Diffusion Limitations III

Lecture 15

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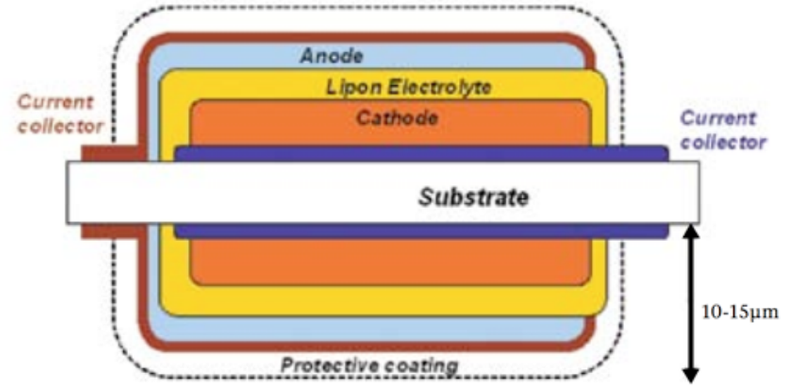
Intercalation in Thin-Film Electrodes

$$\frac{\partial c}{\partial t} = \nabla \cdot D \nabla c$$



Li^+

Li^+

Li^+ $\vec{J} = i_\circ$

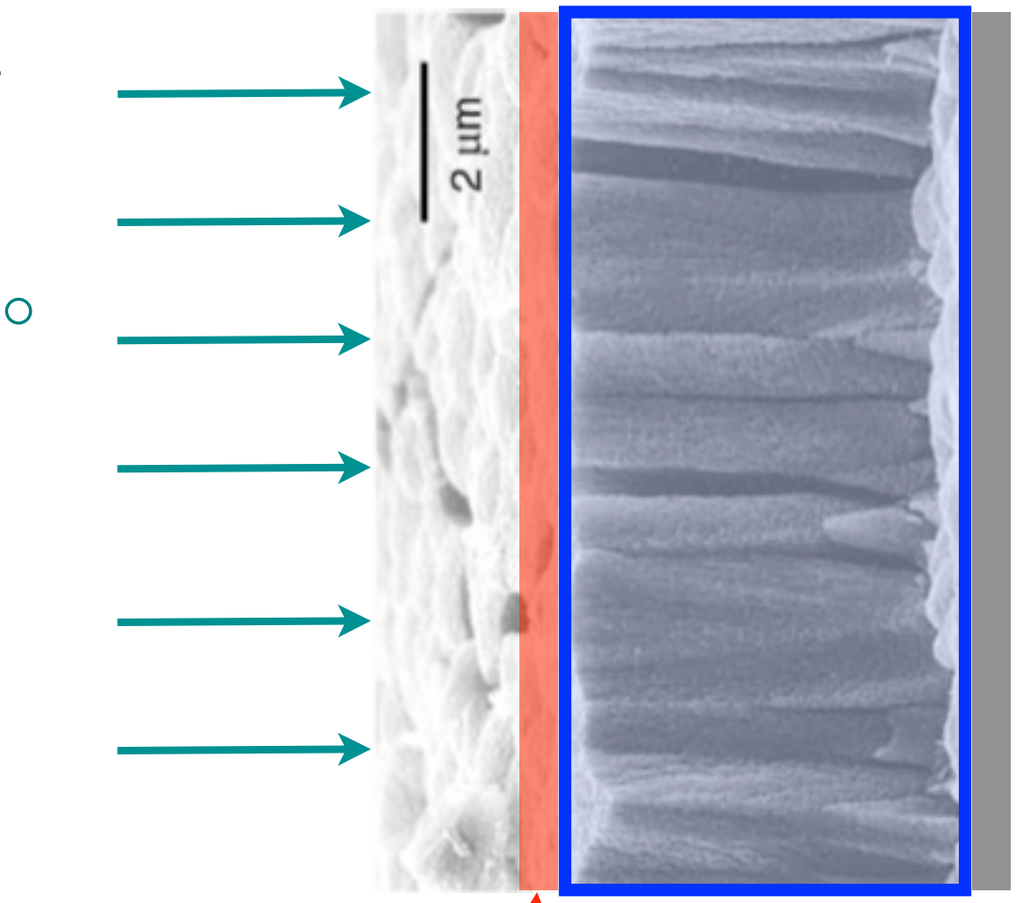
Li^+

Li^+

Li^+

Li^+

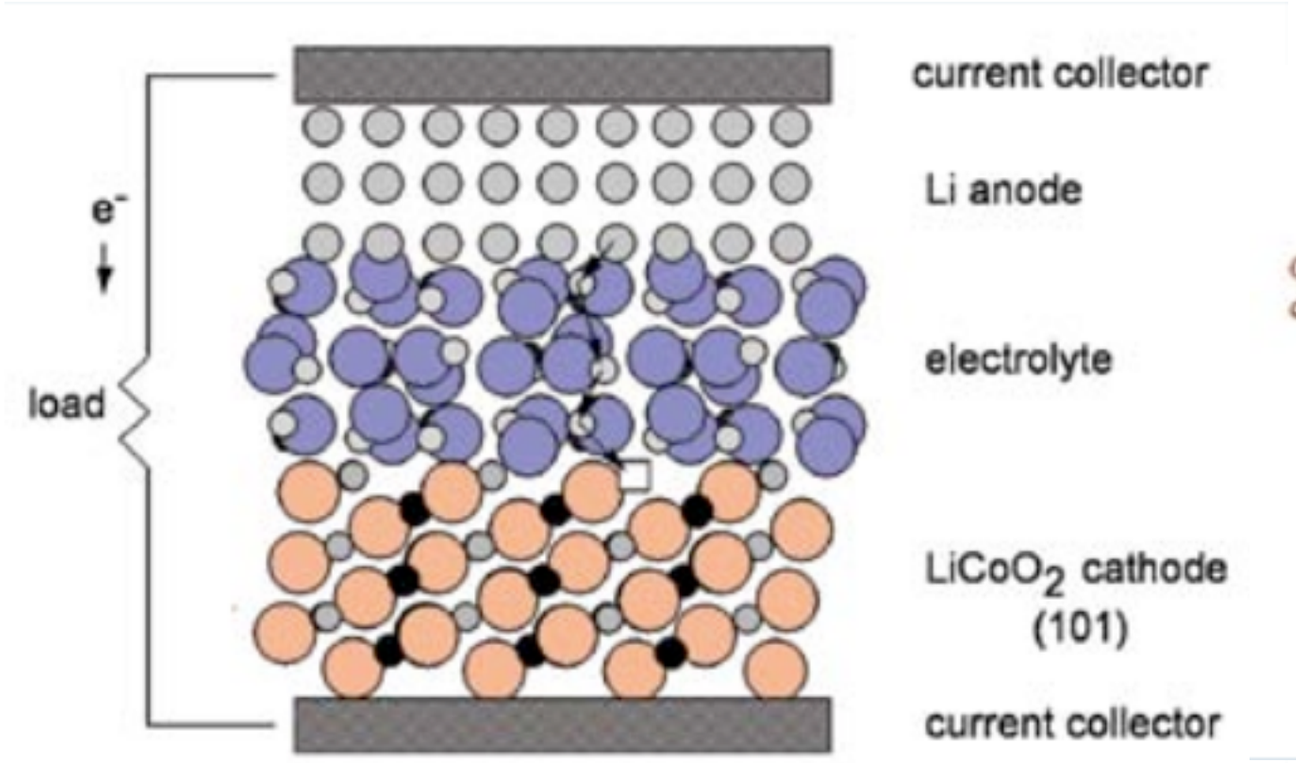
