

Finite Volume Method

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1 Finite-Volume Method for Single Particle Model

Single Particle Model (SPM), is widely used in physics-based battery simulations. In SPM, the homogeneous method is simplified, assuming constant Li^+ concentrations in the electrolyte. Commonly, this method is defined by the following statements:

- Diffusion of lithium inside solid particles is the slowest process in a cell, so its dynamic contribution dominates. Mathematically these particle dynamics could be represented by:

$$\frac{\partial c_s^{+,-}(r,t)}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(D_s^{+,-} \cdot r^2 \cdot \frac{\partial c_s^{+,-}(r,t)}{\partial r} \right) \quad (1)$$

- So, can consider a SPM of a cell, modeling electrodes as a single spherical particle representative of a typical particle within the electrode.
 - Electrolyte concentration and potential dynamics are ignored.
- While crude, SPM is good learning tool for understanding how Li-Ion cells respond to different stimuli; can also be used to give good SOC estimates.
- To simulate SPM, introduce **Finite-Volume Method** (FVM) for discretizing diffusion equation
 - Particle is divided into equal-thickness spherical shells (like an idealized "onion").
 - Each time step, lithium flux from one shell to another is calculated, and the concentration of lithium within each shell is updated.

1.1 Finite-Volume simulation method

Towards FVM implementation, we should define the domain in which particle geometry is conceptualized, as well as the Li^+ flux throughout the electrode.

1.1.1 Geometry

- The particle is modeled with N_r equal-thickness shells
 - So, thickness of any given shell is:

$$dR = \frac{R_s}{N_r} \quad (2)$$

- Must know outer surface area and volume of each shell
 - Innermost shell has a volume $dV_1 = \frac{4}{3}\pi(dR)^3$, outer surface area $S_{a_1} = 4\pi(dR)^2$
 - Next has volume $dV_2 = \frac{4}{3}\pi(2dR)^3$, outer surface area $S_{a_2} = 4\pi(2dR)^2$
 - n th has volume $dV_n = \frac{4}{3}\pi(ndR)^3$, outer surface area $S_{a_n} = 4\pi(ndR)^2$
- The variables dV and S_a in the code are vectors containing volumes and outer surface areas of all shells, respectively.

1.1.2 Flux

In SPM, Li^+ flux does not depend on cell kinetics, due to SPM assumes electrolyte Li^+ constant concentrations.

- In this case, molar flux is converted from continuous function of distance r to discrete function at shell boundaries (units $mol m^{-2} s^{-1}$).

$$N = -D_s \nabla C_s = -D_s \frac{\partial C_s}{\partial r} \approx -D_s \frac{\Delta C_s}{\Delta r} \quad (3)$$

- Flux at boundary between shells n and $n + 1$ is

$$N_n \approx -D_s \frac{c_{n+1} - c_n}{dR} \quad (4)$$

- When N_n is negative, flux enters n th shell from $(n + 1)$ st shell; when it is positive, flux leaves n th shell to $(n + 1)$ st shell.
- The vector N in the code computes this flux at all shell boundaries, except at outer surface of particle, which is computed separately.
- Rate of material transfer equals N multiplied by the surface area of shell through which flux passes: vector M in code (units $mol s^{-1}$).

1.1.3 Concentration

Due to flux is defined by previous governing equations for particle dynamics, the concentration of it, can be represented by the following statements and expressions:

- Net Li^+ flux into n th shell is $S_{a_n} N_n - S_{a_{n-1}} N_{n-1}$ in ($mol s^{-1}$).
- Change in concentration multiplies this flux by Δt , divided by volume of n th shell ($mol s^{-3}$).
- At particle boundary, a flux j is applied (units $mol m^{-2} s^{-1}$).
 - Multiplying j by $S_{a_n} N_n \Delta t / V_n$ gives change in outer-shell concentration due to j .
- Assuming spherical geometries for particles with radius R_s , and representative volume fraction ϵ_s , it could be represented by volume averaging the subsequent specific inter-facial area a_s . Dividing the total surface area of spheres in a given volume by the total volume of a sphere.

$$a_s = \epsilon_s \frac{4\pi R_s^2}{\frac{4}{3}\pi R_s^3} = \frac{3\epsilon_s}{R_s} \quad (m^2 m^{-3}) \quad (5)$$

- Convert cell current from amperes to $mol s^{-1}$ (divide by Faraday constant F), using total surface area $a_s AL$, resulting in the next constant flux equation:

$$j = \frac{i_{app}}{a_s F A L} \quad (mol m^2 s^{-1}) \quad (6)$$

1.1.4 Voltage

- Finally, while SOC depends on average concentration of Li^+ in electrode, voltage depends on *surface* concentration of Li^+ .
- The code calls *cse*, which is what has been termed as $C_{s,e}$ elsewhere, representing **Surface Concentration**.
- When simulating cell using SPM, one particle models negative electrode and a second (using a copy of the code) models positive electrode.

- Cell voltage is then computed as $U_{ocp}^{pos}(y) - U_{ocp}^{neg}(x)$, where $y = \frac{C_{s,e}^+}{C_{s,max}^+}$ and $x = \frac{C_{s,e}^-}{C_{s,max}^-}$ respectively for each electrode. Being x and y , the variables that algebraically define electrode *Open Circuit Potential* (OCP) polynomials.
 - Thus, cell **SOC** can be related either to total amount of lithium in negative or positive electrodes (or, average concentration).
 - When the cell is fully charged, $\frac{C_{s,e}^+}{C_{s,max}^+} = y_{100\%}$ and $\frac{C_{s,e}^-}{C_{s,max}^-} = x_{100\%}$
 - When the cell is fully discharged, $\frac{C_{s,e}^+}{C_{s,max}^+} = y_{0\%}$ and $\frac{C_{s,e}^-}{C_{s,max}^-} = x_{0\%}$
 - State-of-charge varies linearly as electrode stoichiometry varies.

2 References