## Physics-based modeling approach

- Continuum porous-electrode models use physics to derive equations for all internal cell processes using coupled PDEs
- Following variables are of interest in cell:

  - Concentration of Li in solid, $c_s(x, r, t)$, particularly at surface of solid, $c_{s,e}(x, t)$,
  - Concentration of Li in electrolyte, $c_e(x, t)$,
  - Potential in solid, $\phi_s(x, t)$,
  - Potential in electrolyte, $\phi_e(x, t)$, and
  - Rate of lithium movement between phases, $j(x, t)$.

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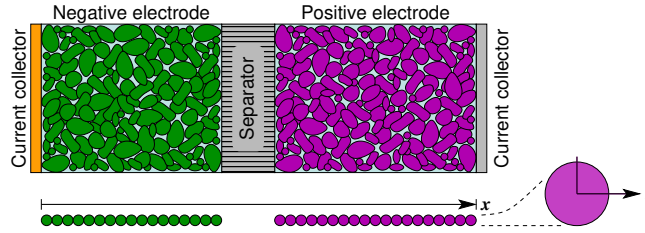
## The porous-electrode model

- These electrochemical variables can be found by solving coupled PDEs (along with associated boundary conditions)

  - Diffusion of Li in solid electrode particles $\frac{\partial}{\partial t} c_s = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s}{\partial r} \right)$
  - Electronic charge balance in particles: $\nabla \cdot (\sigma_{\text{eff}} \nabla \phi_s) = a_s F j$
  - Diffusion of lithium in electrolyte: $\frac{\partial(\varepsilon_e c_e)}{\partial t} = \nabla \cdot (D_{e,\text{eff}} \nabla c_e) + a_s(1 - t_+^0) j$
  - Ionic charge balance in electrolyte: $\nabla \cdot (\kappa_{\text{eff}} \nabla \phi_e + \kappa_{D,\text{eff}} \nabla \ln c_e) + a_s F j = 0$
  - Reaction rate (where $\eta = (\phi_s - \phi_e) - U_{\text{ocp}} - j F R_{\text{film}}$):

$$j = k_0 c_e^{1-\alpha} (c_{s,\max} - c_{s,e})^{1-\alpha} c_{s,e}{}^{\alpha} \left\{ \exp \left( \frac{(1-\alpha)F}{RT} \eta \right) - \exp \left( -\frac{\alpha F}{RT} \eta \right) \right\}$$

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## 1-d example of linear diffusion: time update

- Most model equations are essentially diffusion equations:
  $\frac{\partial c(x,t)}{\partial t} = \nabla \cdot (D \nabla c(x, t)) + f(x, t)$ where $c$ diffuses, $f$ forces
- To help visualize diffusion, let's consider the special case of 1-d diffusion
- Note, in 1-d, $\nabla \cdot (D \nabla c(x, t)) = \frac{\partial}{\partial x} D \frac{\partial}{\partial x} c(x, t)$, so

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}$$

- We can approximate the time derivative using Euler's forward rule

$$\frac{\partial c(x, t)}{\partial t} \approx \frac{c(x, t + \Delta t) - c(x, t)}{\Delta t}$$

# 1-d example of linear diffusion: space update

■ Can approximate the second spatial derivative using forward or backward rule (repeated), or central difference (C.D.) rule

$$\frac{\partial c(x,t)}{\partial x} \approx \frac{c(x+\Delta x, t) - c(x,t)}{\Delta x} \qquad \text{(Fwd.)}$$

$$\frac{\partial c(x,t)}{\partial x} \approx \frac{c(x,t) - c(x-\Delta x, t)}{\Delta x} \qquad \text{(Bkwd.)}$$

$$\frac{\partial^2 c(x,t)}{\partial x^2} \approx \frac{c(x+\Delta x, t) - 2c(x,t) + c(x-\Delta x, t)}{(\Delta x)^2} \qquad \text{(C.D.)}$$

■ Put together, using central-difference, we get

$$c(x, t+\Delta t) = c(x,t) + D\Delta t \frac{c(x+\Delta x, t) - 2c(x,t) + c(x-\Delta x, t)}{(\Delta x)^2}$$

■ This <u>finite difference</u> method requires care—stable only for certain $\Delta t$ and $\Delta x$

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# Code to simulate linear diffusion

■ Code implements C.D. method, mirroring at edges

```matlab
c = 1:32; % initial concentration gradient (mol/(m^3))
D = 2;    % diffusivity (m^2/s)
dt = 0.1; % time step (s)
dx = 1;   % x step (m)

figure(1); clf; colormap(jet(31));
for k = 0:1000,
  % finite-difference diffusion using explicit method, central differences
  c = c + D*dt/(dx^2)*([c(2:end) c(end)] - 2*c + [c(1) c(1:end-1)]);

  if mod(k,100) == 0, % plot a snapshot
    subplot(11,1,k/100+1); image(c); h = ylabel(sprintf('t = %g (s)',k*dt));
    set(gca,'ytick',[],'xticklabel',[],'ticklength',[0 0]); grid on
    set(gca,'xtick',1.5:1:100,'gridlinestyle','-','linewidth',4);
    set(h,'rotation',0,'horizontal','right','vertical','middle')
  end
end
xlabel('x location'); text(16,-14.25,'Diffusion example','horizontal','center');
```
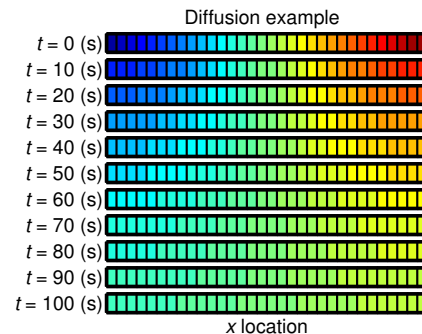
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# Example to demystify diffusion equation

■ At time $t = 0$, the figure shows a concentration gradient ranging from 1 to 32 across the $x$ dimension

■ As time advances, material flows from high- to low-concentration areas

■ By $t = 100$, concentration is nearly uniform

■ Diffusion is actually simple, even though the equation may look frightening

■ Now, you can glance at an equation like

$$\frac{\partial c(x,t)}{\partial t} = \nabla \cdot (D \nabla c(x,t)) + f(x,t)$$

and say "That's just a diffusion equation!"



Diffusion example

$t = 0$ (s)
$t = 10$ (s)
$t = 20$ (s)
$t = 30$ (s)
$t = 40$ (s)
$t = 50$ (s)
$t = 60$ (s)
$t = 70$ (s)
$t = 80$ (s)
$t = 90$ (s)
$t = 100$ (s)

$x$ location

## Summary

- "Porous-electrode" physics-based model of Li-ion battery cell comprises equations to describe:
  - Diffusion of Li in solid electrode particles via $c_s(x, r, t)$ and especially $c_{s,e}(x, t)$
  - Electronic charge balance in particles via $\phi_s(x, t)$
  - Diffusion of lithium in electrolyte via $c_e(x, t)$
  - Ionic charge balance in electrolyte via $\phi_e(x, t)$
  - Reaction rate via $j(x, t)$
- Battery-cell dynamics are dominated by diffusion effects
- While diffusion equation is complicated, actual phenomenon is simple to understand

## For further study

- The porous-electrode partial-differential-equation model presented at the beginning of this lesson is derived from physics first principles in Chapters 3 and 4 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 these topics from which you can learn at `http://mocha-java.uccs.edu/ECE5710/index.html` (Topics 3, 4).