Li^+

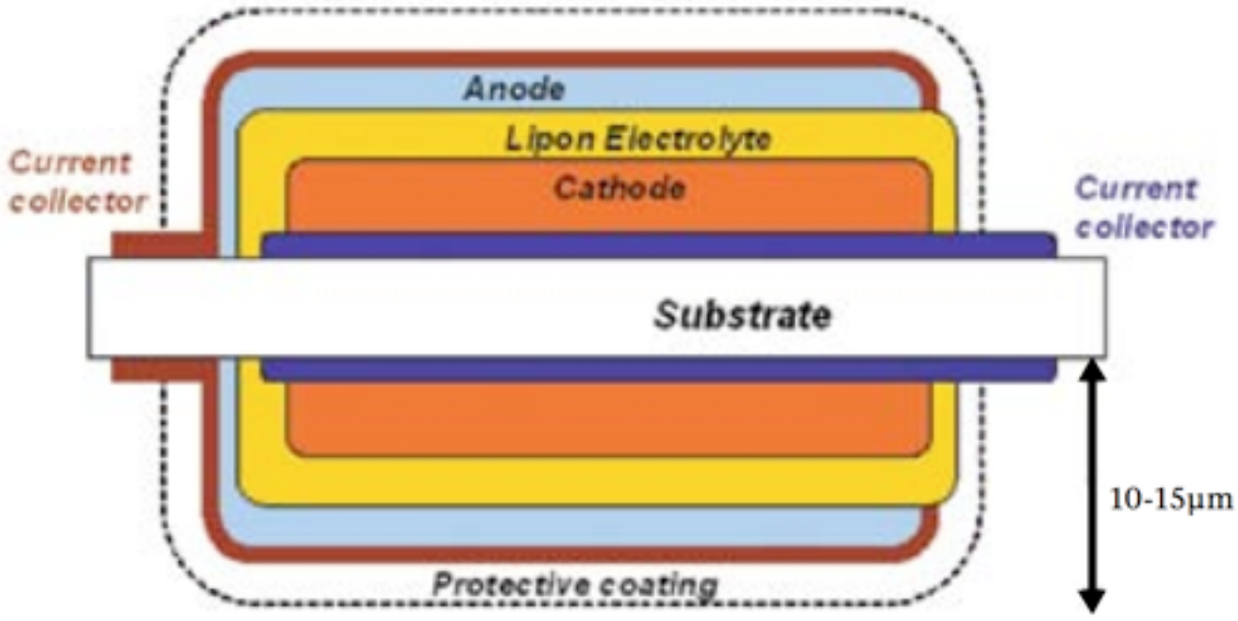


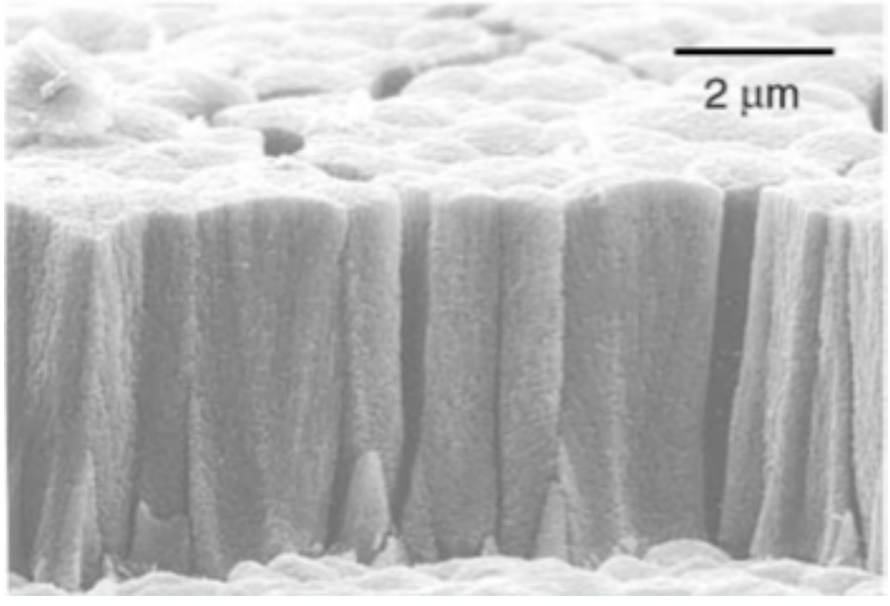
$\frac{\vec{J}}{zF} = \vec{N}$

h_c

Thin Film MicroBatteries



