Multi-dimensional modeling of the electrical, electrochemical, and thermal processes in supercapacitors.

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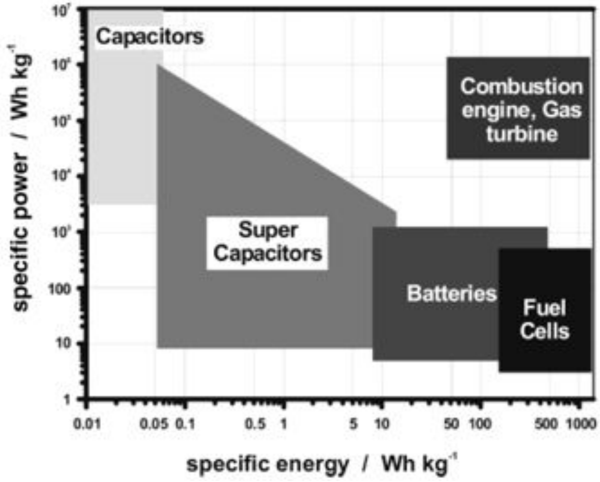
Outline

- What are supercapacitors?
- How do we model their behavior?
- What are the possible sources of inadequacy?

Motivation



From [M. Winter and R. Brodd, Chem. Rev., **104**(10), 4245-4270 (2004)]

Challenges and applications

SC support a broad spectrum of applications, including:

- Low supply current for memory backup in static random-access memory (SRAM)
- Power for cars, buses, trains, cranes and elevators, including energy recovery from braking, short-term energy storage and burst-mode power delivery

SC 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.

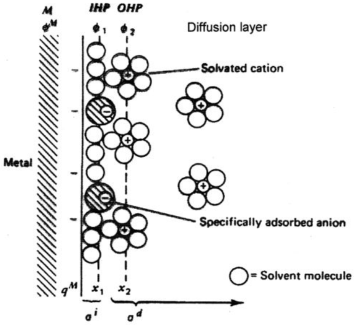
Limitation of current technology related to performance, safety, and lifetime

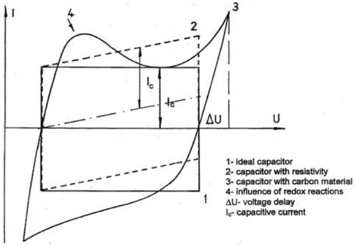
- low operating voltage (safety margin against electrolyte's breakdown)
- current loads only limited by internal resistance
- heat generally defines lifetime (evaporation rate of the liquid electrolyte)
- bridge gap between conventional capacitors and rechargeable batteries

Storage principles

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

- double-layer capacitance – electrostatic storage of the electrical energy achieved by separation of charge in a Helmholtz double layer
- pseudo capacitance – electrochemical storage achieved by faradaic redox reactions with charge-transfer

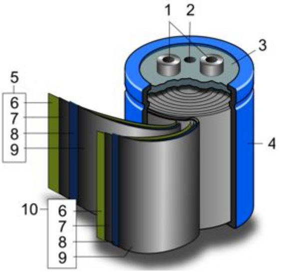




From [E. Frackowiaka and F. Béguin, Carbon, **39**, 937-950 (2001)]

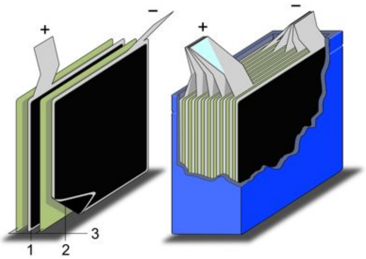
Construction

Wound supercapacitor



1.Terminals, 2.Safety vent, 3.Sealing disc, 4.Aluminum can, 5.Positive pole, 6.Separator, 7.Carbon electrode, 8.Collector, 9.Carbon electrode, 10.Negative pole

