Inadequecy Representation in Models of Supercapacitor Batteries

Danial Faghihi

Center for Predictive Engineering and Computational Science (PECOS)
Institute for Computational Engineering and Sciences (ICES)
The University of Texas at Austin

PECOS Inadequecy Meeting
Wednesday May 24, 2017

Outline

Outline

Governing Equations

electrode

Current density following Ohm's law:

- Matrix phase : $\mathbf{i}_1 = -\sigma \nabla \phi_1$
- Solution phase: $\mathbf{i}_2 = -\kappa \nabla \phi_2$

ϕ_1, ϕ_2: potentials,
σ, κ: electronic/ionic conductivity.

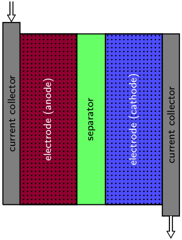
Conservation of charge:

$$-\nabla \cdot \mathbf{i}_1 = \nabla \cdot \mathbf{i}_2 = a i_n$$

a: interfacial area per unit volume
i_n: current transferred from the matrix to the electrolyte

$$i_n = \underbrace{C \frac{\partial}{\partial t} \eta}_{\text{double-layer}} + \underbrace{i_0 (\exp(\frac{\alpha_a F}{RT} \eta) - \exp(-\frac{\alpha_c F}{RT} \eta))}_{\text{faradaic}}$$

overpotential: $\eta = \phi_1 - \phi_2$



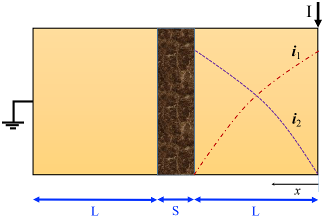
collector

$$\mathbf{i}_1 = -\sigma \nabla \phi_1$$
$$-\nabla \cdot \mathbf{i}_1 = 0$$

seperator

$$\mathbf{i}_2 = -\kappa \nabla \phi_2$$
$$-\nabla \cdot \mathbf{i}_2 = 0$$

High Fidelity Model



- $\eta(\xi, \tau)$ = overpotential in electrode
- $\gamma = \dfrac{\kappa}{\sigma}$: conductivity ratio
- ξ, τ : dimensionless distance/time
- $I(\tau)$: dimensionless current

Modeling Assumptions (Sins)

i. No Faradaic processes: current transferred from matrix to the solution phase goes towards only charging the double-layer at the electrode/electrolyte interface.

ii. ϕ_1 is uniformly distributed over the current collector domain (collector is sufficiently thin)

iii. There is no electron/ion fluxes cross the top and bottom boundaries

iv. The material properties are constant within each layer

High Fidelity (1D) model

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

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

Low Fidelity Model

Modeling Assumptions (Sins)

i. Assuming a quadratically varying profile for overpotential inside the electrodes

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

where a, b, and c can be obtained from PDE+BCs of HF model.

Low Fidelity (0D) model

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

η^{avg} is the solution of following ODE given appropriate initial condition. Spatially averaging the governing equation over the entire domain length

$$\eta^{avg} = \int_0^1 \eta d\xi \qquad \Rightarrow \qquad \frac{\partial \eta^{avg}}{\partial \tau} = I(\tau)$$

QoI : cell voltage

Quantity of Interest

Potential drop across the system

$$\begin{aligned} V^{\text{cell}}(\tau) &= \phi^L_{\text{collector}} - \phi^R_{\text{collector}} \\ &= 2V_0 - 2V^{\text{elect.}} - V^{\text{sep.}} \end{aligned}$$

where

$$V^{\text{elect.}}(\tau) = \phi_1|_{\xi=0} - \phi_2|_{\xi=1} = \frac{1+2\gamma}{1+\gamma}\eta|_{\xi=1} - \frac{\gamma}{1+\gamma}\eta|_{\xi=0} - \frac{\gamma}{(1+\gamma)^2} I$$

and

$$V^{\text{sep.}}(\tau) = I\frac{L_s}{\kappa_s}$$

Outline

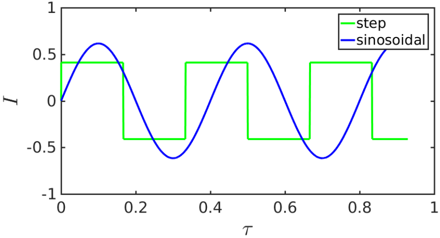
Inadequacy Representation

Objective:

Based on what we know about the models, develop a representation of inadequacy (*error in QoI*, ϵ) as a parametric model $\mathcal{P}(\boldsymbol{\theta})$ such that

$$V_{\rm HF}^{\rm cell} \equiv V_{\rm LF}^{\rm cell} + \mathcal{P}(\boldsymbol{\theta})$$

- Parameters of inadequacy model, $\boldsymbol{\theta}$, needs to be calibrated using the data furnished by HF model for simple scenarios, e.g.

