Multiscale Modelling of Li-batteries

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Homogenisation in Disordered Media
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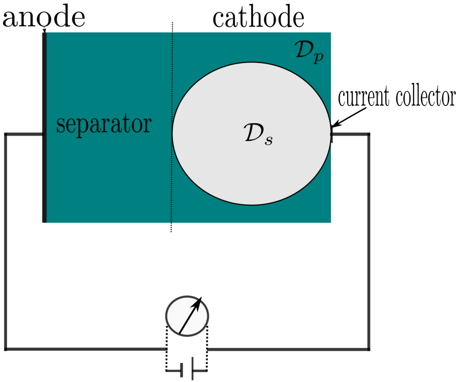
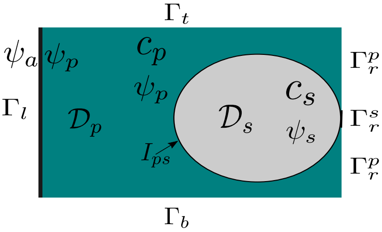
Problem formulation

A fundamental simple Li-battery setup



- $\mathcal{D}_s$ a single intercalation host
- $\mathcal{D}_p$ a binary polymer electrolyte as separator
- a lithium foil as anode

Interfacial reactions



The Butler-Volmer equations account for interfacial reactions on I_{ps} and Γ_l, i.e.,

- Anodic Butler-Volmer equation:

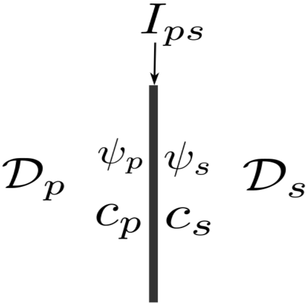
$$\boxed{i_{BV}^l = i_l R_{BV}^l = i_l\left(\mathrm{e}^{\left(\frac{\alpha_{a_l} F \eta_a}{R\theta}\right)} - \mathrm{e}^{\left(-\frac{\alpha_{c_l} F \eta_a}{R\theta}\right)}\right)}$$

- $i_l = F k_{a_l}^{\alpha_{c_l}} k_{c_l}^{\alpha_{a_l}} \left(c_p^m - c_p\right)^{\alpha_{a_l}} \left(c_p\right)^{\alpha_{c_l}}$ is the exchange current density
- $\eta_a = \psi_a - \psi_p$

- Cathodic Butler-Volmer equation:

$$\boxed{i_{BV}^{ps} = i_{ps} R_{BV}^{ps} = i_{ps}\left(\mathrm{e}^{\frac{\alpha_a F}{R\theta}(\eta_{ps}-U)} - (c_s^m - c_s)\mathrm{e}^{-\frac{\alpha_c F}{R\theta}(\eta_{ps}-U)}\right)}$$

- $i_{ps} = F k_{ps}\left(c_p^m - c_p\right)^{\alpha_c} c_p^{\alpha_a}$
- $U = 2.17 + \frac{R\theta}{F}(-0.000558 c_s + 8.1)$ [Doyle 1993]
- $\eta_{ps} = \psi_s - \psi_p$

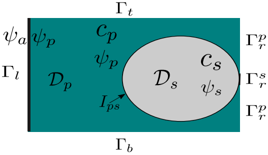


Current-driven battery

Let $\mathcal{D}_p$ be an electrically neutral, dilute, and binary electrolyte

- Charge transport in $\mathcal{D}_p$

$$
\begin{cases}
\frac{\partial c_p}{\partial t} = \Delta c_p & \text{in } \mathcal{D}_p \\
\nabla c_p \cdot \mathbf{n} = \beta_l R^l_{BV} & \text{on } \Gamma_l, \\
\nabla c_p \cdot \mathbf{n} = 0 & \text{on } \Gamma_t \cup \Gamma_b \cup \Gamma^p_r \\
\nabla c_p \cdot \mathbf{n} = \beta_{ps} R^{ps}_{BV} & \text{on } I_{ps} \\
-\mathrm{div}\left(c_p \nabla \psi_p\right) = -\mathcal{R}\Delta c_p & \text{in } \mathcal{D}_p \\
\psi_p = -\eta_a & \text{on } \Gamma_l \\
\nabla \psi_p \cdot \mathbf{n} = \frac{\epsilon_\mathbf{s}}{\epsilon_\mathbf{p}} \nabla \psi_\mathbf{s} \cdot \mathbf{n} & \text{on } I_{ps}
\end{cases}
$$



