

Modelling inadequacy in super capacitors

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1 Introduction

2 Methodology

3 Problem formulation

3.1 Governing equations

Ignoring the influence of the electrolyte concentration, the current density in the matrix and solution phases can be expressed by Ohm's law as

$$i_1 = -\sigma \nabla \Phi_1 \quad (1)$$

$$i_2 = -\kappa \nabla \Phi_2 \quad (2)$$

i and Φ represent current density and potential; subscript indices 1 and 2 denote respectively the solid and the liquid phases. σ and κ are the matrix and solution phase conductivities.

The total current density is given by $i = i_1 + i_2$. Conservation of charge dictates that

$$-\nabla \cdot i_1 = \nabla \cdot i_2 = a i_n \quad (3)$$

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

$$i_n = C \frac{\partial}{\partial t} (\Phi_1 - \Phi_2) + i_0 \left(\exp \frac{\alpha_a F}{RT} \eta - \exp -\frac{\alpha_c F}{RT} \eta \right) \quad (4)$$

C is the double-layer capacitance. i_0 is the exchange current density, α_a and α_c the anodic and cathodic charge transfer coefficients, respectively. F , R , and T stand for Faraday's constant, the universal gas constant and temperature. η is the overpotential relative to the equilibrium potential U_{eq}

$$\eta = \Phi_1 - \Phi_2 - U_{eq} \quad (5)$$

3.1.1 Note

For simplicity, we consider for now a linearized version of the Butler-Volmer kinetics

$$i_{n,f} \approx i_0 \frac{(\alpha_a + \alpha_c)F}{RT} (\Phi_1 - \Phi_2) \quad (6)$$

This is true for overpotentials with absolute value that does not exceed RT/F , which is approximatively 0.05 V at ambient temperature. Admittedly, we will use it beyond its validity range.

U_{eq} is a measure of the state of charge (it “shifts” the equilibrium). For now, we assume it is zero, which makes the supercapacitor behave similarly to a parallel resistor capacitor model. At open circuit, the capacitor slowly discharges back to 0 V.

3.2 Equivalent circuits

The supercapacitor has a sandwich-like configuration of a collector-electrode-separator-electrode. As the current flows from one terminal to the other, each layer contributes to the overall resistance of the device in the same way as resistors connected in series. The goal here is to see if we can assess the impedance of each individual layer of the sandwich in order to build an equivalent circuit model that is able to predict the electrical behaviour of the supercapacitor. Instead of fitting the parameters of the model to “reality” as it is typically done, we would like to infer these from the geometry and material properties used in the finite element model.

The electrical resistance of a conductive material exhibiting a uniform cross section and through which electric current flows uniformly is given by

$$\text{ESR} = \rho l / A \quad (7)$$

Here l measures the length of the material and A is the cross-sectional area. The material resistivity ρ is measured in $\Omega \text{ m}$ and is by definition the inverse of the electrical conductivity. I use ESR to denote the resistance to avoid confusion with the universal gas constant R . It stands for equivalent series resistance.

separator: A uniform flow of the electric current through the separator is a reasonable assumption. We directly use the formula in Eq. (7) with the computed average resistivity of the separator $\langle 1/\kappa \rangle$.

collector: It is yet unclear whether the assumption is verified in the current collectors depending on where the tab terminal is located (boundary area over which we impose the voltage or the current density flowing into

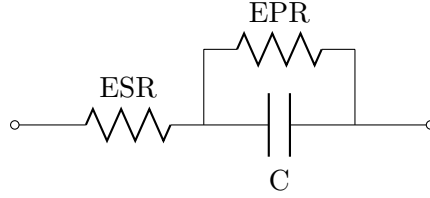


Figure 1: Equivalent circuit for an electrode. ESR = equivalent series resistance. EPR = equivalent parallel resistance. C = capacitance.

the device. However the conductivity σ in the current collector is such that the contribution of the collectors to the overall resistance of the device is insignificant (it is several order of magnitude greater than any of the conductivities in the separator or the electrode).

electrode: The electrode is somewhat thorny. Whereas in the separator, electric current is exclusively carried by the ions in the solution, both the matrix and the solution phases carry a fraction of the current through the electrode. On top of that, uniformity of the current in each phase over the electrode domain is out of question since the current is in the solid phase at the interface with the collector, and, conversely, in the ionic solution at the other end of the electrode, where the electrode meets with the separator. Intuitively though, the electrode resistance must be derivable from the resistance of the solid and the liquid phases taken separately and computed using $\langle 1/\sigma \rangle$ and $\langle 1/\kappa \rangle$, respectively.