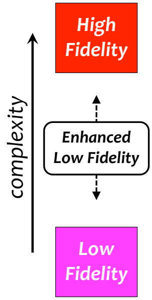


- $\mathcal{P}(\boldsymbol{\theta})$ enables predicting $V^{\rm cell}$ for more complex scenarios outside of the HF data domain along with the associated uncertainty.

Inadequacy Representation

Inadequacy model $\mathcal{P}(\boldsymbol{\theta})$ involves:

- *Deterministic counterpart:* Encapsulates our information about the models.
- *Stochastic counterpart:* Represents the remaining uncertainty due to lack of information about features of full HF system.



- The goal is to construct a class of enhanced low fidelity models (intermediate complexities) based on our knowledge about the system, thus,
  - Deterministic part of $\mathcal{P}(\boldsymbol{\theta})$: $V_{\mathrm{ELF}}^{\mathrm{cell}} - V_{\mathrm{LF}}^{\mathrm{cell}}$
  - Stochastic part of $\mathcal{P}(\boldsymbol{\theta})$: $V_{\mathrm{HLF}}^{\mathrm{cell}} - V_{\mathrm{ELF}}^{\mathrm{cell}}$
- The more complex ELF model:
  - more complex deterministic $\mathcal{P}$ i.e. more parameters
  - more HF data might be required to calibrate
  - less uncertainty in prediction.

Summary of Models and QoI

HF model

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

$$\begin{cases} \dfrac{\partial \eta}{\partial \xi}|_{\xi=0} = & -\dfrac{\gamma I}{1+\gamma} \\ \dfrac{\partial \eta}{\partial \xi}|_{\xi=1} = & \dfrac{I}{1+\gamma} \\ \eta|_{\tau=0} = & \eta_0(\xi) \end{cases}$$

LF model

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

QoI: $V_{\mathrm{LF}}(\tau) = \eta^{avg}(\tau) + C_{\mathrm{LF}} I(\tau)$ where

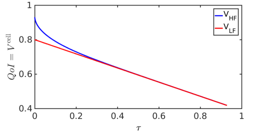
$$\frac{\partial \eta^{avg}}{\partial \tau} = I(\tau)$$

What do we know about HF and LF models?

- structure of HF and LF, i.e. ODE, PDE, etc.
- model respond in a simple (unphysical) case, e.g. constant current.
- XXXX

Knowledge about the models

1. HF model is a PDE with *infinite dimensional* solution space (i.e. function space) while LF model is an ODEs having a *finite dimensional* state vector.
2. for **constant current case**, asymptotic behavior of HF is equivalent to LF, i.e. solution of LF converges to HF after a certain time.



3. **Principles of Fading Memory**[a],[b]
   XXXX

[a] Coleman, B.D. and E. H. Dill., 1971. Thermodynamic restrictions on the constitutive equations of electromagnetic theory.
[b] Coleman, B.D. and Noll, W., 1961. Foundations of linear viscoelasticity.

Constructing ELF model

Delay Differential Equations (DDEs):

- DDEs belong to the class of systems with the functional state, i.e. PDEs which are infinite dimensional.

Constructing ELF model

LF model

$$V_{\mathrm{LF}}(\tau) = \eta^{avg}(\tau) + C_{\mathrm{LF}} I(\tau) \; ; \qquad \frac{\partial \eta^{avg}}{\partial \tau} = I(\tau)$$

$$\text{with IC} : \eta^{avg}(0) = 0, \; \tau > 0$$

Enhancing LF model by creating a delay equation (DDE):

ELF model

$$V_{\mathrm{ELF}}(\tau) = \hat{\eta}(\tau) + C_{\mathrm{ELF}} I(\tau - t_s) \; ; \qquad \frac{\partial \hat{\eta}}{\partial \tau} = I(\tau - t_s)$$

$$\text{with IC} : \hat{\eta}(0) = 0, \; \tau > 0$$
$$\text{and Initial Finction} : I(\tau) = \phi(\tau), \; -t_s \leq \tau \leq 0$$

1. The ELF model (DDEs) belong to the class of systems with the functional state, similar to PDEs are infinite dimensional.
2. ELF model, to some extend, bring the history information of the current.
3. For constant current case, the asymptotic behavior of ELF model is equivalent to those of LF and HF model.

