tag{31}$$

$$\xi = 1 \quad \rightarrow \quad \frac{\partial \eta}{\partial \xi} = I^*\frac{1}{1+\gamma} \tag{32}$$

$$x = 0 : \mathbf{i}_1 = -\sigma\frac{\partial \phi_1}{\partial x} = -I \quad \rightarrow \quad \xi = 0 : \frac{\partial \phi_1}{\partial \xi} = \frac{LI}{\sigma} \tag{33}$$

$$x = L : \mathbf{i}_1 = -\sigma\frac{\partial \phi_1}{\partial x} = 0 \quad \rightarrow \quad \xi = 1 : \frac{\partial \phi_1}{\partial \xi} = 0 \tag{34}$$

Integrating (30) with respect to ξ yields

$$\frac{\partial \phi_1}{\partial \xi} = \frac{-\gamma}{1+\gamma}\frac{\partial \eta}{\partial \xi} + A \tag{35}$$

and using (34) to determine A, results in following relation

$$\frac{\partial \phi_1}{\partial \xi} = \frac{-\gamma}{1+\gamma}\frac{\partial \eta}{\partial \xi} + I^*\frac{\gamma}{(1+\gamma)^2} \tag{36}$$

Integrating (36) between the limits $\xi = 0$ to 1 gives the charge in the dimensionless solid phase potential across the electrode

$$\phi_1|_{\xi=1} - \phi_1|_{\xi=0} = \frac{-\gamma}{1+\gamma}\left(\eta|_{\xi=1} - \eta|_{\xi=0}\right) + I^*\frac{\gamma}{(1+\gamma)^2} \tag{37}$$

Using (37), the dimensionless potential drop across the porous electrode can be written as

$$V_{electrode}^* = \phi_1|_{\xi=0} - \phi_2|_{\xi=1} = \eta|_{\xi=1} + (\phi_1|_{\xi=0} - \phi_1|_{\xi=1}) \tag{38}$$

$$= \frac{1+2\gamma}{1+\gamma}\eta|_{\xi=1} - \frac{\gamma}{1+\gamma}\eta|_{\xi=0} - I^*\frac{\gamma}{(1+\gamma)^2} \tag{39}$$

Having the exact values of overpotentials at the boundaries from HF model (24) and LF model (29) one can obtained the potential across the electrode

$$V^*_{electrode-HF} = I^* \left(\frac{1}{3} + \tau - 2 \sum_{n=1}^{\infty} \frac{1}{n^2 \pi^2} \left(\frac{(-1)^n \gamma}{1+\gamma} + \frac{1}{1+\gamma} \right)^2 \exp(-n^2 \pi^2 \tau) \right) \quad (40)$$

$$V^*_{electrode-LF} = \eta_{LF}^{avg} + I^* \left(\frac{2\gamma+1}{3\gamma+1} + \frac{5}{3} \frac{\gamma}{1+\gamma} - \frac{\gamma}{1+\gamma^2} \right) \quad (41)$$

Substituting the above relation into (13) one can compute the cell voltage as QoI: $Q = V_{cell}$ as

$$V^*_{cell} = \frac{V_{cell}}{2V_0} = 1 - \frac{1}{2} \beta I^* - V^*_{electrode} \quad (42)$$

4 Errors in overpotential and cell voltage

4.1 Error in over potential

Local residual can be obtained by substituting the solution of surrogate (LF) model into the base (HF) model such as

$$\rho(\xi, \tau) = \frac{\partial \eta_{LF}}{\partial \tau} - \frac{\partial^2 \eta_{LF}}{\partial \xi^2}, \quad (43)$$

and with some manipulation one can obtain

$$\rho(\xi, \tau) = \frac{\partial I^*}{\partial \tau} \left(\frac{\xi^2}{2} - \frac{\gamma}{1+\gamma} \xi - \frac{1}{6} + \frac{\gamma}{2(1+\gamma)} \right) \quad (44)$$