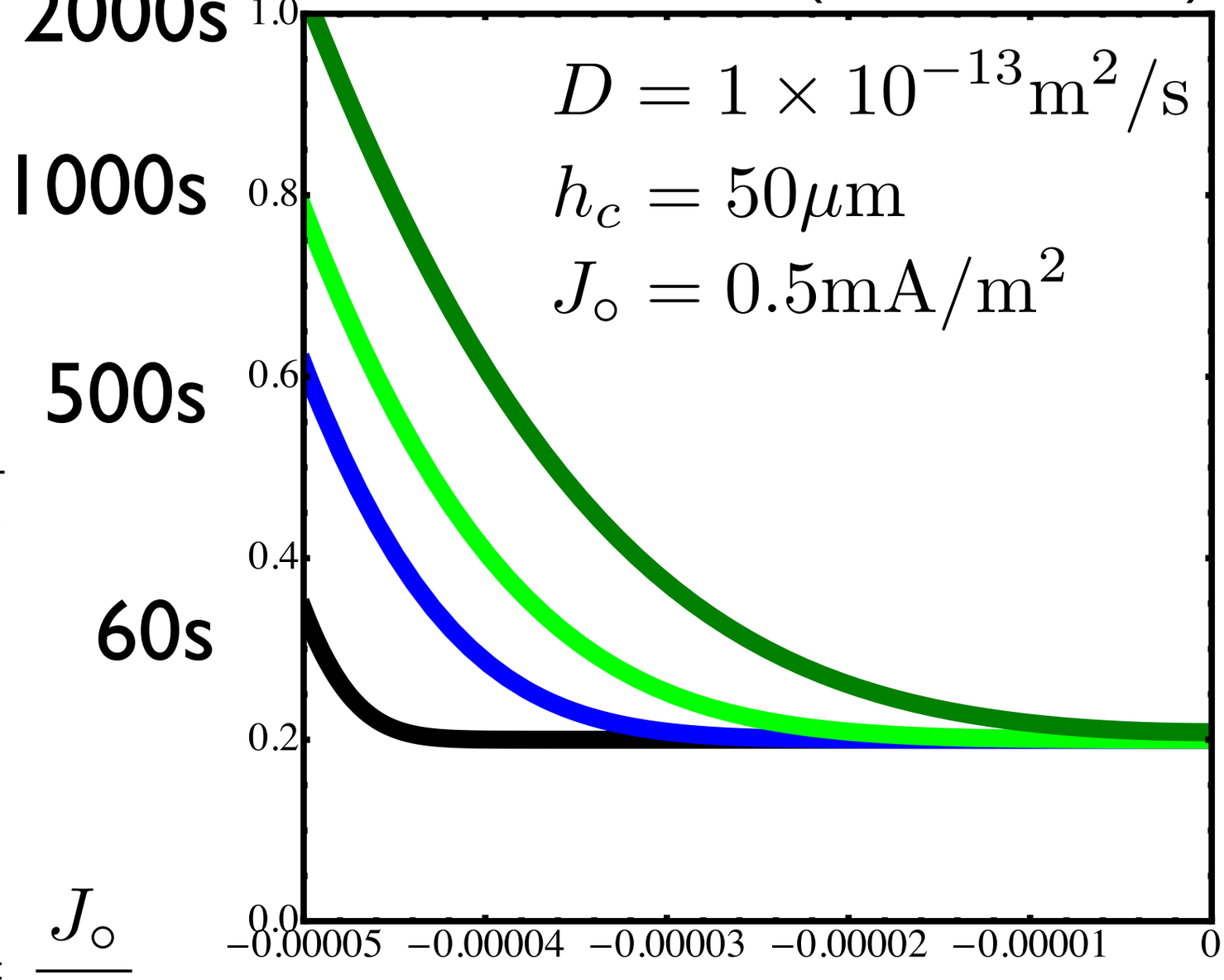


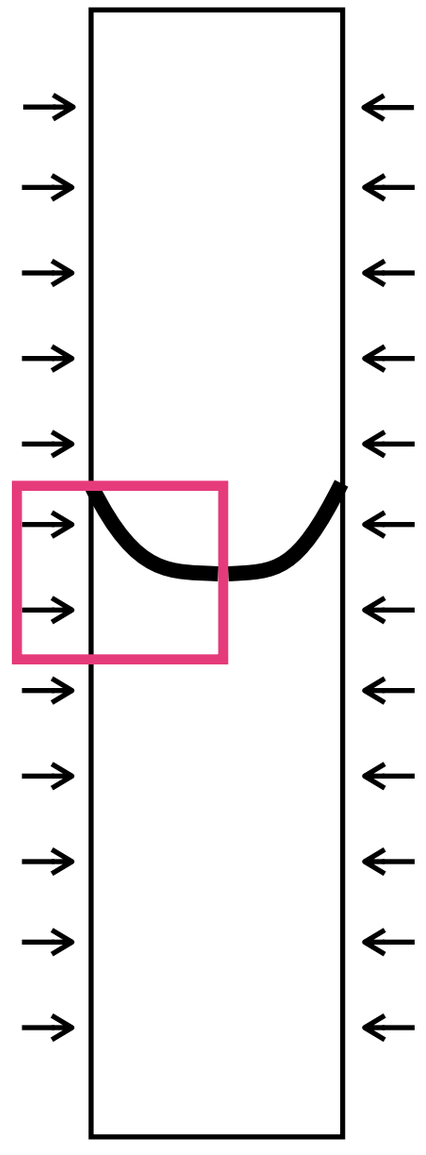


Platelets and Thin Films

$$c - c_\circ = \frac{N_\circ h_c}{D}\left(\frac{Dt}{h_c} + \frac{3x^2 - h_c^2}{6h_c^2} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-Dn^2\pi^2 t/h_c^2)\cos(\frac{n\pi x}{h_c})\right)$$

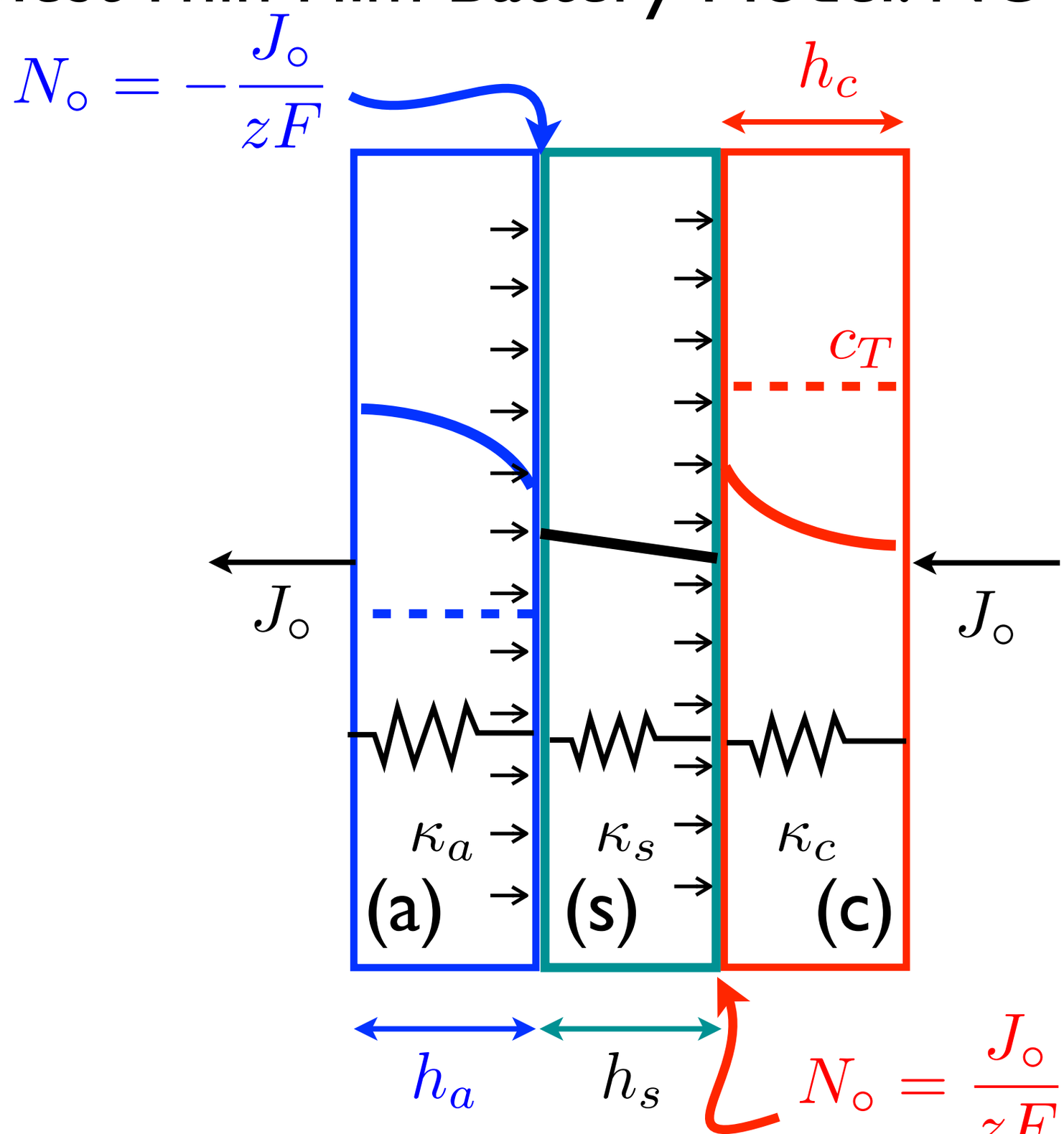
(100 terms)