- $\beta_l = \frac{i_l L_r}{c_r D_p}$
- $\tilde{\psi} := \frac{F\psi}{R\theta}$
- $\eta_a := \psi_a - \psi_p$
- $\tilde{\mathcal{R}} := \frac{R\theta}{F} \frac{D_+ - D_-}{(z_+ M_+ - z_- M_-)F}$

- Intercalation into the solid host $\mathcal{D}_s$

Classical diffusion

$$\begin{cases} a_1 \frac{\partial c_s}{\partial t} = \Delta c_s & \text{in } \mathcal{D}_s \\ \nabla c_s \cdot \mathbf{n} = -\beta_{ps} R_{BV}^{ps} & \text{on } I_{ps} \\ \nabla c_s \cdot \mathbf{n} = 0 & \text{on } \Gamma_r^s \\ -\mathrm{div}\big(\sigma_s \nabla \psi_s\big) = 0 & \text{in } \mathcal{D}_s \\ \sigma_s \nabla \psi_s \cdot \mathbf{n} = \beta_\psi R_{BV}^{ps} & \text{on } I_{ps} \\ \nabla \psi_s \cdot \mathbf{n} = r_s C \frac{I_a}{|\Gamma_r^s|} & \text{on } \Gamma_{\mathrm{r}}^{\mathrm{s}} \end{cases}$$

- $a_1 := \frac{\tau_s}{\tau_p}$
- $\beta_{ps} = \frac{i_{ps} L_r}{D_r c_r}$
- $\tilde{\sigma}_s = \frac{\sigma_s}{\sigma_r}$
- $r_s := \frac{L_r}{\sigma_r} \frac{R\theta}{F}$

Interstitial diffusion[1]

$$\begin{cases} b_1 \frac{\partial c_s}{\partial t} = \Delta \mu_s & \text{in } \mathcal{D}_s \\ \mathbf{j}_s \cdot \mathbf{n} = -\beta_{ps} R_{BV}^{ps} & \text{on } I_{ps} \\ \mathbf{j}_s \cdot \mathbf{n} = 0 & \text{on } \Gamma_r^s \\ \nabla(\Delta c_s) \cdot \mathbf{n} = 0 & \text{on } \Gamma_r^s \\ -\mathrm{div}\big(\sigma_s \nabla \psi_s\big) = 0 & \text{in } \mathcal{D}_s \\ \sigma_s \nabla \psi_s \cdot \mathbf{n} = \beta_\psi R_{BV}^{ps} & \text{on } I_{ps} \\ \nabla \psi_s \cdot \mathbf{n} = r_s C \frac{I_a}{|\Gamma_r^s|} & \text{on } \Gamma_{\mathrm{r}}^{\mathrm{s}} \end{cases}$$

- $b_1 := \frac{\tau_M}{\tau_p}$
- $\mu_s(c_s) = f_r'(c_s) - \lambda \Delta c_s$
- $\mathbf{j}_s = \nabla\big(f_r'(c_s) - \lambda \Delta c_s\big)$
- $\beta_\psi = \frac{i_{ps} L_r}{\sigma_r} \frac{F}{R\theta}$

