Inadequecy Representation in Models of Supercapacitor Batteries

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Outline

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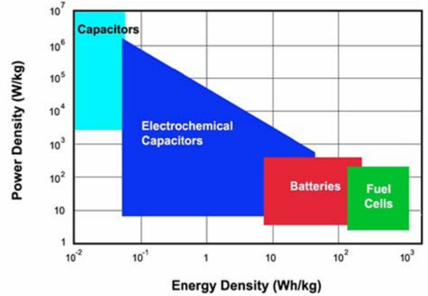
What are supercapacitors?

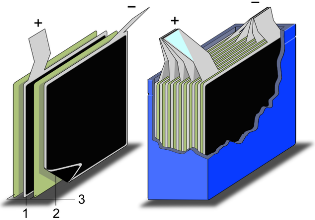
Supercapacitors are intermediate power/energy storage/supply devices that bridge the gap between *electrolytic capacitors* and *rechargeable batteries*. They can provide

- higher energy density (capacitance) than capacitors
- higher power density (faster charge delivery) than batteries
- many more charge and discharge cycles than batteries

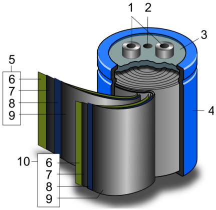


Supercapacitors are suitable in applications where a large amount of power is needed for a relatively short time, where a very high number of charge/discharge cycles or a longer lifetime is required. e.g. Low supply current for memory backup in SRAM, power for cars, etc.

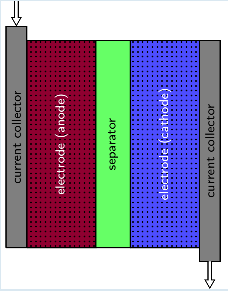
What are supercapacitors?



Supercapacitor with stacked electrodes



Wound supercapacitor



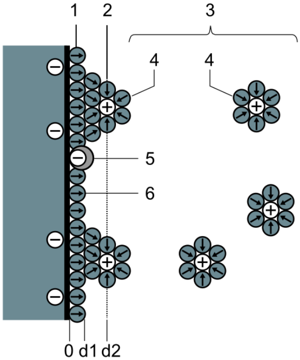
Unit cell:

- Anode current collector
- Porous anode electrode: solid matrix filled with liquid electrolyte
- Separator: electronic insulator and ion permeable
- Porous cathode electrode: solid matrix and liquid electrolyte
- Cathode current collector.

Storage principles

Capacitance value of an electrochemical capacitor is determined by two storage principles

- *double-layer capacitance:* electrostatic storage of the electrical energy by separation of charge in a double layer at the interface between electrode/electrolyte .
- *pseudocapacitance:* electrochemical storage achieved by faradaic redox reactions with electron charge-transfer between electrolyte and electrode.



1. Inner Helmholtz plane, 2. Outer Helmholtz plane, 3. Diffuse layer, 4. Solvated ions (cations) **5. Specifically adsorbed ions (redox ion, which contributes to the pseudocapacitance),** 6. Molecules of the electrolyte solvent

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.

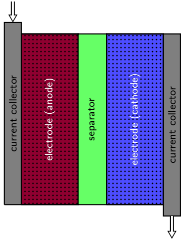
Conservation of charge:

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

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

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

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



collector

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

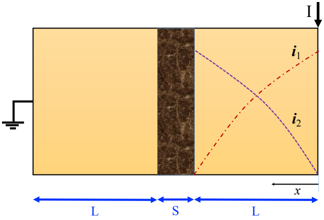
$$-\nabla \cdot \mathbf{i}_1 = 0$$

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

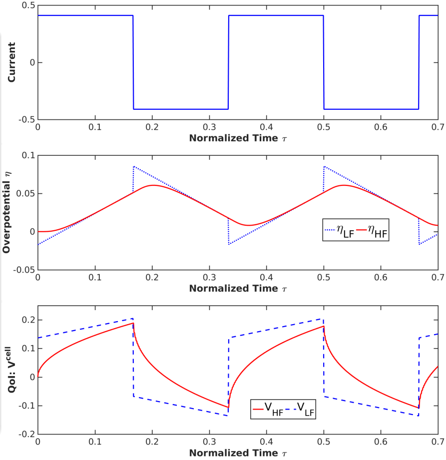
$$\begin{aligned} V^{\text{cell}}(\tau) &= \phi^L_{\text{collector}} - \phi^R_{\text{collector}} \\ &= 2V_0 - 2V^{\text{elect.}} - V^{\text{sep.}} \end{aligned}$$

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

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



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Model Inadequacy

We are interested in Error in QoI: $\epsilon = V_{\mathrm{HF}}^{\mathrm{cell}} - V_{\mathrm{LF}}^{\mathrm{cell}} \equiv V_{\mathrm{HF}}^{\mathrm{electrode}} - V_{\mathrm{LF}}^{\mathrm{electrode}}$
Given what we know about high fidelity model η_{HF}, we can formulate inadequacy representation.

- Solution of low fidelity model converges to high fidelity over time i.e. modeling error is larger for higher frequency current.
- 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:

$$\begin{aligned} V_{\mathrm{HF}}^{\mathrm{electrode}} &= A(\gamma)\int_0^\tau I(\tau')\mathcal{K}(\tau-\tau')d\tau' + B(\gamma)I(\tau) \\ V_{\mathrm{LF}}^{\mathrm{electrode}} &= C(\gamma)\int_0^\tau I(\tau')d\tau' + D(\gamma)I(\tau) \end{aligned}$$

  Solving PDE using Laplace transform

$$\mathcal{K}(\tau-\tau') = \sum_{n=1}^{\infty} e^{-n^2\pi^2(\tau-\tau')}$$

- The stochastic inadequacy representation needs to account for the incomplete and uncertain history information available to the LF model.

Model Inadequacy

Inadequacy representation

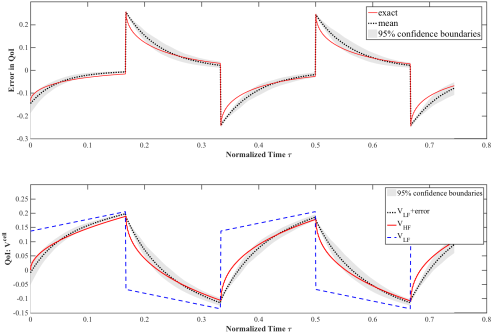
Auxiliary Stochastic ODE:

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

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.



- The ODE accounts for some of hidden features of HF i.e. the term $\lambda\epsilon$ takes care of the Kernel $\mathcal{K}$ and the term $\alpha \dfrac{\partial I}{\partial \tau}$ accounts for discontinuity of I.
- It needs to be trained by HF data i.e. calibrating parameters of inadequacy representation $(\alpha, \beta, c, \lambda_{mean})$.