The electrode capacitance of an electrode is given by

$$C = aClA \quad (8)$$

and its equivalent parallel resistance

$$\text{EPR} = \frac{RT}{Fai_0lA} \quad (9)$$

This will need some more explanation but in short if we approximate the electrode by a ladder network as shown in Figure 2 and take the low frequency limit, we get

$$\text{ESR} = \frac{1}{3} \frac{(\rho_1 + \rho_2)l}{A} + \frac{1}{3} \frac{\rho_1 \rho_2 l}{(\rho_1 + \rho_2)A} \quad (10)$$

Here I use ρ_1 and ρ_2 to designate the electronic and ionic resistivity of the electrode, respectively $\langle 1/\sigma \rangle$ and $\langle 1/\kappa \rangle$.

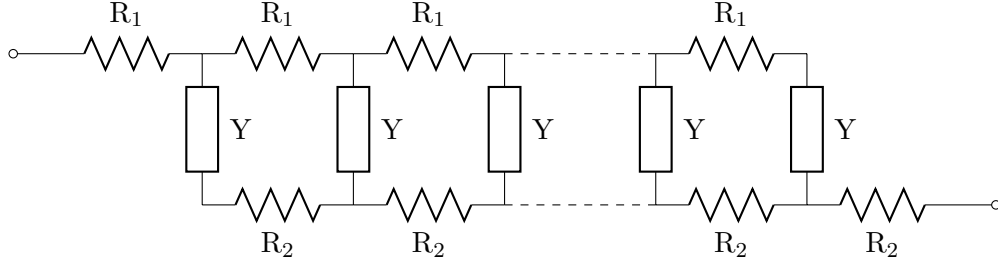


Figure 2: Ladder. With $R_1 = \rho_1 dx/A$, $R_2 = \rho_2 dx/A$, and $Y = aC dx A$.

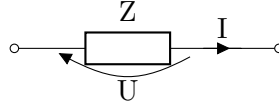


Figure 3: Electrical impedance.

4 Electrochemical impedance spectroscopy

dynamic relation between current and voltage is given by the complex and frequency dependent impedance $Z(f)$

Impedance spectroscopy is a widely used experimental technique to investigate electrochemical systems. measures the impedance of the energy storage device over a range of frequencies. The frequency response allows

4.1 Definitions

By definition, the impedance Z is the measure of the opposition that an electrical element or circuit presents to a current when a voltage is applied. It is the frequency domain ratio of the voltage to the current

$$Z = \frac{U}{I} \quad (11)$$

It is a complex number.

$$Z = |Z|e^{j \arg(Z)} = R + jX \quad (12)$$

The magnitude of the impedance $|Z|$ acts just like a resistance. It gives the drop in voltage amplitude across an impedance Z for a given current I . The phase $\theta = \arg(Z)$ tells by how much the current lags the voltage. The real part $R = |Z| \cos \theta$ and imaginary part $X = |Z| \sin \theta$ of the impedance are

called resistance and reactance, respectively. They are both measured in ohms (Ω). If $X > 0$, the reactance is said to be inductive. If $X < 0$, the reactance is capacitive. If $X = 0$, then the impedance is purely resistive. An inductor has a purely reactive impedance proportional to the signal frequency f and inductance L , $X_L = 2\pi fL$. The impedance of a capacitor is inversely proportional to the frequency f and capacitance C , $X_C = \frac{1}{2\pi fC}$.

4.2 Measurement

4.2.1 Discharge curve

Mostlikely the most common test for energy storage devices. The device is discharged in one of the three discharge mode (constant current, constant power, or constant load). The device's voltage and current are plotted versus time. Other quantities such as power, energy, capacity... Different criteria can terminate the discharge process (see input).

```
<discharge_curve>
  <discharge_mode>constant_power</discharge_mode>
  <max_discharge_time>3600.0</max_discharge_time> <!-- second -->
  <discharge_power>0.8</discharge_power> <!-- watt -->
  <discharge_stop_at>voltage_lower_than</discharge_stop_at>
  <discharge_voltage_limit>0.7</discharge_voltage_limit> <!-- volt -->

  <initial_voltage>2.2</initial_voltage> <!-- volt -->
  <time_step>0.05</time_step> <!-- second -->
</discharge_curve>
```

4.2.2 Charge curve

The device is charge by applying a constant current. This is

4.2.3 Cyclic Charge-Discharge

Study how the energy storage device behaves as it stores and then release energy. The test starts either with a charge ot discharge step and repeats the charge-discharge process through a number of cycles.

