Transport in Rechargeable Batteries

Lecture 21

(in all its glory)

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Transferring Charge to the Particles

Current density is distributed among the particles of active material

Effective current density per particle in porous media

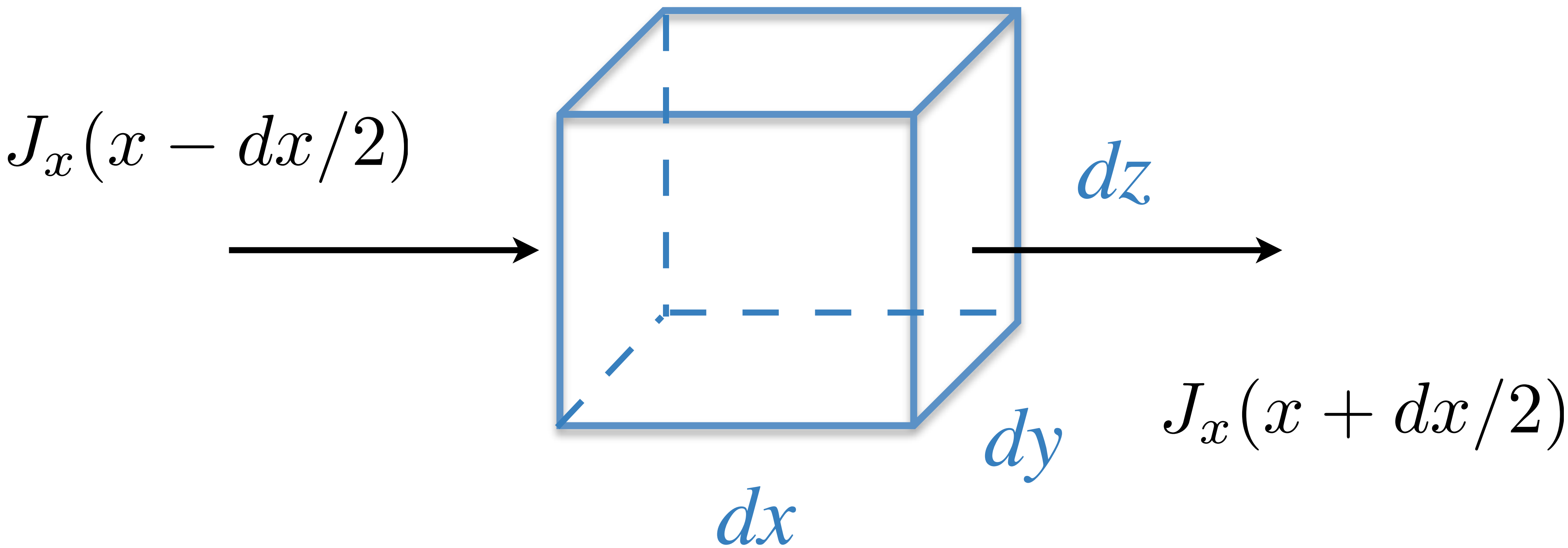
$$a = \frac{\text{area per particle}}{\text{volume per particle}} \times \text{fraction of active material}$$

$$a = \frac{4\pi r_p^2}{\frac{4}{3}\pi r_p^3}(1-\epsilon) \qquad a = \frac{3(1-\epsilon)}{r_p}$$

Current per particle

$$I_\circ^p = I_\circ / a$$

Equations of Continuity



$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{J}_\rho \qquad \frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{J}_i$$

Entropy Generation and the Second Law

$$\dot{\sigma} = \frac{\partial s}{\partial t} + \nabla \cdot \vec{J}_s \geq 0$$

At equilibrium:

$$\dot{\sigma} = 0$$

Away from equilibrium:

$$\dot{\sigma} > 0$$

Joule heating redefined as:

$$\dot{Q} = T\dot{\sigma}$$

Local Equilibrium and Entropy Maximization

Assume that first + second law applies at the volume element level

$$du = T ds + \sum_{i=1}^{N} \mu_i dc_i + \phi d\rho$$

Try to account for how much "stuff" accumulates:

$$\frac{\partial u}{\partial t} = T \frac{\partial s}{\partial t} + \sum_{i=1}^{N} \mu_i \frac{\partial c_i}{\partial t} + \phi \frac{\partial \rho}{\partial t}$$

We want to know how the material is dissipating heat!

$$\frac{\partial s}{\partial t} = -\frac{1}{T} \frac{\partial u}{\partial t} + \sum_{i=1}^{N} \frac{\mu_i}{T} \frac{\partial c_i}{\partial t} + \frac{\phi}{T} \frac{\partial \rho}{\partial t}$$

Local Equilibrium and Entropy Maximization

Use continuity Equations:

$$\frac{\partial s}{\partial t} = -\frac{1}{T}\nabla \cdot \vec{J}_u + \sum_{i=1}^{N} \frac{\mu_i}{T}\nabla \cdot \vec{J}_i + \frac{\phi}{T}\nabla \cdot \vec{J}_\rho$$

remember

$$A\nabla\vec{B} = -\vec{B}\cdot\nabla A + \nabla\cdot(A\vec{B})$$

$$\frac{\partial s}{\partial t} = \dot{\sigma} - \nabla \cdot \vec{J}_s$$

$$\vec{J}_s = \frac{1}{T}\left(-\vec{J}_u + \sum_{i=1}^{N} \frac{\mu_i}{T}\vec{J}_i + \frac{\phi}{T}\vec{J}_\rho\right)$$

$$\dot{\sigma} = \nabla\frac{1}{T}\cdot\vec{J}_u - \sum_{i=1}^{N}\nabla\frac{\mu_i}{T}\cdot\vec{J}_i - \nabla\frac{\phi}{T}\cdot\vec{J}_\rho$$