Moreover, error in overpotential produced by using the surrogate model is defined as

$$\epsilon(\xi, \tau) = \eta_{HF} - \eta_{LF} \quad (45)$$

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

$$\frac{\partial \epsilon}{\partial \tau} = \frac{\partial^2 \epsilon}{\partial \xi^2} - \rho(\xi, \tau) \quad (46)$$

Having,

$$\frac{\partial \epsilon}{\partial \xi} = \frac{\partial(\eta_{HF} - \eta_{LF})}{\partial \xi} = \frac{\partial \eta_{HF}}{\partial \xi} - (I^* \xi - I^* \frac{\gamma}{1+\gamma}) \quad (47)$$

along with (22), the boundary conditions of PDE (46) can be written as,

$$\xi = 0 \quad \rightarrow \quad \frac{\partial \epsilon}{\partial \xi} = 0 \quad (48)$$

$$\xi = 1 \quad \rightarrow \quad \frac{\partial \epsilon}{\partial \xi} = 0.$$

Initial condition of (46) can be easily obtained as

$$\epsilon(\xi, \tau = 0) = \eta_{HF}(\xi, \tau = 0) - \eta_{LF}(\xi, \tau = 0) = \epsilon_0(\xi) \quad (49)$$

Having the BCs and IC, one can write the exact solutions of the PDE (46) as

$$\epsilon(\xi, \tau) = \sum_{n=1}^{\infty} \phi_n \exp(-(n\pi)^2 \tau) \cos(n\pi\xi) - A_n \cos(n\pi\xi) \int_0^\tau \exp\left(-(n\pi)^2(\tau - S)\right) \frac{\partial I^*}{\partial \tau} dS \quad (50)$$

$$\phi_n = 2 \int_0^1 \epsilon_0(\xi) \cos(n\pi\xi)d\xi \tag{51}$$

$$A_n = \frac{1}{3(n\pi)^3(1+\gamma)} \left[-6\gamma\sin(n\pi) - \sin(n\pi) + 2(n\pi)^2\sin(n\pi) + 6(n\pi)\gamma + 6(n\pi)\cos(n\pi) - \gamma(n\pi)^2\sin(n\pi) \right].$$

For the special case of $\rho(\xi,\tau) = 0$, e.g. constant current, the exact solution of (46) can be written as,

$$\epsilon(\xi,\tau) = A_0 + \sum_{n=1}^{\infty} A_n \exp\left(-(n\pi)^2\tau\right) \cos(n\pi\xi) \tag{52}$$

$$A_0 = \int_0^1 \epsilon_0(\xi)d\xi \tag{53}$$

$$A_n = \int_0^1 \epsilon_0(\xi) \cos(n\pi\xi)d\xi.$$

4.2 Error in cell voltage

Through the information about the evolution of the error and information from the local residual, it might be possible to formulate the error in QoI, cell voltage, incurred from solving the low-fidelity equation without having to solve the high-fidelity system of equations,

$$\mathcal{E} = Q(\eta_{HF}) - Q(\eta_{LF}) = V^*_{cell}(\eta_{HF}) - V^*_{cell}(\eta_{LF}). \tag{54}$$

Using (42) above equation is equivalent to

$$\mathcal{E} = V^*_{electrode}(\eta_{HF}) - V^*_{electrode}(\eta_{LF}). \tag{55}$$

Substituting $V^*_{electrode}$ from (38) and using the relation for error in over potential (45), one can write

$$\mathcal{E} = \frac{1+2\gamma}{1+\gamma}\epsilon(\xi = 1, \tau) - \frac{\gamma}{1+\gamma}\epsilon(\xi = 0, \tau) \tag{56}$$

5 Numerical Example: Constant and Cyclic Current

We consider numerical examples with imposing constant and cyclic currents, when the supercapcitor is initially fully discharged ($\phi_1(x; t = 0) = \phi_2(x; t = 0) = 0$). The values of the parameters considered in this example are presented in Table 1. The applied currents are shown in Figure (3a).

