Physics-based models of degradation mechanisms

- In course 4, you learned how Li-ion battery cells age
- There are numerous mechanisms
  - Some are continuously occurring, such as SEI growth
  - Others are atypical, such as Li plating, current-collector corrosion
- Physics-based controls need mathematical models of mechanisms they are to limit
- Good models exist for some mechanisms, but not for all
- Good news: to make big improvements need only to model most prevalent/severe
- In this lesson, we look at SEI growth (prevalent) and Li plating (severe)

SEI-layer formation and growth (FOM)

- Ramadass et al. proposed model describing formation, growth of SEI, solvent reaction as mechanism (cf. resources, later)
- Side-reaction rate described as (where $\eta_s = \phi_s - \phi_e - U_s^{\text{ref}} - FR_{\text{film}}(j_s + j)$)

$$j_s = -\frac{i_{0,s}}{F}\exp\left(-\frac{\alpha_s F}{RT}\eta_s\right)$$

- Once j_s calculated, power and capacity fade described by

$$R_{\text{film}} = R_{\text{SEI}} + \frac{\delta_{\text{film}}}{\kappa_P} \quad \text{where} \quad \frac{\partial \delta_{\text{film}}}{\partial t} = -\frac{M_P}{\rho_P} j_s$$

$$\frac{\partial Q}{\partial t} = \int_0^{L_n} a_n A F j_s \,\mathrm{d}x$$

Simplified SEI model

- BMS must be able to j_s very quickly and accurately
- Solving coupled PDE equations of FOM too complicated
- Can develop extremely simple 0-d SEI growth, capacity and resistance fade model

$$j_{s,k} = \frac{AB + A\sqrt{B^2 + (1 - 2CA)}}{(1 - 2CA)}$$

where (cf. resources section for details)

$$A = -\frac{i_{0,s}}{F}\exp\left(\frac{F\left(U_s^{\text{ref}} - U_n^{\text{ref}}(\theta^{\text{n}})\right)}{2RT}\right), \quad B = \frac{-i_{\text{app}}}{2a_n L^{\text{n}} A i_0}, \quad C = \frac{F}{2i_0}$$

Summary of SEI-growth model

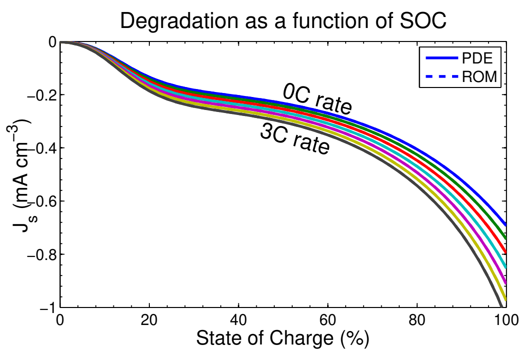
- Total process for determining side-reaction rate, resulting film-resistance growth, capacity loss can be summarized as

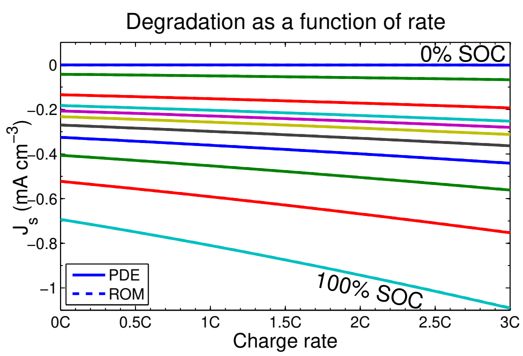
$$
\begin{aligned}
\theta^{\mathrm{n}} &= \theta^{\mathrm{n}}_{0\%} + \mathrm{SOC}_{\mathrm{cell}}\left(\theta^{\mathrm{n}}_{100\%} - \theta^{\mathrm{n}}_{0\%}\right) \\
j_{s,k} &= \frac{AB + A\sqrt{B^2 + (1-2CA)}}{(1-2CA)} \\
R_{\mathrm{film},k} &= R_{\mathrm{film},k-1} - \left(\frac{M_P\,\Delta t}{\rho_P \kappa_P}\right) j_{s,k-1} \\
Q_k &= Q_{k-1} + \left(a_n A F L^{\mathrm{n}} \Delta t\right) j_{s,k-1}
\end{aligned}
$$

where A, B, and C are computed as shown on previous slide

Results

- Figures compare ROM vs. FOM (PDE) predictions of degradation rate... indistinguishable at this scale