Supercapacitor with stacked electrodes



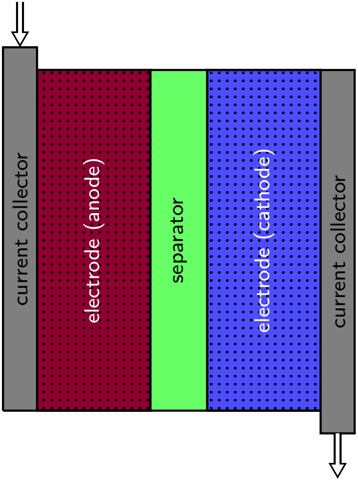
1.Positive electrode, 2.Negative electrode, 3.Separator

From [Wikipedia contributors, *Electric double-layer capacitor* (Accessed 29 October 2014)]

Schematic of an electrochemical capacitor

Multiphysics components:

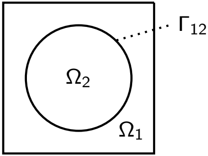
- electrochemical
- electrical
- thermal



Governing equations

Solid phase Ω_1

$$\nabla \cdot i_1 = 0$$
$$i_1 = -\sigma \nabla \Phi_1$$



Liquid phase Ω_2

$$\frac{\partial c_j}{\partial t} = -\nabla \cdot N_j$$
$$N_j = -D_j \left(\nabla c_j - z_j \frac{F}{RT} c_j \nabla \Phi_2 \right)$$
$$\nabla \cdot i_2 = 0$$
$$i_2 = F \sum_j z_j N_j$$
$$\sum_j z_j c_j = 0$$

Solid-liquid interface Γ_{12}

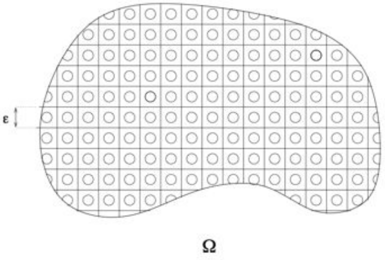
$$i_n = C \frac{\partial \eta}{\partial t} + f(\eta, c_j)$$
$$f(\eta, c_j) = i_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta \right) - \exp\left(-\frac{\alpha_c F}{RT} \eta \right) \right]$$
$$\eta = \Phi_1 - \Phi_2$$
$$i_2 \cdot n = -i_1 \cdot n = i_n$$
$$z_j F N_j \cdot n = -\frac{dq_j}{dq} i_n$$

Homogenization of the system in the porous medium

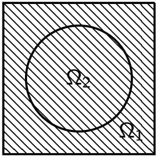
- Properties of the medium (electrical conductivity, specific capacitance, etc.) can be derived from (i) respective properties of its constituents, (ii) the media porosity and (iii) pores structure
- Derivation is usually complex (c.f. discussion with Brendan Sheehan)

For a binary 1:1 electrolyte : $\kappa = \frac{F^2}{RT}\frac{1}{2}D\left(\frac{1}{t_-}+\frac{1}{t_+}\right)c$

$$t_+ = \frac{D_+}{D_+ + D_-}; \quad t_- = \frac{D_-}{D_+ + D_-}; \quad D = \frac{2D_+D_-}{D_+ + D-}$$



From [G. Allaire, Lecture notes on homogenization theory (2010)]



$$\Omega = \Omega_1 \cup \Omega_2$$

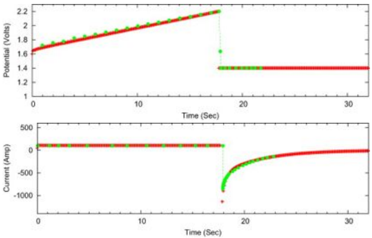
$$\epsilon_2 \frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c) - ai_n\left(t_- \frac{dq_+}{dq} + t_+ \frac{dq_-}{dq}\right)$$

$$i_2 = -\kappa\nabla\Phi_2 - \left(\frac{t_+ - t_-}{f}\right)\kappa\nabla \ln c$$

$$i_1 = -\sigma\nabla\Phi_1$$

$$-\nabla \cdot i_1 = \nabla \cdot i_2 = ai_n$$

Simplified electrochemical model

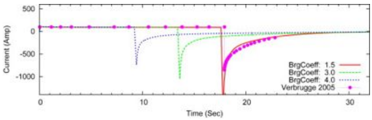


From [S. Allu et al., J. Power Sources, **256**, 369-382 (2014)]

