



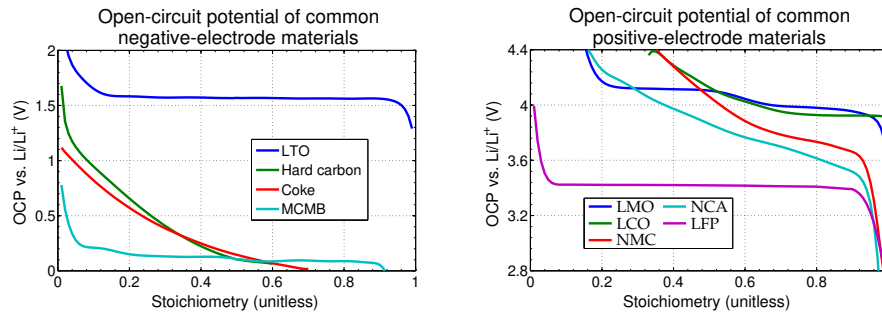
## Open-circuit voltage (OCV)

- While using PDEs in a BMS is unreasonable, some cell-level variables can be understood quite easily from them
  - In this lesson: OCP, capacity, SOC, (single-particle approximate) voltage
- Open-circuit voltage is steady-state terminal voltage when cell is allowed to rest
- Steady-state condition means that both  $c_{s,e}$  and  $c_e$  are uniform
- OCV can be related to *open-circuit potentials* of the electrodes  $U_{ocv}^{cell} = U_{ocv}^{pos} - U_{ocv}^{neg}$
- High cell voltages (for high energy density), require high positive-electrode potential and low negative-electrode potential (vs. Li/Li<sup>+</sup>)



## Example OCP curves

- OCP curves for common electrode materials plotted below



- Negative and positive plotted versus  $x = c_s^{neg} / c_{s,max}^{neg}$  and  $y = c_s^{pos} / c_{s,max}^{pos}$  where  $c_{s,max}^{reg}$  is amount of Li stored when electrode crystal lattice structure completely full



## Cell total capacity $Q$

- In “ideal” case, cell uses capacity from  $c_s = 0$  to  $c_s = c_{s,max}$
- Practical cells don't use entire range
  - Use only from  $x_{0\%}$  to  $x_{100\%}$  in negative and  $y_{0\%}$  to  $y_{100\%}$  in positive electrode
- In terms of physical cell-model parameter values,

$$Q^{neg} = AFL^{neg} \varepsilon_s^{neg} c_{s,max}^{neg} |x_{100\%} - x_{0\%}| / 3600 \text{ Ah}$$

$$Q^{pos} = AFL^{pos} \varepsilon_s^{pos} c_{s,max}^{pos} |y_{100\%} - y_{0\%}| / 3600 \text{ Ah}$$

- These capacities are matched, by definition of compatible  $x_{0\%}$ ,  $x_{100\%}$ ,  $y_{0\%}$ ,  $y_{100\%}$
- Notice that cell total capacity is not a function of temperature, rate, and so forth



## Cell state of charge (SOC)

- Cell SOC can be related either to total amount of lithium in negative or positive electrodes (or, average concentrations)
- When the cell is fully charged,  $c_{s,avg}^{neg}/c_{s,max}^{neg} = x_{100\%}$  and  $c_{s,avg}^{pos}/c_{s,max}^{pos} = y_{100\%}$
- When the cell is fully discharged,  $c_{s,avg}^{neg}/c_{s,max}^{neg} = x_{0\%}$  and  $c_{s,avg}^{pos}/c_{s,max}^{pos} = y_{0\%}$  (where  $x_{0\%} < x_{100\%}$  and  $y_{0\%} > y_{100\%}$ )
- State-of-charge varies linearly as electrode stoichiometry varies
- Therefore, we can compute cell-level state of charge  $z$  as either

$$z = \frac{c_{s,avg}^{neg}/c_{s,max}^{neg} - x_{0\%}}{x_{100\%} - x_{0\%}} = \frac{c_{s,avg}^{pos}/c_{s,max}^{pos} - y_{0\%}}{y_{100\%} - y_{0\%}}$$



## Single-particle model

- Diffusion of lithium inside solid particles is slowest process in a cell, so its dynamic contribution dominates
- So, can consider a single-particle model (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 input stimuli; can also be used to give good SOC estimates
- To simulate SPM, introduce finite-volume method for discretizing diffusion equation
  - Particle 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
  - Imposed cell current forces lithium into/out of the outermost shell



## Finite-volume simulation method (geometry)

- Particle modeled with  $N_r$  equal-thickness onion-like “shells”
  - So, thickness of any given shell is  $dR = R_s / N_r$
- Must know outer surface area and volume of each shell
  - Innermost shell has volume  $dV_1 = \frac{4}{3}\pi(dR)^3$ , outer surface area  $Sa_1 = 4\pi(dR)^2$
  - Next has volume  $dV_2 = \frac{4}{3}\pi(2dR)^3 - dV_1$ , outer surface area  $Sa_2 = 4\pi(2dR)^2$
  - $n$ th has volume  $dV_n = \frac{4}{3}\pi(n dR)^3 - \frac{4}{3}\pi((n-1)dR)^3$ , area  $Sa_n = 4\pi(n dR)^2$
- The variables  $dV$  and  $Sa$  in the code (coming up!) are vectors containing volumes and outer surface areas of all shells, respectively