Li-plating FOM

- Arora expresses rate of irreversible Li loss due to plating using

$$\eta_s(x,t) = \phi_s(x,t) - \phi_e(x,t) - U_s^{\mathrm{ref}} - FR_{\mathrm{film}}\, j_s(x,t)$$

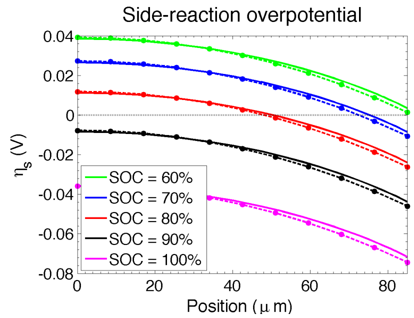
as (where $i_{0,s} = k_{n,s}(c_e)^{\alpha_{a,s}}$ and $\alpha_{a,s} \neq \alpha_{c,s}$ in general)

$$j_s(x,t) = \min\left(0, \frac{i_{0,s}}{F}\left[\exp\left(\frac{\alpha_{a,s}F}{RT}\eta_s(x,t)\right) - \exp\left(-\frac{\alpha_{c,s}F}{RT}\eta_s(x,t)\right)\right]\right)$$

- Plating is semi-irreversible in sense that it includes anodic rate, but doesn't allow overall positive side-reaction flux
- Plating occurs only at spatial locations in negative electrode where $\eta_s(x,t) < 0$
- Enforced by "min" in j_s equation, which sets $j_s(x,t) = 0$ for values of x where $\eta_s(x,t) \geq 0$; otherwise, keeps result of computation when $\eta_s(x,t) < 0$.

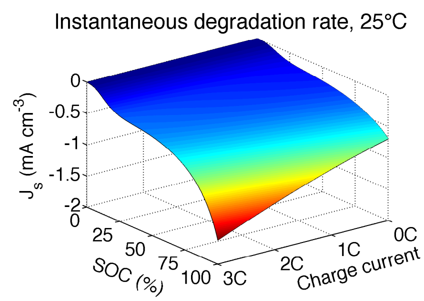
Li-plating ROM

- 0-d model doesn't work very well since Li-plating phenomena is very nonlinear
  - Average η_s (predicted well by 0-d ROM) is not what matters when predicting plating rates
  - Instead, local values for η_s matter
- So, use 1-d ROM of cell to produce signals needed to compute $\eta_s(x,t)$
- Figure shows comparison between Li-plating FOM (solid line) and ROM for 1C charge pulses, starting at different initial SOC values



Summary

- To control degradation, must have a model of degradation and model must have controllable inputs (e.g., cell current, temperature, SOC range, etc.)
- Can make simple 0-d ROM of SEI-growth FOM that approximates FOM very well
  - Figure shows Li-loss rate for this model
  - "Works" because average values over electrode width approximate phenomenon reasonably well
- 0-d ROM can't approximate Li-plating well
- But, 1-d ROM based on ideal-cell model gives very good predictions of Li-plating



Resources for SEI models

- One model of SEI growth is presented in
  - FOM in: Ramadass, P., Haran, B., Gomadam, P.M., White, R., Popov, B.N., "Development of First Principles Capacity Fade Model for Li-Ion Cells," *J. Electrochemical Society,* 151, A196–A203, 2004
  - ROM in: Plett, G.L., "Algebraic solution for modeling SEI layer growth," *ECS Electrochemistry Letters*, 2(7), A63–A65, 2013
- A more mature model of SEI growth is presented in
  - FOM in: Safari, M., Morcrette, M., Teyssot, A., and Delacourt, C., "Multimodal physics-based aging model for life prediction of Li-ion batteries," *J. Electrochem. Soc.*, 156(3), A145–A153, 2009.
  - ROM in: Plett, G.L., "Reduced-order multi-modal model of SEI layer growth for management and control of lithium-ion batteries," in *IEEE Conference on Control Technology and Applications 2017*, Kohala Coast, Hawai'i (2017)

Resources related to Li plating

- Model of Li plating in
  - FOM in: Arora, P., Doyle, M., White, R.E., "Mathematical Modeling of the Lithium Deposition Overcharge Reaction in Lithium-Ion Batteries Using Carbon-Based Negative Electrodes," *J. Electrochemical Society*, 146(10) 3543–3553, 1999
  - Early 0-d ROM results in: Perkins, R.D., Randall, A.V., Zhang, X., Plett, G.L., "Controls Oriented Reduced Order Modeling of Lithium Deposition on Overcharge," *Journal of Power Sources*, 209, 318–325, 2012
  - 1-d "ROM" based on PBROM presented earlier this week works far better than 0-d ROM in Perkins et al.