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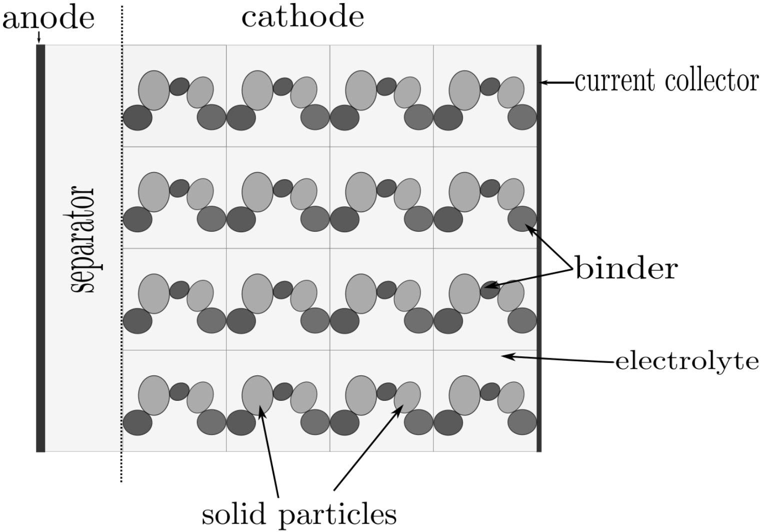
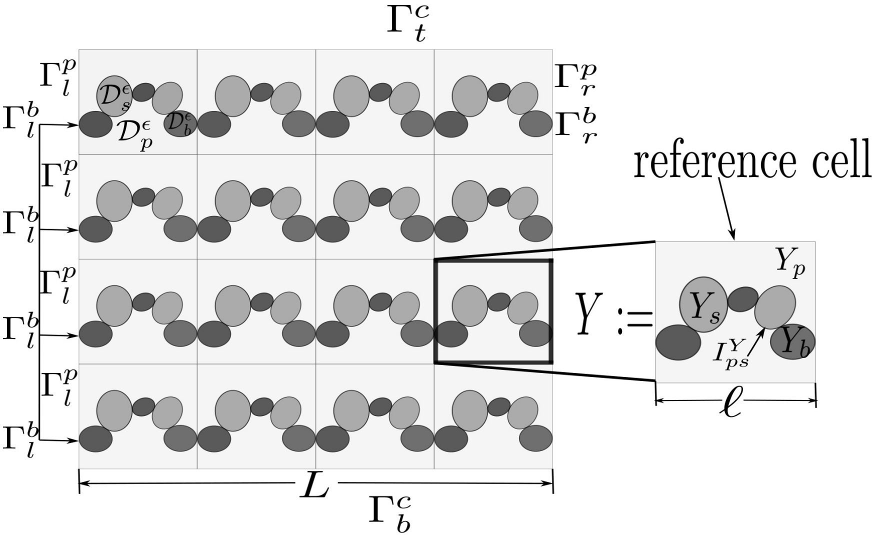
[1] M. Bazant, Theory of chemical kinetics and charge transfer based on nonequilibrium thermodynamics. Accounts of Chemical Research, 2013.

Microscopic composite cathode formulation





- We can identify two characteristic length scales: a macroscale L and microscale ℓ
- The heterogeneity parameter is defined by $\epsilon = \ell/L$

Microscopic formulation for interstitial diffusion

- For the microscopic variables $u^\epsilon(\mathbf{x}, t) = u(\mathbf{x}, \mathbf{y}, t)$ where $u \in \{c_p, \psi_p, c_s, \psi\}$, consider

- Microscopic description in $\mathcal{D}_p^\epsilon$

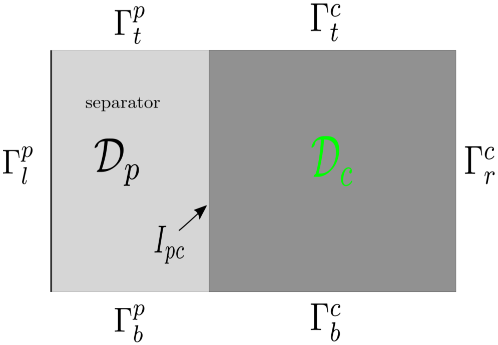
$$\begin{cases} \frac{\partial c_p^\epsilon}{\partial t} = \mathrm{div}\big(\nabla c_p^\epsilon\big) & \text{in } \mathcal{D}_p^\epsilon \\ \quad \nabla c_p^\epsilon \cdot \mathbf{n} = \epsilon \beta_{ps} R_{BV}^{ps} & \text{on } I_{ps}^\epsilon \\ -\mathrm{div}\big(c_p^\epsilon \nabla \psi_p^\epsilon\big) = -\mathcal{R}\mathrm{div}\big(\nabla c_p^\epsilon\big) & \text{in } \mathcal{D}_p^\epsilon \\ \quad \nabla \psi_p^\epsilon \cdot \mathbf{n} = \frac{\epsilon_s}{\epsilon_p} \nabla \psi_s^\epsilon \cdot \mathbf{n} & \text{on } I_{ps}^\epsilon \end{cases}$$

