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NONUNIFORM DEGRADATION OF LITHIUM-ION BATTERIES – 3D MODELING

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Introduction & Objectives

MODALIS² addresses the following design challenges

- The need for faster development of batteries with higher energy densities
- Improved battery safety during operation and transportation
- Optimization of cyclability
- Lower development costs
- Better understanding of material interactions within the cell

Our contribution to MODALIS²

- Implementation of a prototype within Simcenter STAR-CCM+ for the simulation of battery materials with new electrode materials accounting for battery aging: Solid-electrolyte interphase (SEI) growth, lithium plating (LiP), and mechanical degradation mechanisms
- Investigation of nonuniform aging in-plane and in-thickness direction

Modeling Approach

3D macro-homogeneous electrode modeling [1]

- Conservation of an electrically neutral binary salt

$$\chi \partial_t c = \nabla \cdot (D \nabla c) - \frac{\boldsymbol{i} \cdot \nabla t_+^0}{z_+ \nu_+ F} + (1 - t_+^0) \frac{a \sum_k i_k}{z_+ \nu_+ F}$$

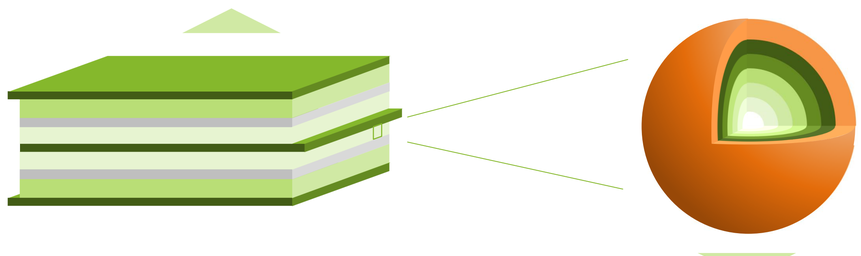
χ: porosity; c: Li⁺/salt concentration; D: effective diffusivity; t_+^0: cation transference number; $\boldsymbol{i}$: electric current density; a: specific interface area

- Reaction kinetics at solid-electrolyte interface

$$i_q = i_{0,q} \prod_k \left(\frac{c_k}{c_{ref,k}}\right)^{\gamma_k} \left[e^{\frac{\alpha_A F}{RT}\eta_q} - e^{-\frac{\alpha_C F}{RT}\eta_q}\right] \quad \text{with} \quad \eta_q = \Delta\varphi - U_q - \frac{\delta_{SEI}}{\sigma_{SEI}} \sum_k i_k$$

$i_{(0,)r}$: (specific) reaction current; c_k: reacting species concentrations; $c_{ref,k}$: reference concentrations; γ_k: rate exponents; $\alpha_{A/C}$: anodic/cathodic charge transfer coeff.; η_q: overpotential; $\Delta\varphi$: electric potential jump; U_q: equilibrium potential; σ_{SEI}: ionic conductivity of SEI film

- Charge and energy conservation in solid and electrolyte phase (not detailed here)



1D microscale particle modeling [2]

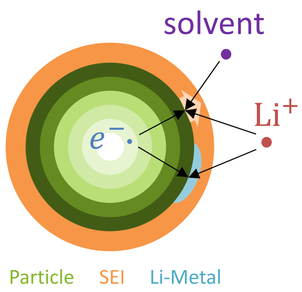
- Conservation of intercalated lithium

$$\partial_t c_s = \frac{1}{r^2} \partial_r \left[r^2 D_s \left(\partial_r c_s - \frac{\Omega c}{RT} \partial_r \sigma_h\right)\right]$$

- Hydrostatic stress (linear elasticity)

$$\sigma_h = \frac{2\Omega E}{9(1-\nu)} \left[\frac{3}{R^3} \int_0^R (c_s\, r^2) dr - c_s\right]$$

c_s: lithium concentration in solid; D_s: diffusivity; Ω: partial molar volume; E: Youngs modulus; ν: Poisson ratio; R: particle radius



