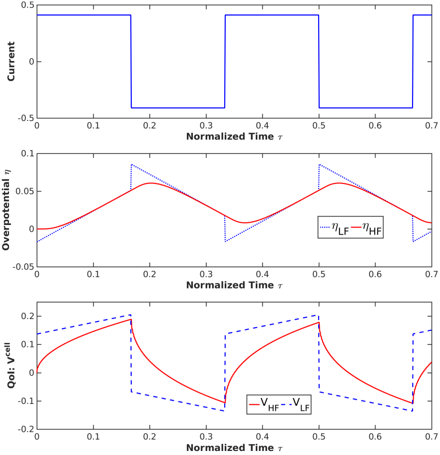
Models of Supercapacitors

- $\eta(\xi,\tau)$ = overpotential in electrode: $\eta = \phi_{solid} - \phi_{liquid} - U_{eq}$
- γ = conductivity ratio of solid and liquid
- ξ, τ = dimensionless distance and time
- $I(\tau)$ = applied current



High Fidelity (1D) model

$$\frac{\partial \eta_{HF}}{\partial \tau} = \frac{\partial^2 \eta_{HF}}{\partial \xi^2}$$

$$\begin{cases} \frac{\partial \eta_{HF}}{\partial \xi}\big|_{\xi=0} & = & -\frac{\gamma}{1+\gamma} I(\tau) \\ \frac{\partial \eta_{HF}}{\partial \xi}\big|_{\xi=1} & = & \frac{1}{1+\gamma} I(\tau) \\ \eta_{HF}\big|_{\tau=0} & = & \eta_0(\xi) \end{cases}$$

Low Fidelity (0D) model

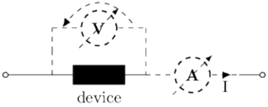
$$\eta_{LF} = \frac{1}{2} I \xi^2 - I \frac{\gamma}{1+\gamma}\xi + \eta^{avg}(\tau) - I\frac{2\gamma - 1}{6(1+\gamma)}$$

where $\frac{\partial \eta^{avg}}{\partial \tau} = I$

Quantity of Interest

Potential drop across the system

$$V^{cell}(\tau) = \phi^L_{collector} - \phi^R_{collector} = \frac{1+2\gamma}{1+\gamma}\eta|_{\xi=1} - \frac{\gamma}{1+\gamma}\eta|_{\xi=0} - \frac{\gamma}{(1+\gamma)^2} I$$



Model Inadequacy

- The high fidelity model accounts for the time history of the current. Such history does not appear with right dependency in the low fidelity model:

$$V_{HF}^{cell} = A(\gamma)\int_0^\tau I(\tau')K(\tau-\tau')d\tau' + B(\gamma)I(\tau)$$
$$V_{LF}^{cell} = C(\gamma)\int_0^\tau I(\tau')d\tau' + D(\gamma)I(\tau)$$

- The stochastic inadequacy representation needs to account for the incomplete and uncertain history information available to the low-fidelity model.
- Solution of low fidelity model converges to high fidelity over time i.e. modeling error is larger for higher frequency current.

Inadequacy representation

Error in QoI: $\epsilon = V_{HF}^{cell} - V_{LF}^{cell}$

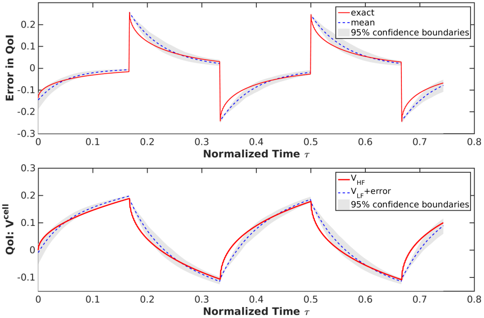
Auxiliary Stochastic ODE:

$$\frac{\partial \epsilon}{\partial \tau} = -\lambda\epsilon + \alpha\frac{\partial I}{\partial \tau}$$

where λ is a stochastic process with following time evolution:

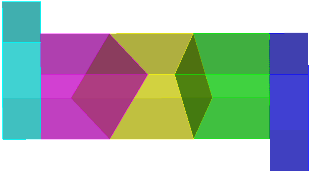
$$\frac{\partial \lambda}{\partial \tau} = -c(\lambda - \lambda_{mean}) + \beta\frac{\partial W}{\partial \tau}$$

where $W(\tau)$ is a Wiener process.

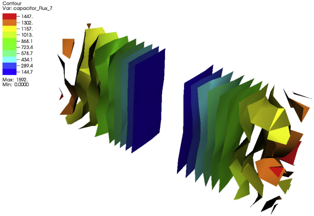


Model Inadequacy

- The equivalent circuit models and transmission lines are not able to fully capture the behavior of real supercapacitors.
- The high-fidelity 3D finite element model makes it possible to understand better how physical electrochemistry and other design parameters affects super capacitor behavior. But this comes at a cost of complex operation mode with high performance computing requirement.
- Similar procedure will be pursue to formulate inadequacy of the 1D model with respect to finite element 3D model.
- The 1D model enhanced with stochastic inadequacy representation, can be utilized to provide low cost computational predictions for analyzing electrochemical impedance spectroscopy data, computing heat production in thermal analysis, etc.



3D finite element mesh of supercapacitor[1].



Spatial distribution of the current density for parallel plate supercapacitor configuration[2].

[1] Lebrun-Grandie and Turcksin. *Cap: C++ library for modeling energy storage devices*. ORNL-CEES.

[2] Allu, Velamur Asokan, Shelton, Philip, Pannala. *Journal of Power Sources* 256 (2014): 369-382.