Table 1: Values of parameters for the illustrative example.

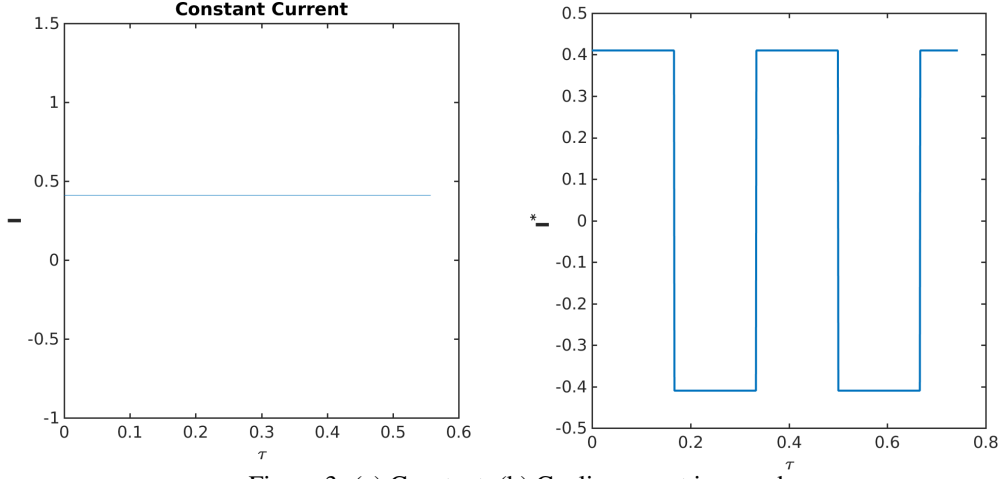|	
κ	0.0195174 sec/m
σ	52.1 sec/m
L	50e-6 m
C	0.03134 F/m^2
a	4.19956e7/C m
V_0	1.25 $volt$
I_{unscaled}	200 Amp/m^2
κ_s	0.0311627 sec/m
S	25e-6 m

Figure 3: (a) Constant; (b) Cyclic current imposed.

5.1 Constant Current Discharge

Solution of LF model: Figures (4) shows the variation of solution of LF model (29) in the normalized time and space. η_{LF}^{avg} in this equation is the solution of (25) such as

$$\eta_{LF}^{avg}(\tau) = \int_0^\tau I^*(\tau')d\tau' = I^*\tau \tag{57}$$

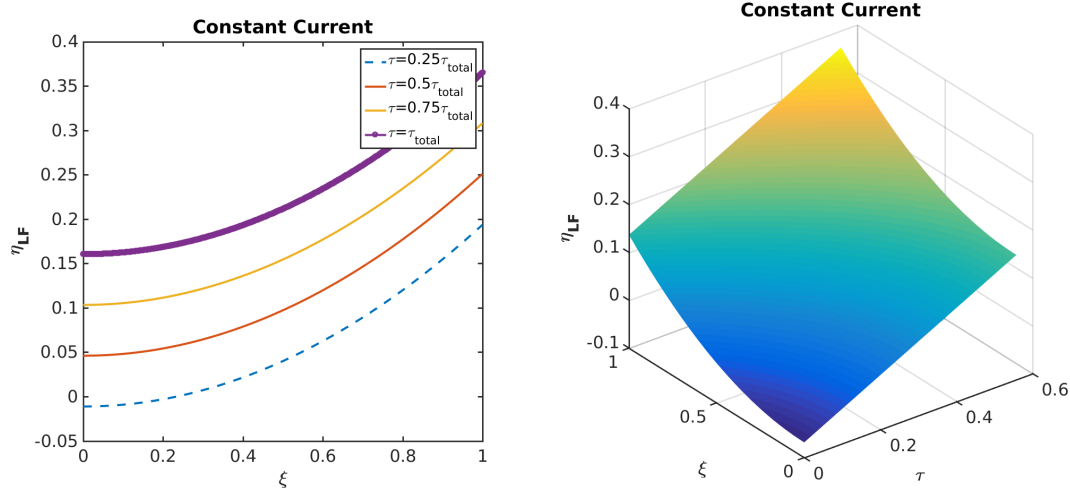*Solution of HF model:* Solution of the HF model is shown in Figures (5). The following PDE+BCs is