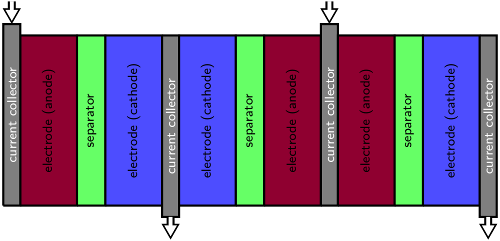
Governing equations

$$aC\frac{\partial}{\partial t}(\Phi_2 - \Phi_1) = \nabla \cdot (\kappa \nabla \Phi_2)$$
$$aC\frac{\partial}{\partial t}(\Phi_1 - \Phi_2) = \nabla \cdot (\sigma \nabla \Phi_1)$$

- Effective transport property is proportional to ϵ^{ζ}, where ϵ is the void fraction and ζ is the Bruggeman's coefficient
- Higher value of ζ implies higher tortuosity and lower effective transport coefficients



Multi-domain multi-operator formulation



electrode (both anode and cathode)

$$aC\frac{\partial}{\partial t}(\Phi_1 - \Phi_2) = \nabla \cdot (\sigma \nabla \Phi_1)$$

$$aC\frac{\partial}{\partial t}(\Phi_2 - \Phi_1) = \nabla \cdot (\kappa \nabla \Phi_2)$$

boundary current collector

$$\sigma \frac{\partial \Phi_1}{\partial n} = I_{charge/discharge} \text{ or } \Phi_1 = 0$$

current collector

$$\nabla \cdot (\sigma \nabla \Phi_1) = 0$$

separator

$$\nabla \cdot (\kappa \nabla \Phi_2) = 0$$

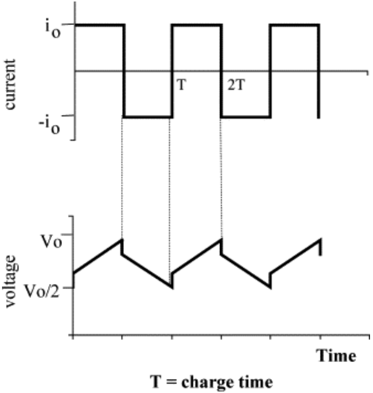
interface electrode/separator

$$\sigma \frac{\partial \Phi_1}{\partial n} = 0$$

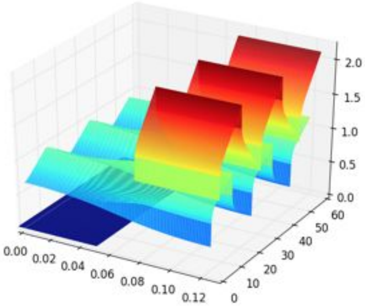
interface electrode/collector

$$\kappa \frac{\partial \Phi_2}{\partial n} = 0$$

Charge/discharge cycles



From [J. Miller, Electrochemica Acta, **52**, 1703-1708 (2006)]

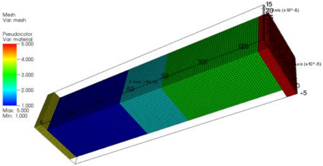


Evolution of Φ_S and Φ_l during charge and discharge cycles

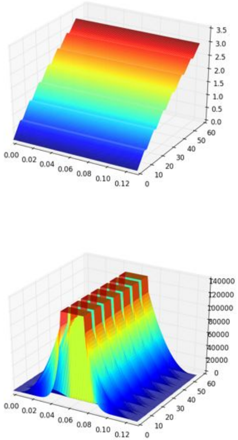
Thermal transport

Coupling Electrochemical/Electrical to Thermal

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + q$$



- ◇ Heat generation takes place in separator
- ◇ Temperature uniform through the thickness of the sandwich
- ◇ However full cell simulation could display significant temperature gradients