$$N_\circ = \frac{J_\circ}{zF}$$

The Simplest Thin Film Battery Model: NO Reaction Zone



$$\phi = U_c(c(x = h_c, t)) - U_a(c(x = h_a, t)) - \frac{h_c}{\kappa_c} i - \frac{h_a}{\kappa_a} i - \frac{h_s}{\kappa_s} i$$

Major Results and Other Approximations

Total intercalated charge

$$Q = J_\circ A t_d \qquad \text{thin film}$$

$$Q = 2 J_\circ A t_d \qquad \text{platelet}$$

short time approximate solution, $t < \dfrac{h_c^2}{D}$

(can use error function solution)

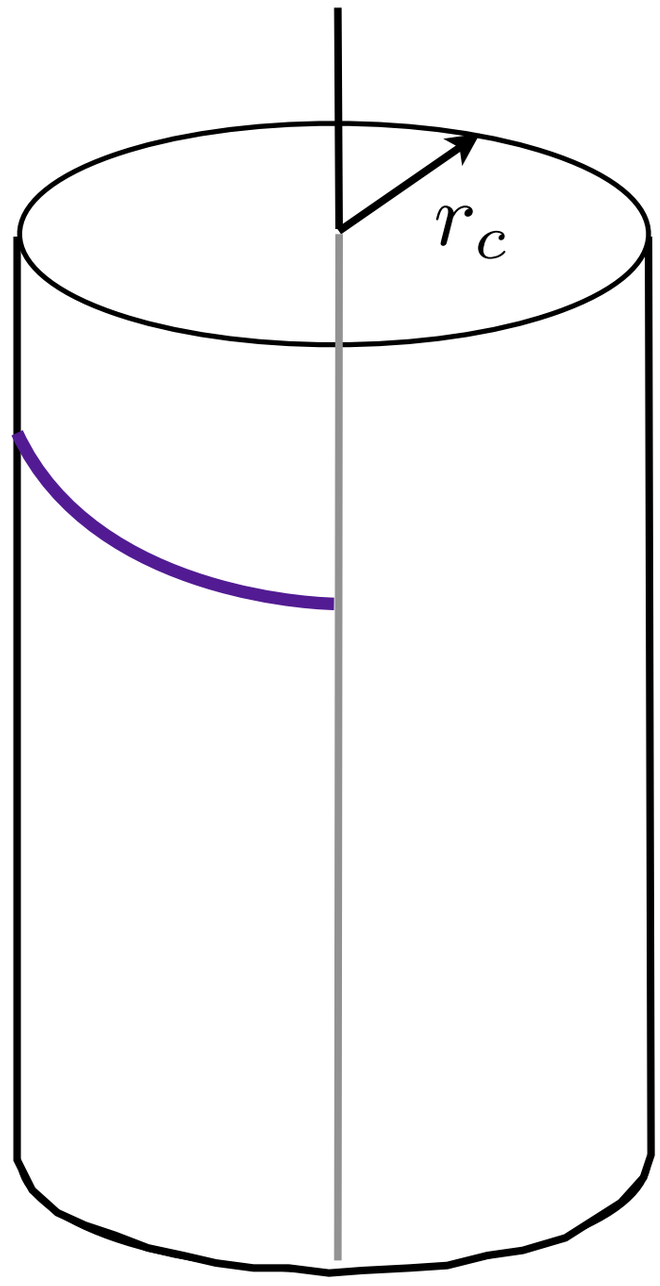
$$c(x = \pm h_c, t) \sim c_\circ + \frac{2 J_\circ t^{1/2}}{F \pi^{1/2} D^{1/2}}$$