Figure 4: Solution of LF model for constant current.

solved using finite difference methods:

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

$$\text{BCs}: \quad \frac{\partial \eta}{\partial \tau}\big|_{\xi=0} = -I^* \frac{\gamma}{1+\gamma} \quad ; \quad \frac{\partial \eta}{\partial \tau}\big|_{\xi=1} = I^* \frac{1}{1+\gamma} \tag{58}$$

$$\text{IC}: \quad \eta(\xi, \tau = 0) = 0 \tag{59}$$

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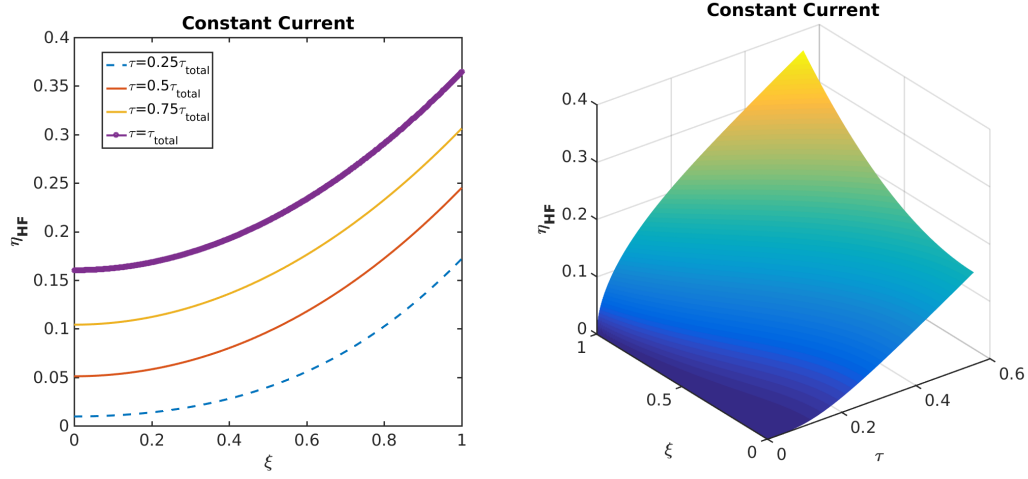
Figure 5: Solution of HF model for constant current.

Evolution of error: The local residual $\rho(\xi, \tau)$ can be computed from (44). However, $\frac{\partial I}{\partial \tau} = 0$ resulting in zero local residual.

Having the solution of HF model one can obtain the exact error $\epsilon_{\text{exact}} = \eta_{HF} - \eta_{LF}$. This can be compared with the evolution of error that is obtained from solving the following PDE (Figures 6 and 7).

$$\frac{\partial \epsilon}{\partial \tau} = \frac{\partial^2 \epsilon}{\partial \xi^2} - \rho(\xi, \eta)$$

BCs : $\qquad\qquad \frac{\partial \epsilon}{\partial \xi}|_{\xi=0} = \frac{\partial \epsilon}{\partial \xi}|_{\xi=1} = 0$ $\qquad\qquad$ (60)