Colombic efficiency and energy efficiency can be measured.

```
<cyclic_charge_discharge>
  <first_step>charge</first_step>
  <cycles>3</cycles>

  <charge_mode>constant_current</charge_mode>
  <charge_current>0.75</charge_current> <!-- ampere -->
  <charge_stop_at>voltage_greater_than</charge_stop_at>
  <charge_voltage_limit>2.7</charge_voltage_limit> <!-- volt -->
  <charge_rest_time>5.0</charge_rest_time> <!-- second -->

  <discharge_mode>constant_load</discharge_mode>
  <discharge_load>300.0</discharge_load> <!-- ohm -->
  <discharge_stop_at>voltage_lower_than</discharge_stop_at>
  <discharge_voltage_limit>1.1</discharge_voltage_limit> <!-- volt -->
  <discharge_rest_time>5.0</discharge_rest_time> <!-- second -->

  <initial_voltage>0.0</initial_voltage> <!-- volt -->
```

```
<time_step>0.05</time_step> <!-- second -->
</cyclic_charge_discharge>
```

Test uses constant current or constant power charging.

4.2.4 Ragone chart

Real capacitors have limitations on the power or current that can be drawn from them, mainly because of they present some electrical resistance that causes power-losses during discharge. Due to internal losses, the energy available for use is in general less than the energy stored in the ESD.

mainly used for a rough comparison of energy storage technologies across orders of magnitude in either power or energy capability.

```
<ragone_chart>
  <discharge_mode>constant_power</discharge_mode>
  <discharge_power_lower_limit>1.0e-6</discharge_power_lower_limit> <!-- watt -->
  <discharge_power_upper_limit>1.0e2</discharge_power_upper_limit> <!-- watt -->
  <steps_per_decade>6</steps_per_decade>

  <initial_voltage>2.7</initial_voltage> <!-- volt -->
  <discharge_stop_at>voltage_lower_than</discharge_stop_at>
  <discharge_voltage_limit>1.2</discharge_voltage_limit> <!-- volt -->

  <time_step>1800.0</time_step> <!-- second -->
  <min_steps_per_discharge>200</min_steps_per_discharge>
  <max_steps_per_discharge>300</max_steps_per_discharge>
</ragone_chart>
```

4.2.5 Cyclic Voltammetry

4.3 Finite element discretization

The finite element matrix formulation is derived in the usual fashion by multiplying the two potentials equations by test functions φ_i and integrating over the whole domain. It yields

$$(M + \Delta t K)\Phi^{n+1} = \Delta t f + M\Phi^n \quad (13)$$

where the unknown vector $\Phi = (\Phi_1, \Phi_2)^T$ contains the solid phase and electrolyte potentials at all nodes of the domain triangulation $\mathcal{T}^h(\Omega)$. The superscript n denotes the time discretization, $\Phi^n = \Phi(t^n)$ and $\Delta t = t^{n+1} - t^n$ is the time step. The approximation of the solution for the solid phase and electrolyte potentials at time $t = t^{n+1}$ are given by $\Phi_k^h(x, t^{n+1}) = \sum_j \Phi_{k,j}(t^{n+1})\varphi_{j,\Phi_k}(x)$, $k = 1, 2$. M is the mass matrix

$$M = \begin{pmatrix} \langle \varphi_{i,\Phi_1} | aC\varphi_{j,\Phi_1} \rangle_\Omega & -\langle \varphi_{i,\Phi_1} | aC\varphi_{j,\Phi_2} \rangle_\Omega \\ -\langle \varphi_{i,\Phi_2} | aC\varphi_{j,\Phi_1} \rangle_\Omega & \langle \varphi_{i,\Phi_2} | aC\varphi_{j,\Phi_2} \rangle_\Omega \end{pmatrix} \quad (14)$$