Cylindrical Structures

$$c - c_\circ = -\frac{N_\circ r_c}{D}\left(\frac{2Dt}{r_c^2} + \frac{r^2}{2r_c^2} - \frac{1}{4} - 2\sum_{n=1}^{\infty}\exp(-D\alpha_n^2 t/r_c^2)\frac{J_\circ(r\alpha_n/r_c)}{\alpha_n^2 J_\circ(\alpha_n)}\right)$$

Effective intercalated charge

$$Q = 2\pi r_c l J_\circ t_d$$



short time approximate solution, $t < \frac{r_c^2}{D}$

$$c(x = r_c, t) \sim c_\circ + \frac{2J}{F}\left(\frac{t}{D}\right)^{1/2}$$

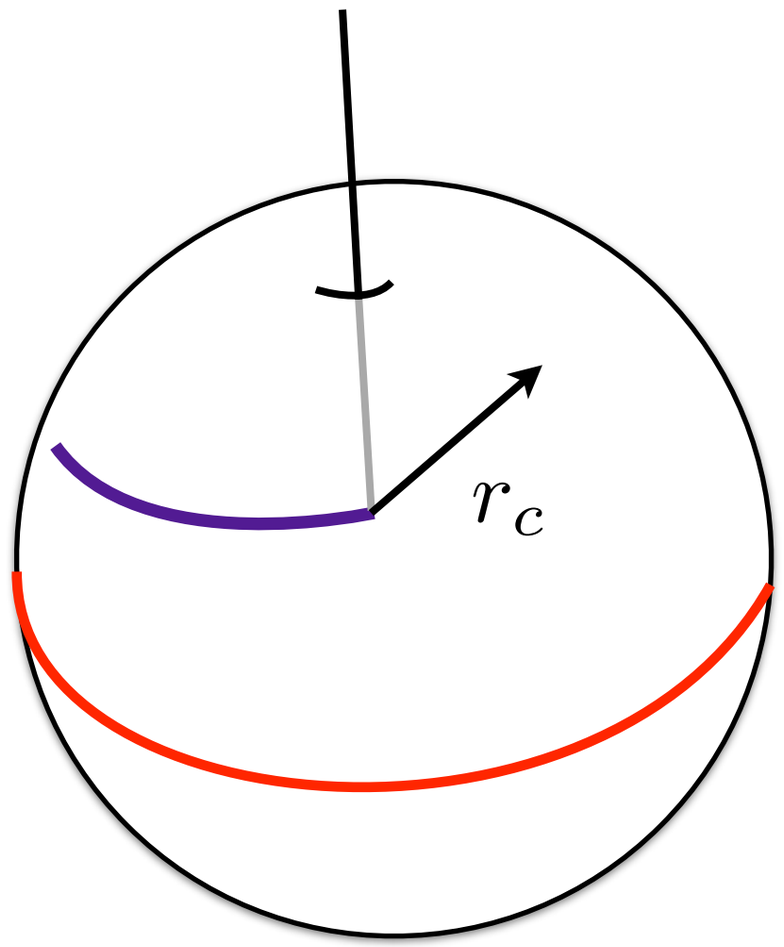
$$N_\circ = \frac{J_\circ}{zF}$$

Spherical Particles

$$c - c_\circ = \frac{N_\circ r_c}{D}\left(\frac{3Dt}{r_c^2} + \frac{r^2}{2r_c^2} - \frac{3}{10} - 2\frac{r_c}{r}\sum_{n=1}^{\infty}\exp(-D\alpha_n^2 t)\frac{\sin(r\alpha_n)}{\alpha_n^2 r_c^2 \sin(\alpha_n r_c)}\right)$$