Inadequacy Representation: Deterministic

- Deterministic part of $\mathcal{P}^{\mathrm{d}}(\boldsymbol{\theta})$: $V_{\mathrm{ELF}}^{\mathrm{cell}} - V_{\mathrm{LF}}^{\mathrm{cell}}$
- The objective is not to solve the full ELF system, rather using it to motivates form of inadequacy model.
- Using Taylor expansion:

$$V_{\mathrm{ELF}}(\tau) = \hat{\eta}(\tau) + C_{\mathrm{ELF}}\left(I(\tau) - t_s \frac{\partial I}{\partial \tau} + \frac{1}{2} t_s^2 \frac{\partial^2 I}{\partial \tau^2} + \cdots\right)$$

  with

$$\frac{\partial \hat{\eta}}{\partial \tau} = I(\tau) - t \frac{\partial^2 \hat{\eta}}{\partial \tau^2} - \frac{1}{2} t_s^2 \frac{\partial^3 \hat{\eta}}{\partial \tau^3} + \cdots$$

- One can increase the complexity of the ELF and corresponding $\mathcal{P}^{\mathrm{d}}$ by considering more Taylor expansion terms.

Inadequacy Representation: Deterministic

Constructing $\mathcal{P}_1^{\mathrm{d}}(\boldsymbol{\theta})$ using one Taylor expansion term of ELF:

$$V_{\mathrm{LF}} = \eta^{avg} + C_{\mathrm{LF}} I \quad \text{with} \quad \frac{\partial \eta^{avg}}{\partial \tau} = I$$

$$V_{\mathrm{ELF}} = \hat{\eta} + C_{\mathrm{ELF}}(I - t_s \frac{\partial I}{\partial \tau}) \quad \text{with} \quad \frac{\partial \hat{\eta}}{\partial \tau} = I - t_s \frac{\partial^2 \hat{\eta}}{\partial \tau^2}$$

Substituting above relations in $\epsilon_1^{\mathrm{d}} = V_{\mathrm{ELF}} - V_{\mathrm{LF}}$ and evaluating $\frac{\partial \epsilon_1^{\mathrm{d}}}{\partial \tau}$ and little manipulation, one can derive:

$$\mathcal{P}_1^{\mathrm{d}}(\boldsymbol{\theta}) : \quad \frac{\partial \epsilon_1^{\mathrm{d}}}{\partial \tau} + \lambda^2 \epsilon_1^{\mathrm{d}} = \alpha \frac{\partial I}{\partial \tau} + \beta I$$

where $\lambda^2 = 1/t_s^2, \ \alpha = C_{\mathrm{ELF}} - C_{\mathrm{LF}} - \frac{1}{t_s} C_{\mathrm{LF}}, \ \beta = C_{\mathrm{ELF}} - C_{\mathrm{LF}} - 1$

Inadequacy Representation: Deterministic

Using second terms of the Taylor expansions, and following similar derivation, motivates an inadequacy representation such as:

$$\mathcal{P}_2^{\mathrm{d}}(\boldsymbol{\theta}): \quad \frac{\partial^2 \epsilon_2^{\mathrm{d}}}{\partial \tau^2} + \lambda^2 \frac{\partial \epsilon_2^{\mathrm{d}}}{\partial \tau} + \mu^2 \epsilon_2^{\mathrm{d}} = \alpha I + \beta \frac{\partial I}{\partial \tau} + \rho \frac{\partial^2 I}{\partial \tau^2}$$

writing the above relation as system of 1st order ODEs

$$\mathcal{P}_2^{\mathrm{d}}(\boldsymbol{\theta}): \begin{cases} x_1'(\tau) = & x_2(\tau) \\ x_2'(\tau) = & f(\tau) \quad -\mu^2 x_1(\tau) - \lambda^2 x_2(\tau) \end{cases}$$

where $\epsilon_2^{\mathrm{d}} = x_1(\tau)$

and $f(\tau) = \alpha I + \beta \dfrac{\partial I}{\partial \tau} + \rho \dfrac{\partial^2 I}{\partial \tau^2}$

Inadequacy Representation: Deterministic

Constant current case:

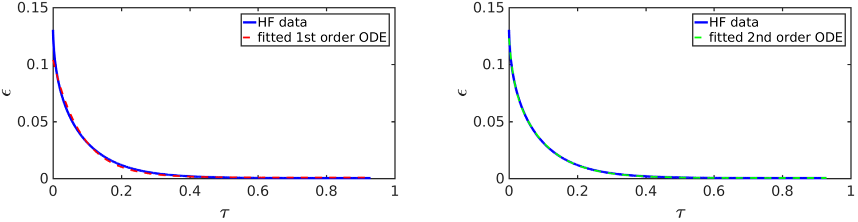
Under constant current assumption, it can be shown that

$$V_{\mathrm{ELF}} \equiv V_{\mathrm{LF}} + \sum_{i=1}^{n} C_i \exp(-\frac{\tau}{t_{si}})$$

where number of terms in the Prony series n determine the complexity of the ELF model.