The stiffness matrix K is defined by

$$K = \begin{pmatrix} \langle \nabla \varphi_{i,\Phi_1} | \sigma \nabla \varphi_{j,\Phi_1} \rangle_\Omega & 0 \\ 0 & \langle \nabla \varphi_{i,\Phi_2} | \kappa \nabla \varphi_{j,\Phi_2} \rangle_\Omega \end{pmatrix} \quad (15)$$

The stiffness matrix may be modified to take into consideration the faradaic processes (linearized version of the Butler-Volmer kinetics).

$$K += \begin{pmatrix} \langle \varphi_{i,\Phi_1} | a \frac{a_{i0} F (\alpha_a + \alpha_c)}{RT} \varphi_{j,\Phi_1} \rangle_\Omega & -\langle \varphi_{i,\Phi_1} | \frac{a_{i0} (\alpha_a + \alpha_c) F}{RT} \varphi_{j,\Phi_2} \rangle_\Omega \\ -\langle \varphi_{i,\Phi_2} | \frac{a_{i0} F (\alpha_a + \alpha_c)}{RT} \varphi_{j,\Phi_1} \rangle_\Omega & \langle \varphi_{i,\Phi_2} | \frac{a_{i0} (\alpha_a + \alpha_c) F}{RT} \varphi_{j,\Phi_2} \rangle_\Omega \end{pmatrix} \quad (16)$$

The right-hand side f accounts for the prescribed solid current density on the cathode current collector tab (current divided by tab surface area)

$$f = \begin{pmatrix} \langle \varphi_{i,\Phi_1} | n \cdot \sigma \nabla \Phi_1 \rangle_{\partial\Omega} \\ 0 \end{pmatrix} \quad (17)$$

4.4 Verification

The exact transient solution for a supercapacitor under galvanostatic charge conditions is given in [?]. The model includes both double-layer charging and faradaic processes approximated with linear kinetics.

The overpotential and interfacial current density expressed dimensionless form, η^* and i_n^* respectively, are functions of the dimensionless current density δ , dimensionless exchange current density ν^2 , and the ratio of the solution phase to matrix phase conductivities β .

$$\delta = I \frac{FL}{\kappa RT}, \quad \nu^2 = \frac{a_{i0} (\alpha_a + \alpha_c) FL^2}{RT} \left(\frac{1}{\sigma} + \frac{1}{\kappa} \right), \quad \beta = \frac{\kappa}{\sigma}$$

$$\begin{aligned} \eta^* = & \frac{\delta(1 + \beta) \exp(-\nu^2 \tau)}{\nu^2} - \frac{\delta (\cosh(\nu[1 - X]) + \beta \cosh(\nu X))}{\nu \sinh(\nu)} \\ & + 2\delta \sum_{n=1}^{\infty} \frac{\beta \cos(n\pi) + 1}{\nu^2 + n^2 \pi^2} \cos(n\pi X) \exp(-(n^2 \pi^2 + \nu^2) \tau) \end{aligned} \quad (18)$$

$$\begin{aligned} i_n^* = & -2\delta \sum_{n=1}^{\infty} \frac{\beta \cos(n\pi) + 1}{(\nu^2 + n^2 \pi^2)(\beta + 1)} n^2 \pi^2 \cos(n\pi X) \exp(-(n^2 \pi^2 + \nu^2) \tau) \\ & - \frac{\delta \nu (\cosh(\nu[1 - X]) + \beta \cosh(\nu X))}{(\beta + 1) \sinh(\nu)} \end{aligned} \quad (19)$$

with

$$X = \frac{x}{L}, \quad \tau = \frac{t}{aC(1/\kappa + 1/\sigma)L^2}, \quad \eta^* = \frac{\eta F}{RT}. \quad (20)$$

The potential drop across the porous electrode is computed as

$$V^* = \frac{\eta^*|_{X=0} + \beta\eta^*|_{X=1} - \delta\beta}{1 + \beta} \quad (21)$$

The total voltage (two porous electrode with a separator between them) can be evaluated using

$$U = 2\frac{RT}{F}V^* + I\frac{L_s}{\kappa} \quad (22)$$

where L_s is the thickness of the separator. Electrical resistivity in the current collectors is very low. Their contribution to the total voltage is not accounted for in the exact solution. It is assumed that there is little or no effect on the verification procedure.