Fluxes and Conjugate Forces

Flux Quantity	Conjugate Force	Empirical Law
$\vec{J}_Q$ (heat)	$-\frac{1}{T^2}\nabla T$	$\vec{J}_Q = -K\nabla T$ (Fick's second law)
$\vec{J}_i$ (mass)	$-\nabla \mu$	$\vec{J}_i = -M_i c_i \nabla \mu_i$ (Fick's second law)
$\vec{J}_\rho$ (charge)	$-\nabla \phi$	$\vec{J}_\rho = -\kappa\nabla \phi$ (Ohm's law)

Fluxes and Driving Forces

$$J_Q = J_Q(F_Q, F_\rho, F_1, ..., F_N, ...)$$

Assume "small" deviations from equilibrium

$$J_Q = \frac{\partial J_Q}{\partial F_Q} F_Q + \frac{\partial J_Q}{\partial F_\rho} F_\rho + \frac{\partial J_Q}{\partial F_1} F_1 + ... + \frac{\partial J_Q}{\partial F_N} F_N + ...$$

$$J_\rho = \frac{\partial J_\rho}{\partial F_Q} F_Q + \frac{\partial J_\rho}{\partial F_\rho} F_\rho + \frac{\partial J_\rho}{\partial F_1} F_1 + ... + \frac{\partial J_\rho}{\partial F_N} F_N + ...$$

$$J_1 = \frac{\partial J_1}{\partial F_Q} F_Q + \frac{\partial J_1}{\partial F_\rho} F_\rho + \frac{\partial J_1}{\partial F_1} F_1 + ... + \frac{\partial J_1}{\partial F_N} F_N + ...$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$J_N = \frac{\partial J_N}{\partial F_Q} F_Q + \frac{\partial J_N}{\partial F_\rho} F_\rho + \frac{\partial J_N}{\partial F_1} F_1 + ... + \frac{\partial J_N}{\partial F_N} F_N + ...$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

The Onsager Matrix

$$\begin{pmatrix} J_Q \\ J_\rho \\ J_1 \\ . \\ . \\ . \\ J_N \\ .. \end{pmatrix} = \begin{pmatrix} L_{QQ} & L_{Q\rho} & L_{Q1} & ... & L_{QN} & ... \\ L_{\rho Q} & L_{\rho\rho} & L_{\rho 1} & ... & L_{\rho N} & ... \\ L_{1Q} & L_{1\rho} & L_{11} & ... & L_{1N} & ... \\ \vdots & & \ddots & ... & \vdots & ... \\ L_{NQ} & L_{N\rho} & L_{N1} & ... & L_{NN} & ... \end{pmatrix} \begin{pmatrix} F_Q \\ F_\rho \\ F_1 \\ . \\ . \\ . \\ F_N \\ .. \end{pmatrix}$$

$$\vec{J} = \overleftrightarrow{L} \vec{F}$$

Onsager's Symmetry Principle

The Entropy production is non-negative if and only if:

$$L_{\alpha\beta} = L_{\beta\alpha}$$

or

$$\frac{\partial J_\alpha}{\partial F_\beta} = \frac{\partial J_\beta}{\partial F_\alpha}$$

or

$$|| \overleftrightarrow{L} || > 0$$

Irreversible Thermodynamics Consequences

- Ionic character favors the appearance of electromigration effects that accelerate intercalation during discharge and work against it during recharge
- Heat dissipation induces chemical diffusion to undesirable places
- Mass diffusion can be slowed down by mass diffusion (!)

Interdiffusion of Charged Species

$$\vec{J}_1 = -M_1 \nabla \mu_1 - z_1 F M_1 \nabla \phi - \sum_{j=1, j \neq 1}^{N} M_{1j} \nabla \mu_j$$

diffusion term

electromigration

osmotic pressure or chemical wind

$$\vdots \qquad \vdots \qquad \vdots$$

$$\vec{J}_i = -M_i \nabla \mu_i - z_i F M_i \nabla \phi - \sum_{i=1, j \neq i}^{N} M_{ij} \nabla \mu_j$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\vec{J}_N = -M_i \nabla \mu_N - z_N F M_N \nabla \phi - \sum_{j=1, j \neq N}^{N} M_{Nj} \nabla \mu_j$$

Electrical and Ionic Conductivity

$$\vec{J}_\rho = -\sigma_T \nabla \phi - \sum_{i=1}^{N} z_i F M_i \nabla \mu_i$$

conductivity term

electromigration

linear superposition of conductivities

$$\sigma_T = \sigma_1 + \sigma_2 + \ldots + \sigma_N$$

ionic conductivity

$$\sigma_i = \frac{(z_i F)^2 D_i c_i}{RT}$$

transference number

$$t_i = \frac{\sigma_i}{\sigma_T} \qquad \sigma_i = t_i \sigma_T$$