IC : $\quad \epsilon(\xi, \tau = 0) = \eta_{HF}(\xi, \tau = 0) - \eta_{LF}(\xi, \tau = 0)$ $\qquad\qquad$ (61)
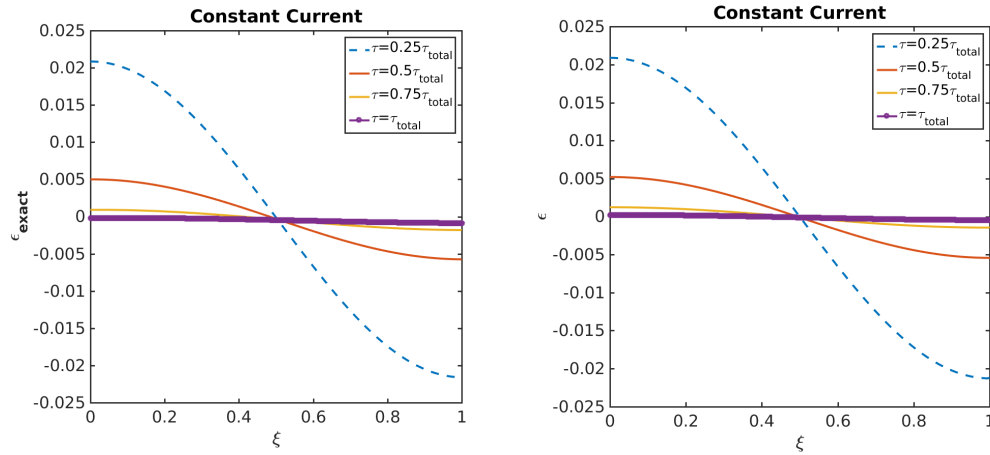

Figure 6: Solution of error $\epsilon(\xi, \tau)$ at different normalized time and space : (top) exact error using HF model, (bottom) error using (45).
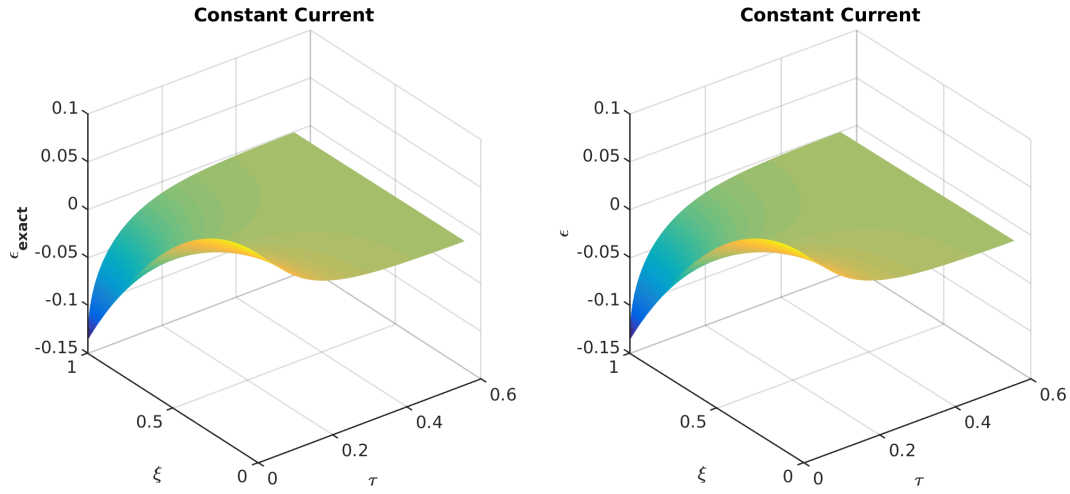
Figure 7: Solution of error $\epsilon(\xi, \tau)$ at different normalized time and space : (top) exact error using (45) and solution of HF model, (bottom) error using (46).