Effective intercalated charge

$$Q = \pi r_c^2 J_\circ t_d$$



short time approximate solution, $t < \frac{r_c^2}{D}$

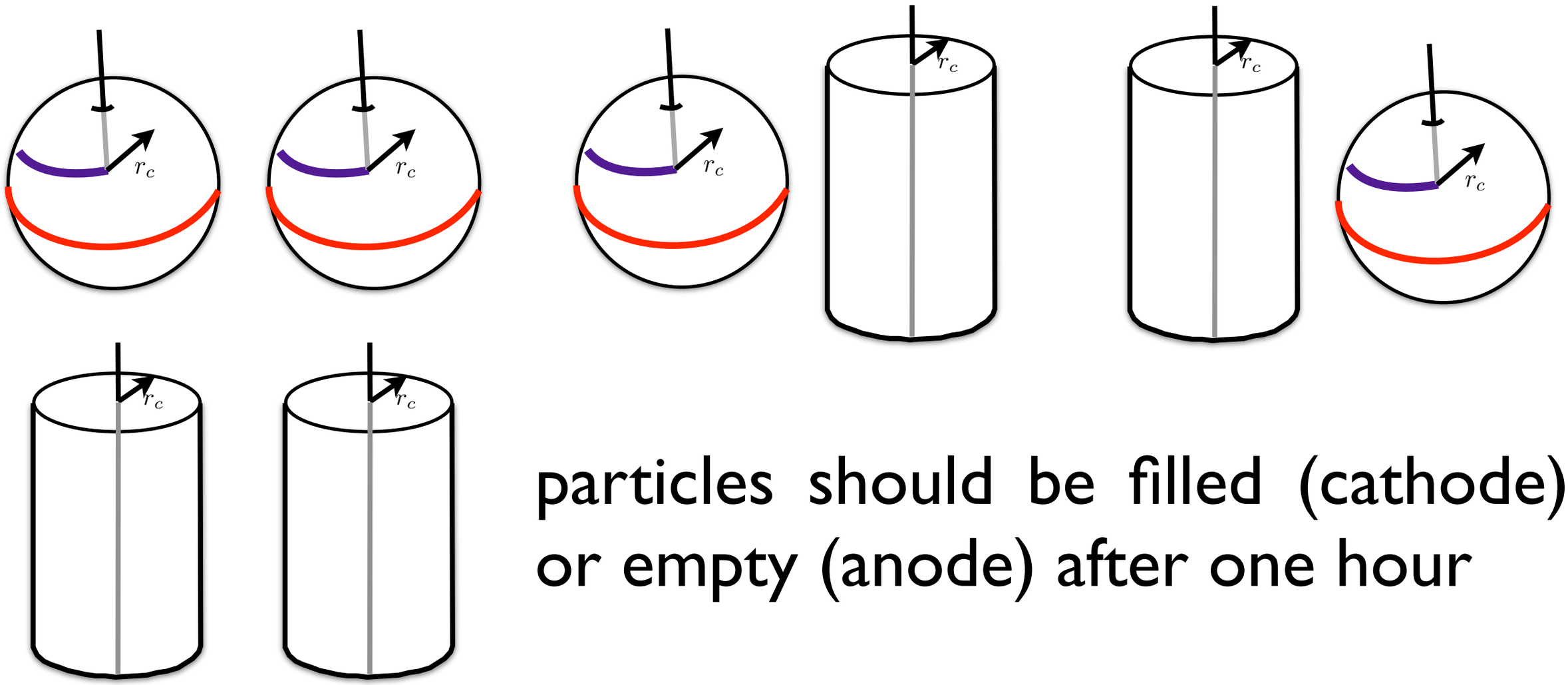
$$c(x = r_c, t) \sim c_\circ + \frac{3J}{F}\left(\frac{t}{D}\right)^{1/2}$$

$$N_\circ = \frac{J_\circ}{zF}$$

Typical Diffusion Values in Lithium-Ion Batteries

material	value (m^2/s)	limit [mol/m^3]
graphite	5×10^{-13}	28464
$LiMn_2O_4$	1×10^{-13}	23720
$LiCoO_2$	1×10^{-15} to 5×10^{-16}	51555
$LiFePO_4$	1×10^{-14} to 1×10^{-20}	237
$LiPF_6$ in EC/DMC	9×10^{-11} to 2.58×10^{-10}	4744

Effective Particle Architectures



particles should be filled (cathode) or empty (anode) after one hour

material	value (m^2/s)	limit [mol/m^3]
graphite	5×10^{-13}	28464
$LiMn_2O_4$	1×10^{-13}	23720