Surface film growth

The kinetically limited growth of the solid electrolyte interphase layer and lithium plating due to parasitic side reactions is described via the Butler-Volmer equation

$$i_{SEI} = i_{0,SEI} \left[\frac{c_{solv}\, c}{1\ \text{kmol}^2\ \text{m}^{-6}}\right]^{0.5} \left[e^{\frac{0.05\,F}{RT}\eta_{SEI}} - e^{-\frac{0.95\,F}{RT}\eta_{SEI}}\right]$$

$$i_{LiP} = i_{0,LiP} \left[\frac{c}{1\ \text{kmol m}^{-3}}\right]^{0.3} \left[e^{\frac{0.3\,F}{RT}\eta_{LiP}} - e^{-\frac{0.7\,F}{RT}\eta_{LiP}}\right]$$

Thickness evolution: $\partial_t \delta = \partial_t \delta_{SEI} + \partial_t \delta_{LiP} = \frac{i_{SEI} M_{SEI}}{\rho_{SEI} F} + \frac{i_{LiP} M_{LiP}}{\rho_{LiP} F}$

M_q: molecular weight; ρ_q: density

Loss of active material (LAM)

Cyclic mechanical stresses lead to particle fracture and, hence, to loss of the electrical contact. The Basquin power law yields the maximum number of cycles, N_{max}, until failure for given yield stress, σ_{yield}, and amplitude stress, σ_{ampl}. Under uniform cycling conditions and linear damage accumulation, the damage after n cycles can be estimated as [3]

$$\text{damage} = \frac{n}{N_{max}} = n \left(\frac{\sigma_{ampl}}{\sigma_{yield}}\right)^{\frac{1}{m}} \quad \xrightarrow{n=1} \quad \frac{\text{damage}}{\text{cycle}} = \left(\frac{\sigma_{ampl}}{\sigma_{yield}}\right)^{\frac{1}{m}} \propto \frac{\text{LAM}}{\text{cycle}}$$

An instantaneous evolution equation of the particle volume fraction ε is given by [4]

$$\dot{\varepsilon} = -\varepsilon_0\, p_{LAM} \left|\overline{\max_{0 \le r \le R} (|\dot{\sigma}_h|)}\right|$$

ε_0: initial particle volume fraction; p_{LAM}: active material loss coefficient

Surface cracking

Like for the LAM, the used surface fracture model is based on a power law – Paris' law. An instantaneous evolution law of the specific interface area is given by [4]

$$\dot{a} = a_0 \frac{\dot{\varepsilon}}{\varepsilon_0} + p_{crack} |\dot{\sigma}_h|_{r=R}|, \quad \sigma_h|_{r=R} > 0$$