Time evolution of cell voltage Having the solutions of overpotential furnished by HF and LF model, the time evolution of the normalized voltage can be computed using (42). The results are shown in Figures (8).
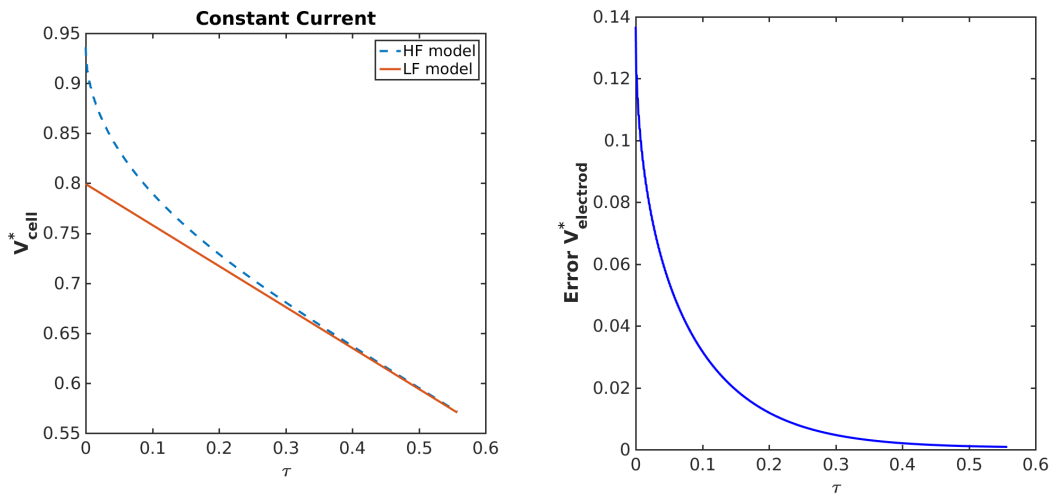

Figure 8: (a) Change in voltage across the porous electrode with dimensionless time for constant current. (b) error in V_{cell}

5.2 Cyclic Current

Solution of LF model: Figures (9) show the variation of solution of LF model (29) in the normalized time and space.

$$\eta_{LF}^{avg}(\tau) = \int_0^\tau I^*(\tau')d\tau' \tag{62}$$

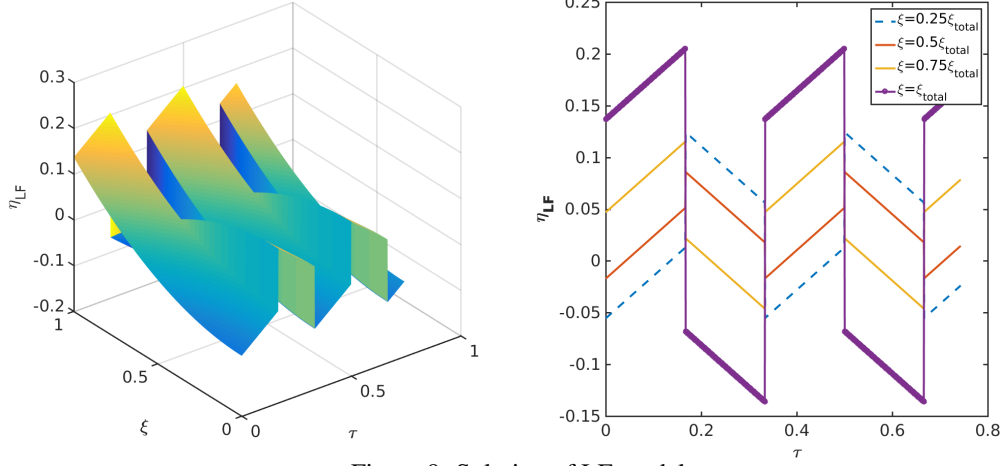*Solution of HF model:* Solution of the HF model is shown in Figures (10). The following PDE+BCs is

Figure 9: Solution of LF model.