- Microscopic description in $\mathcal{D}_s^\epsilon$

$$\begin{cases} b_1 \frac{\partial c_s^\epsilon}{\partial t} = \mathrm{div}\Big(\nabla\big(f_r'(c_s^\epsilon) - \lambda \Delta c_s^\epsilon\big)\Big) & \text{in } \mathcal{D}_s^\epsilon \\ \quad \nabla\big(f_r'(c_s^\epsilon) - \lambda \Delta c_s^\epsilon\big) \cdot \mathbf{n} = -\epsilon \beta_{ps} R_{BV}^{ps} & \text{on } I_{ps}^\epsilon \\ -\mathrm{div}\big(\sigma^\epsilon \nabla \psi^\epsilon\big) = 0 & \text{in } \mathcal{D}_s^\epsilon \cup \mathcal{D}_b^\epsilon \\ \quad \sigma^\epsilon \nabla \psi^\epsilon \cdot \mathbf{n} = \epsilon \beta_\psi R_{BV}^{ps} & \text{on } I_{ps}^\epsilon \end{cases}$$

where $\sigma^\epsilon(\mathbf{x}) = \sigma(\mathbf{x}/\epsilon) = \sigma_s \chi_{Y_s}(\mathbf{y}) + \sigma_b \chi_{Y_b}(\mathbf{y})$

Homogenization of cathode in $\mathcal{D}_c$



- The upscaling procedure relies on the following asymptotic expansion

$$u^\epsilon(\mathbf{x}, t) = \sum_{i=0}^{\infty} \epsilon^i u_i(\mathbf{x}, \mathbf{y}, t)$$

with $u \in \{c_p, \psi_p, c_s, \psi\}$

Upscaled charge transpot equations

$$\begin{cases} p\dfrac{\partial C_p^c}{\partial t} = \mathrm{div}(\hat{D}_p \nabla C_p^c) + \bar{\beta}_p R_{BV}^{ps} & \text{in } \mathcal{D}_c \\ \mathrm{div}\big(C_p^c \hat{M}_p \nabla \Psi_p^c\big) = \mathcal{R}\mathrm{div}(\hat{D}_p \nabla C_p^c) & \text{in } \mathcal{D}_c \\ q b_1 \dfrac{\partial C_s}{\partial t} - \mathrm{div}\Big(\hat{D}_s \nabla \Big(f_r'(C_s) + \mathrm{div}\frac{\lambda}{q}\hat{D}_s \nabla C_s\Big)\Big) = \bar{\beta}_{ps} R_{BV}^{ps} & \text{in } \mathcal{D}_c \\ -\mathrm{div}\big(\hat{\Sigma}\nabla\Psi\big) = \bar{\beta}_\psi R_{BV}^{ps} & \text{in } \mathcal{D}_c \end{cases}$$

- $p = \frac{|Y_p|}{|Y|} \qquad q = 1 - p$
- $\Lambda = \frac{|I_{ps}^Y|}{|Y|}$
- $\bar{\beta}_i = \Lambda \beta_i \;\; i \in \{p,\, s,\, \psi,\, ps\}$

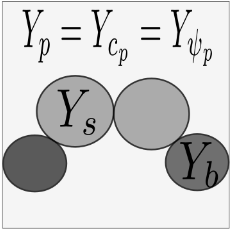
- The effective material tensors $\hat{D}_p = \{\bar{d}_{ik}^{c_p}\}_{i,k=1}^{d}$, $\hat{M}_p = \{\bar{d}_{ik}^{\psi_p}\}_{i,k=1}^{d}$, $\hat{D}_s = \{\bar{d}_{ik}^{s}\}_{i,k=1}^{d}$, and $\hat{\Sigma} = \{\bar{d}_{ik}^{\psi}\}_{i,k=1}^{d}$ are defined by

$$\bar{d}_{ik}^{w} = \frac{1}{|Y|} \sum_{j=1}^{d} \int_{Y_w} \left(\delta_{ik} - \delta_{ij} \frac{\partial \xi_w^k}{\partial y_j}\right) \mathrm{d}\mathbf{y},$$

and

$$d_{ik}^{\psi} = \frac{1}{|Y|} \sum_{j=1}^{d} \int_{Y_s \cup Y_b} \sigma^{\epsilon}(\mathbf{y}) \left(\delta_{ik} - \delta_{ij} \frac{\partial \xi_{\psi}^k}{\partial y_j}\right) \mathrm{d}\mathbf{y},$$