The following input is used for the energy storage device.

```
<geometry>
  <electrode_width>50.0e-6</electrode_width> <!-- metre -->
  <separator_width>25.0e-6</separator_width> <!-- metre -->
  <collector_width>5.0e-6</collector_width> <!-- metre -->
  <sandwich_height>25.0e-6</sandwich_height> <!-- metre -->
  <tab_height>5.0e-6</tab_height> <!-- metre -->
</geometry>
<material_properties>
  <differential_capacitance>0.03134</differential_capacitance> <!-- farad per square metre -->
  <separator_void_volume_fraction>0.6</separator_void_volume_fraction>
  <electrode_void_volume_fraction>0.67</electrode_void_volume_fraction>
  <electrolyte_conductivity>0.067</electrolyte_conductivity> <!-- siemens per metre -->
  <solid_phase_conductivity>52.1</solid_phase_conductivity> <!-- siemens per metre -->
  <collector_electrical_resistivity>28.2e-9</collector_electrical_resistivity> <!-- ohm metre -->
  <bruggemans_coefficient>1.5</bruggemans_coefficient>
  <electrode_tortuosity_factor>2.3</electrode_tortuosity_factor>
  <separator_tortuosity_factor>1.29</separator_tortuosity_factor>
  <pores_characteristic_dimension>1.5e-9</pores_characteristic_dimension> <!-- metre -->
  <pores_geometry_factor>2.0</pores_geometry_factor>
  <exchange_current_density>0.7463e-5</exchange_current_density> <!-- ampere per square metre -->
</material_properties>
```

The supercapacitor, initially fully discharged, undergoes constant current charge at 5 mA which correspond to a total current density $I = 200 \text{ A/m}^2$ throughout the electrode. This yields $\delta = 19.8191$, $\nu^2 = 0.0495684$, and $\beta = 0.000374614$. The voltage U at time $t = 0.1 \text{ s}$ is computed as the grid resolution is increased.

The discretization error is calculated using the exact transient solution given above in Eq. (22).

$$\text{error } \% = \left| \frac{U_{\text{computed}} - U_{\text{exact}}}{U_{\text{exact}}} \right| \times 100 \quad (23)$$

In order to ensure that temporal discretization error does not interfere in the spatial convergence study, the time step Δt is refined until a plateau is

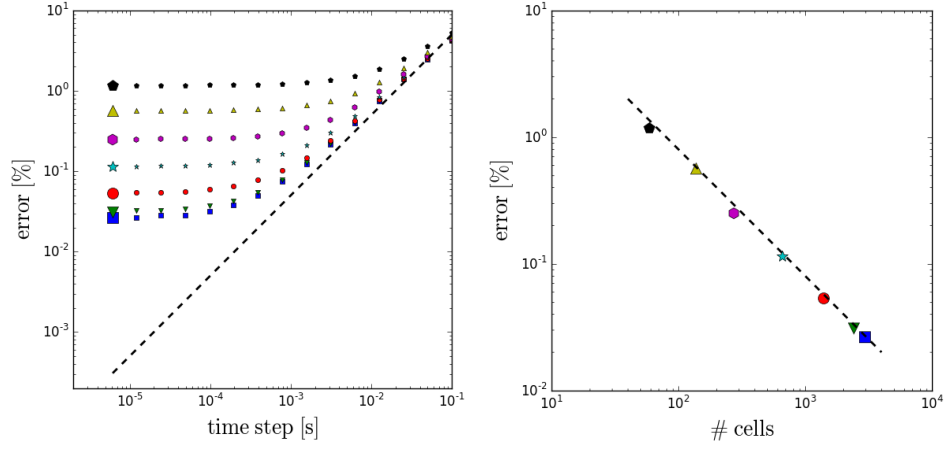


Figure 4: Discretization error in the total voltage with piecewise-linear basis function in 2-D. Left: Eliminating the temporal discretization errors. Right: Convergence of the spatial error.

reached, as can be seen on Fig. 4 on the left. The spatial error is then plotted against the number of grid cells in Fig. 4 (right). The results correspond to a two-dimensional problem ($d = 2$) using piecewise-linear basis functions φ_i (degree $p = 1$). The slope on the log-log graph is -1 which is the expected behavior $-(p + 1)/d$.

5 Results

6 Discussion