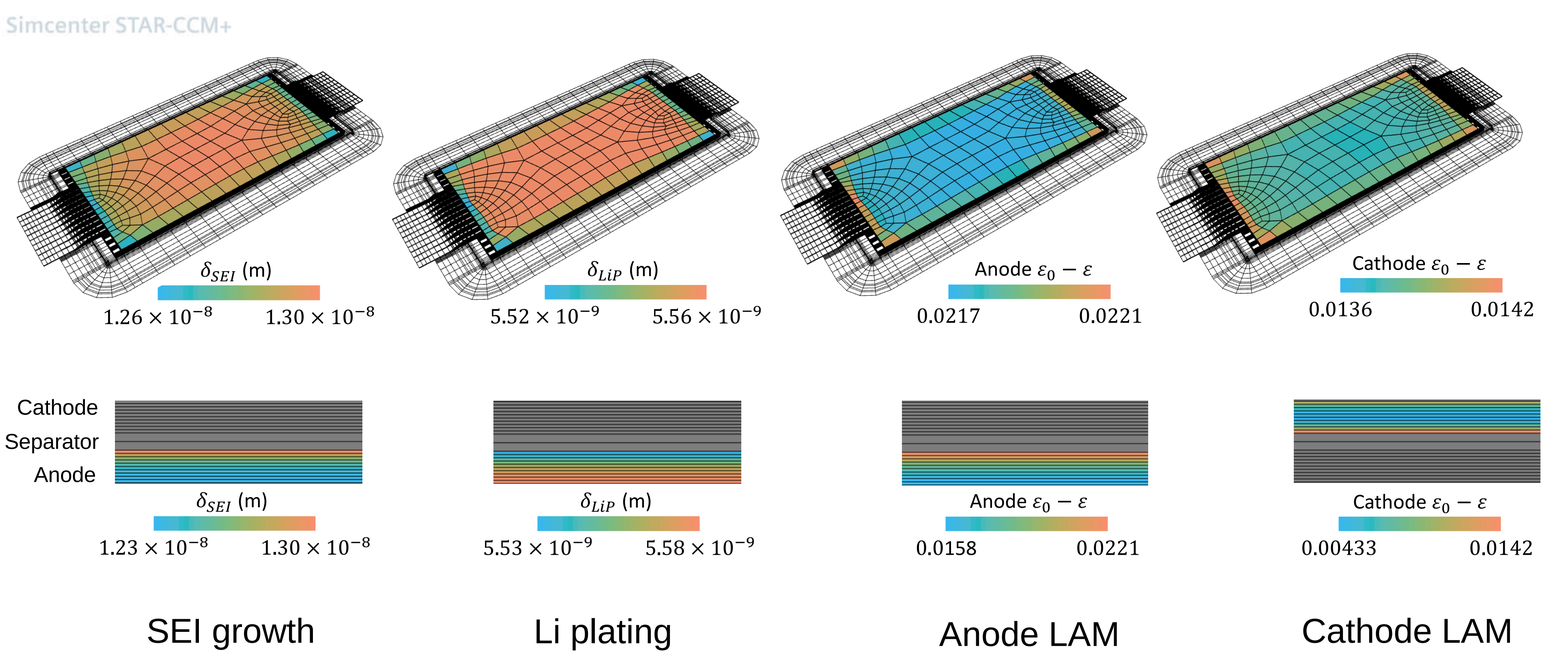
a_0: initial specific interface area; p_{crack}: surface cracking coefficient

Results & Discussion

Toy-problem Stack of 15 electrochemical cells discretized by ~200,000 finite volume cells; drive cycle (10x): CC/CV charging at 2C/4.2V until 95% SOC, 200s rest, CC discharging at 2C until 60% SOC, 200s rest.

In-plane The thermal boundary conditions are such that the highest temperatures are observed at the center of the battery cell, where the temperature-dependency of multiple material parameters leads to increased SEI growth rates. LAM is pronounced close to the battery tabs, where the highest stress change rates are observed.

In-thickness As expected, SEI growth and LAM are highest near the separator. The operation conditions are such that the Li-metal, with initially specified homogeneous profile, is dissolved faster than it is deposited, especially close to the separator.



SEI growth | Li plating | Anode LAM | Cathode LAM

Conclusion & Outlook

- In the studied case, aging is more heterogeneous in thickness direction, but the in-plane variation of the different aging profiles is still significant
- Consideration of cathode dissolution, the influence of manufacturing uncertainties, other cell geometries and more realistic cycling conditions will be considered in following works
- Modeling of all-solid-state batteries is the next step in the MODALIS² project

References

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[2] Y. Dai, L. Cai, E. White, *J. Power Sources*, Bd. 247, pp. 365-376, 2014.
[3] I. Laresgoiti, S. Käbitz, M. Ecker, D. U. Sauer, *J. Power Sources,* 300, (2015) 112-122.
[4] J. M. Reniers, G. Mulder, and D. A. Howey, *J. Electrochem. Soc*, 166(14) (2019) A3189-A3200.