where $w \in \{c_p, \psi_p, s\}$

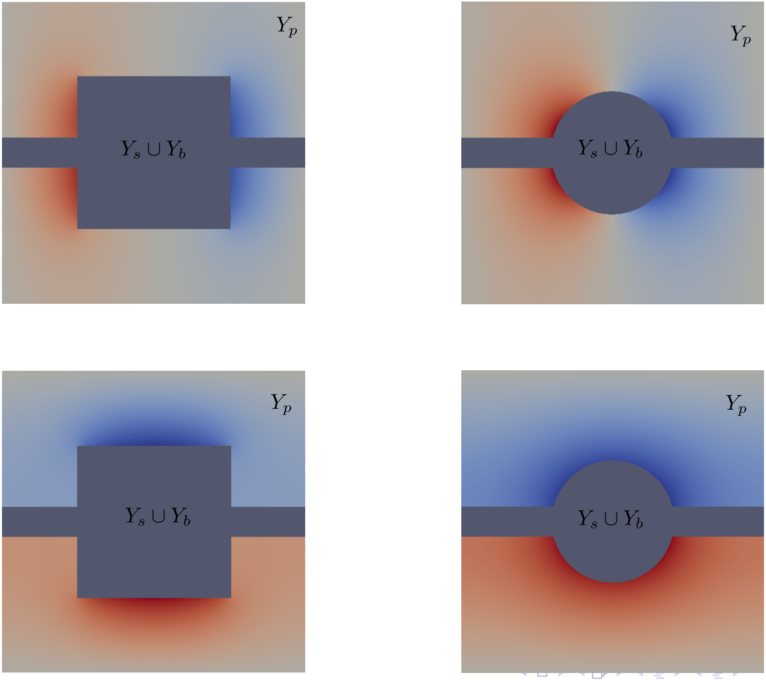
$Y :=$ 

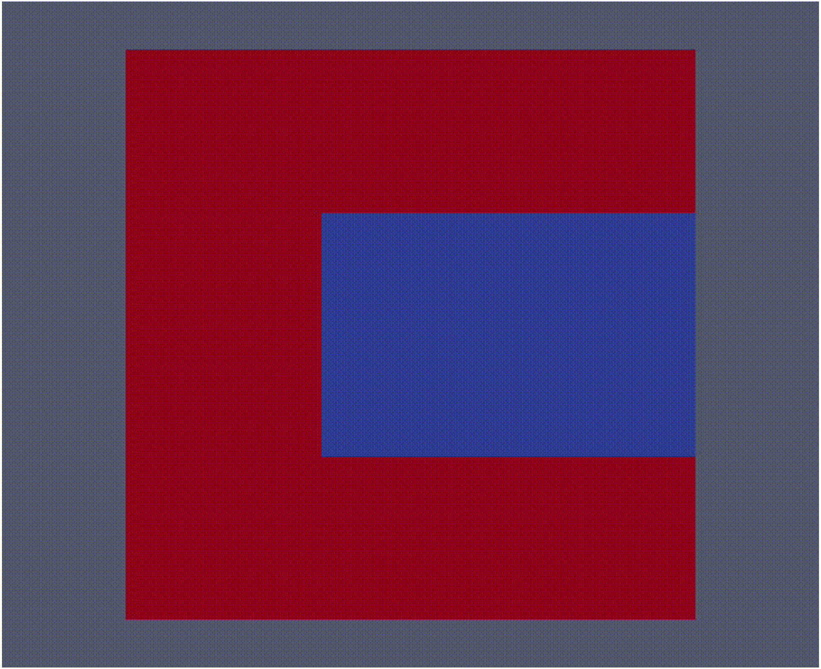
- The correctors ξ_w^k, $w \in \{c_p, \psi_p, s\}$, and ξ_ψ^k, $0 \le k \le d$, solve the cell problems

$$\boxed{\xi_w^k : \begin{cases} -\displaystyle\sum_{i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right) = 0 & \text{in } Y_w, \\ \left(\nabla \xi_w^k + y_k\right) \cdot \mathbf{n} = 0 & \text{on } I_{ps}^Y, \end{cases}}$$

and

$$\boxed{\xi_\psi^k : \begin{cases} -\displaystyle\sum_{i,j=1}^{d} \sigma^\epsilon \frac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_\psi^k}{\partial y_j}\right) = 0 & \text{in } Y_s \cup Y_b, \\ \left(\nabla \xi_\psi^k + y_k\right) \cdot \mathbf{n} = 0 & \text{on } I_{ps}^Y \end{cases}}$$


Y_p
$Y_s \cup Y_b$
Y_p
$Y_s \cup Y_b$
Y_p
$Y_s \cup Y_b$
Y_p
$Y_s \cup Y_b$



Conclusion

- Derived effective macroscopic transport formulations for Li-batteries allowing us to apply classical numerical methods without ending up with high-dimensional numerical problems
- The upscaled formulation gives analytical guidance for design optimization without the need for numerical computations

Acknowledgements

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