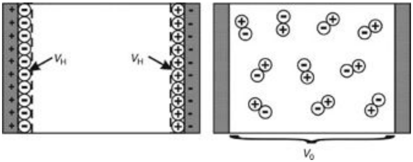
Evolution of T (above) and of q^{irr} (below)

Heat generation in double layer capacitors

$$q = q^{rev} + q^{irr}$$

- $q^{irr} = \sigma|\nabla\Phi|^2$: Joule heating (ohmic losses $\propto RI^2$ when current traverse resistive material)
- $q^{rev} = \pm\frac{2k_BT}{e}\ln(\frac{V_H}{V_0})|\sigma\nabla\Phi|$: changes in entropy (ions in the electrolyte of a double layer capacitor are arranged in the electric field during charging and are spreading themselves again during discharging)

ion distribution in the electrolyte for charged (left) and discharged (right) condition



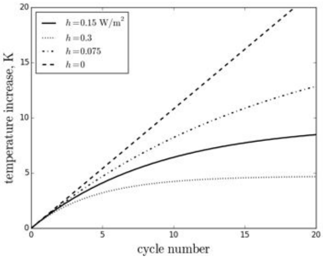
From [J. Schiffer et al., J. Power Sources, **160**, 765-772 (2006)]

Heat management

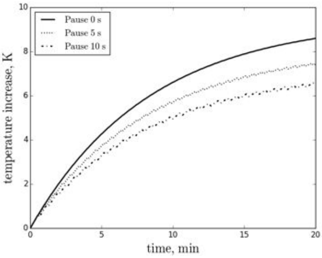
Heat exchange between layers and/or with the surrounding

$$-\lambda \frac{\partial T}{\partial n} = h(T - T_{\infty})$$

- ◇ Steady-state strongly dependent on heat transfer coefficient h
- ◇ Yet large uncertainty on its value



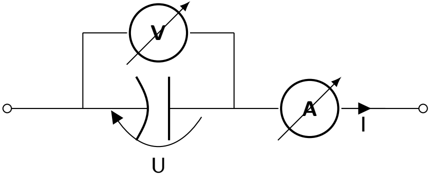
temperature rise of the cell as a function of the cycle number



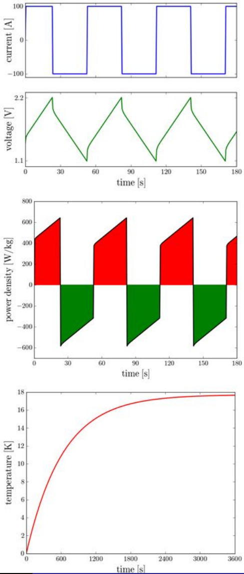
impact of the cycle duration

Quantities of interest

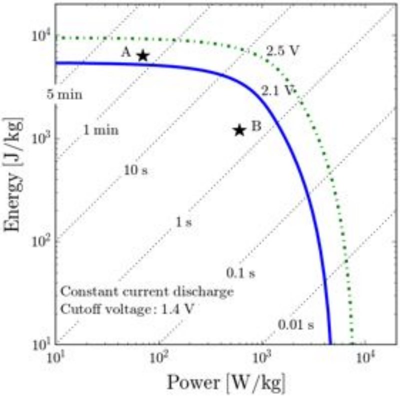
Only total current and voltage are measurable.



- ◇ Power $P = UI/m$
- ◇ Energy $E = \int_0^t P dt'$
- ◇ Efficiency
- ◇ Temperature (surface...)