solved using finite difference methods:

$$\frac{\partial \eta_{HF}}{\partial \tau} = \frac{\partial^2 \eta_{HF}}{\partial \xi^2}; \quad \text{BCs}: \frac{\partial \eta_{HF}}{\partial \tau}\Big|_{\xi=0} = -I^* \frac{\gamma}{1+\gamma}; \quad \text{IC}: \eta_{HF}(\xi, \tau = 0) = 0$$
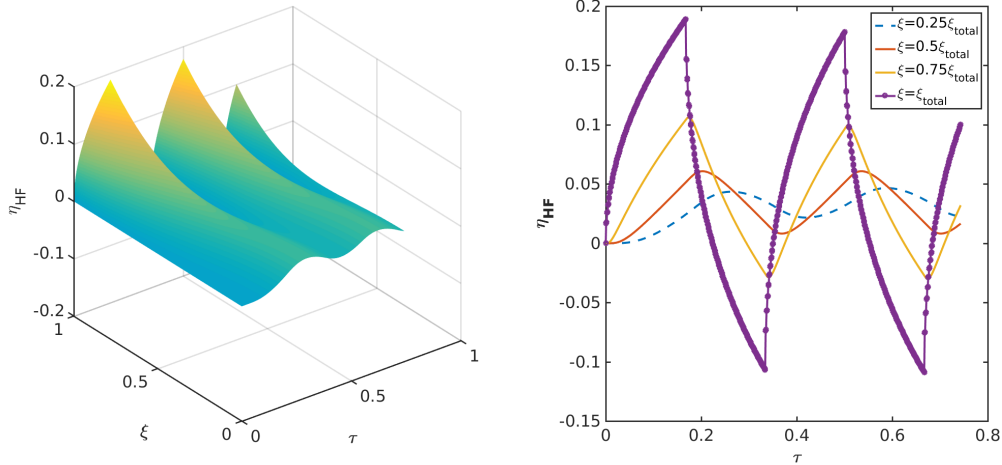

Figure 10: Solution of HF model.

Time evolution of cell voltage: Having the solutions of overpotential furnished by HF and LF model, the time evolution of the normalized voltage can be computed using (42). The results are shown in Figures (8).

Error in cell voltage: Both (55) and (56) can be computed having solution of HF model. The results are shown in Figure (11).
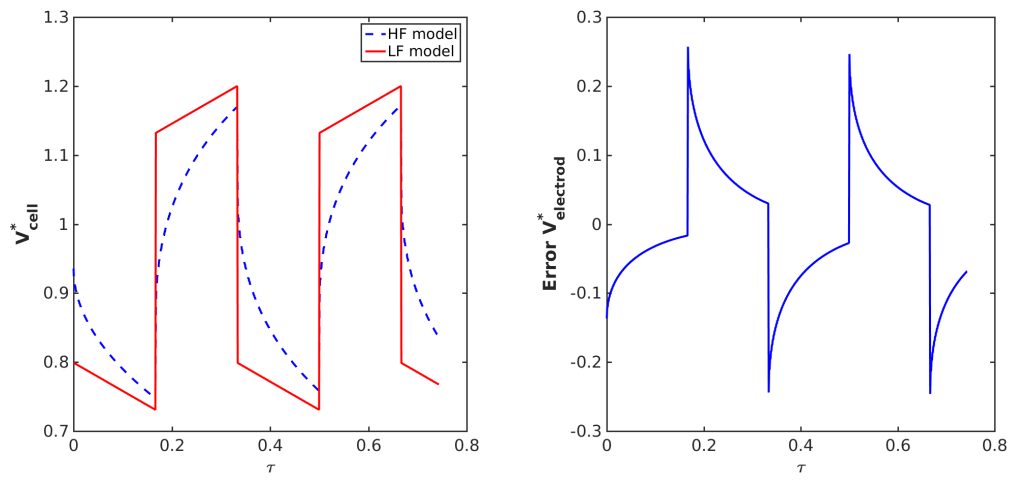
Figure 11: (a) Change in voltage across the porous electrode with dimensionless time. (b) Error in $V\,cell$ using HF and LF models (56).