## Finite-volume simulation method (flux)

- Now, convert molar flux from continuous function of distance  $r$  to discrete function at shell boundaries (units  $\text{mol m}^{-2} \text{s}^{-1}$ )

$$N = -D_s \nabla c_s = -D_s \frac{\partial c_s}{\partial r} \approx -D_s \frac{\Delta c_s}{\Delta r}$$

- Flux at boundary between shells  $n$  and  $n + 1$  is  $N_n \approx -D_s \frac{c_{n+1} - c_n}{\Delta R}$
- 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  $\mathbf{N}$  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  $\mathbf{N}$  multiplied by the surface area of shell through which flux passes: vector  $\mathbf{M}$  in code (units  $\text{mol s}^{-1}$ )



## Finite-volume simulation method (concentration)

- Net Li flux into  $n$ th shell is  $Sa_n N_n - Sa_{n-1} N_{n-1}$  ( $\text{mol s}^{-1}$ )
- Change in concentration multiplies this flux by  $\Delta t$ , divided by volume of  $n$ th shell ( $\text{mol m}^{-3}$ )
- At particle boundary, a flux  $j$  is applied ( $\text{mol m}^{-2} \text{s}^{-1}$ )
  - Multiplying  $j$  by  $Sa_n \Delta t / V_n$  gives change in outer-shell concentration due to  $j$
- Assuming particles spherical with radius  $R_s$ , have volume fraction  $\varepsilon_s$ , define

$$a_s = \frac{\text{total surface area of spheres in a given volume}}{\text{total volume of a sphere}} = \varepsilon_s \frac{4\pi R_s^2}{\frac{4}{3}\pi R_s^3} = \frac{3\varepsilon_s}{R_s} \text{ m}^2 \text{ m}^{-3}$$

- Convert cell current from A to  $\text{mol s}^{-1}$  (divide by  $F$ ), using total surface area  $a_s AL$ ,

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



## Finite-volume simulation method (voltage)

- Finally, while SOC depends on average concentration of Li in electrode, voltage depends on *surface* concentration of Li
- The code calls this  $c_{se}$ , which is what we have termed  $c_{s,e}$  elsewhere
- 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  $U_{\text{ocp}}^{\text{pos}}(y) - U_{\text{ocp}}^{\text{neg}}(x)$ , where  $y = c_{s,e}/c_{s,\text{max}}$  and  $x = c_{s,e}/c_{s,\text{max}}$



## SPM code: Setting up problem

- First segment of code sets up problem for one electrode
  - Initialize constants, input profile, geometry

```
R = 10e-6; % particle radius [m]
Cmax = 12000; % [mol/m^3]
c0 = 9500; % initial concentration [mol/m^3]
j0 = 5000*R/3/1800; % lithium flux [mol/m^2/sec]
D = 1e-14; % solid diffusivity, [m^2/s]

jk = [j0*ones(1,1800), zeros(1,3600)]; % discharge and rest
jk = [jk -jk]; % discharge and rest, then charge and rest

% Simulation control
Nr = 20; % number of "shells" radially
dR = R/Nr; % width of each "shell"
Sa = 4*pi*(R*(1:Nr)/Nr).^2; % outer surface area of each shell
dV = (4/3)*pi*((R*(1:Nr)/Nr).^3 - (R*(0:Nr-1)/Nr).^3); % vol. of ea. shell
dt = 1; % time steps of 1 second
```



## SPM code: Simulation loop

- Remainder of code simulates SPM over time
  - Initialize, loop through input profile, plot results

```
c = c0*ones(1,Nr); % initialize concentration profile versus "r" dimension
cse = zeros(size(jk)); % concentration at surface
cse(1) = c0;

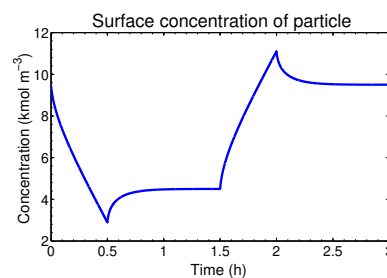
for timestep = 1:length(jk),
    N = -D*diff(c)/dR; % flux at surfaces between "bins"
    M = N.*Sa(1:end-1); % total moles crossing surfaces
    c = c + ([0 M] - [M 0])*dt./dV; % conc. change via diffusion
    c(end) = c(end) - jk(timestep)*Sa(end)*dt./dV(end); % at boundary
    cse(timestep+1) = c(end);
end

figure(1); clf; plot((0:length(jk))/3600, cse/1000);
title('Surface concentration of particle')
xlabel('Time (h)'); ylabel('Concentration (kmol m^{-3})')
```



## Summary

- In this lesson, you learned:
  - How to find OCV from electrode OCPs
  - How to compute total capacity and SOC
  - How to use finite-volume method to simulate a single particle
- Example output from sample code plotted to right
- To simulate full cell using SPM method, simulate two (positive, negative electrode) particles
  - Then, convert surface concentrations to OCPs
  - Then, compute voltage from OCPs





## For further study

- The single-particle model is presented in Chapter 3 of
  - Plett, Gregory L., *Battery Management Systems, Volume 1: Battery Modeling*
  - See also <http://mocha-java.uccs.edu/BMS1/index.html>.
- There are detailed lecture notes and lecture videos on the topics in this lesson from which you can learn at <http://mocha-java.uccs.edu/ECE5710/index.html> (Topics in section 3).