Results from simulation



Low-fidelity thermal model

Homogenized anisotropic heat conduction equation with uniform heat source.

- Heat flux $-\lambda \nabla T$

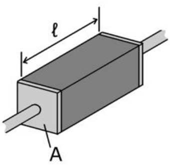
$$\lambda = \begin{bmatrix} \lambda_x & 0 & 0 \\ 0 & \lambda_y & 0 \\ 0 & 0 & \lambda_z \end{bmatrix}$$

$$\lambda_x = \frac{\lambda^{el} 2w^{el} + \lambda^{sep} w^{sep} + \lambda^{cc} 2w^{cc}}{2w^{el} + w^{sep} + 2w^{cc}}$$

$$\lambda_y = \lambda_z = \frac{2w^{el} + w^{sep} + 2w^{cc}}{\frac{2w^{el}}{\lambda^{el}} + \frac{w^{sep}}{\lambda^{sep}} + \frac{2w^{cc}}{\lambda^{cc}}}$$

- Heat source $Q = RI^2$

$$R = \frac{2w^{el}}{A}\left(\frac{1}{\kappa^{el}} + \frac{1}{\sigma^{el}}\right) + \frac{w^{sep}}{A}\frac{1}{\kappa^{sep}} + \frac{2w^{cc}}{A}\frac{1}{\sigma^{cc}}$$



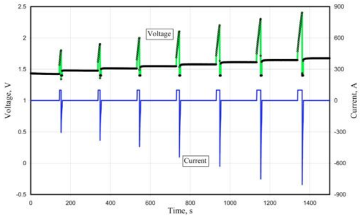
Resistive material with uniform cross section ($R = \rho l / A$)

Or even cruder 0-D

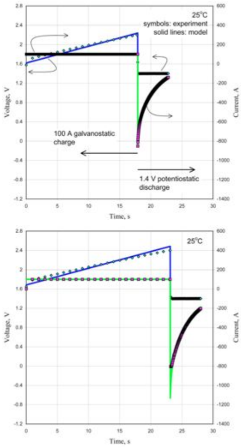
$$mC_p \frac{\partial T}{\partial t} = Q - H(T - T^{ambient})$$

Results from experiment as the reality

- supercapacitor initially at 0 V
- charged to 1.7 V at constant current 100 A
- constant 1.4 V applied for 5 s then allowed to rest for 3 min
- sequence repeated for a series of potentials from 1.8 to 2.4 V with increments of 0.1 V

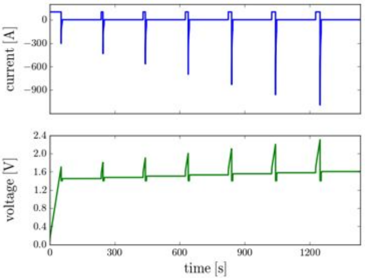


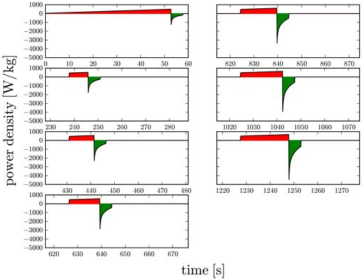
[From M. Verbrugge and P. Liu, J. Electrochem. Soc., **152**(5) D79-D87 (2005)]

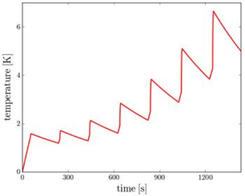


Maximum voltage at end of charge are 2.2 V (upper) and 2.4 V (lower).

Compare against simulation with electrochemical model







Conclusions and future work

- Relatively simple multi-physics problem that couples electrochemical, electrical and thermal
- Same formulation can handle multiple dimensions
- High dimensional parameter spaces for optimization and UQ
- Quantify impact of unmodelled physics (e.g., explicit faradaic charge transfer in the electrode or entropic heat generation)
- Can use upscaled quantities either from more detailed simulations or from experiment