Also, it can be shown that $V_{\mathrm{ELF}} \to V_{\mathrm{HF}}$ as $n \to \infty$.

Calibrating against HF data:



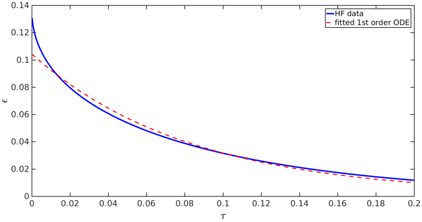
Inadequacy Representation: Deterministic

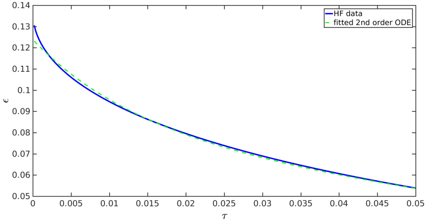
Constant current case:

Calibrating inadequacy models against HF data:

- $\mathcal{P}_1^{\mathrm{d}} : \lambda = 3.47; \beta = 0.0223$
- $\mathcal{P}_2^{\mathrm{d}} : \lambda = 9.55; \mu = 28.82; \alpha = 0.532$

If finite number of exponential decay enhancements, n, is taken into account for constructing ELF, the motivated inadequacy model is incapable of capturing HF data in a small time scale.

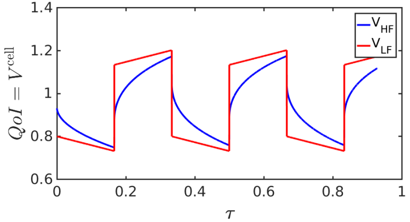




Similar results are also expected for step current case.

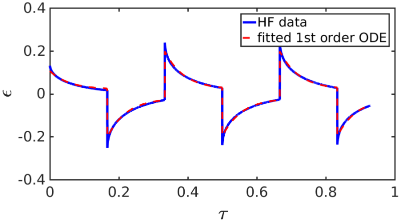
Inadequacy Representation: Deterministic

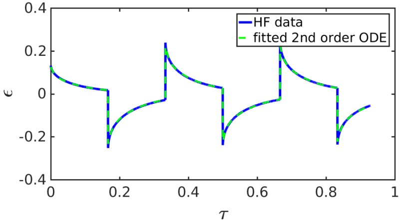
Step current case:



Calibrating inadequacy models against HF data:

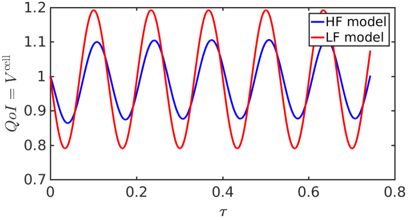
- $\mathcal{P}_1^{\mathrm{d}} : \lambda = 4.2273; \beta = 0.8766; \alpha = 0.2764$
- $\mathcal{P}_2^{\mathrm{d}} : \lambda = 10.64; \mu = 34.03; \alpha = 9.018; \beta = 23.9858; \rho = 0.3048$





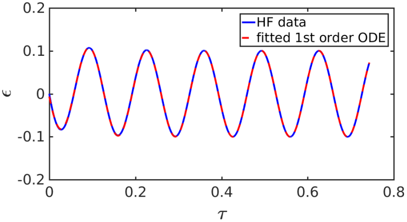
Inadequacy Representation: Deterministic

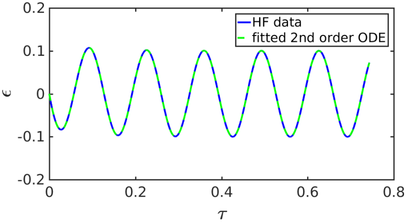
Sinusoidal current case: High Frequency



Calibrating inadequacy models against HF data:

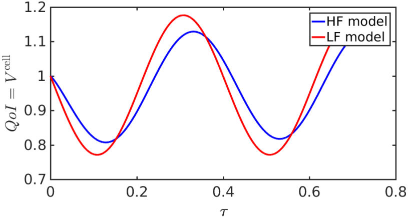
- $\mathcal{P}_1^{\mathrm{d}} : \lambda = 3.8389; \beta = 0.4342; \alpha = -0.2555$
- $\mathcal{P}_2^{\mathrm{d}} : \lambda = 9.4434; \mu = 29.7492; \alpha = 1333.9; \beta = -18; \rho = 0.3079$





Inadequacy Representation: Deterministic

Sinusoidal current case: Low Frequency



- $\mathcal{P}_1^{\mathrm{d}} : \lambda = 3.3459; \beta = 0.0932; \alpha = -0.2352$
- $\mathcal{P}_2^{\mathrm{d}} : \lambda = 8.8651; \mu = 26.6081; \alpha = 36.35; \beta = -15.38; \rho = 0.1415$