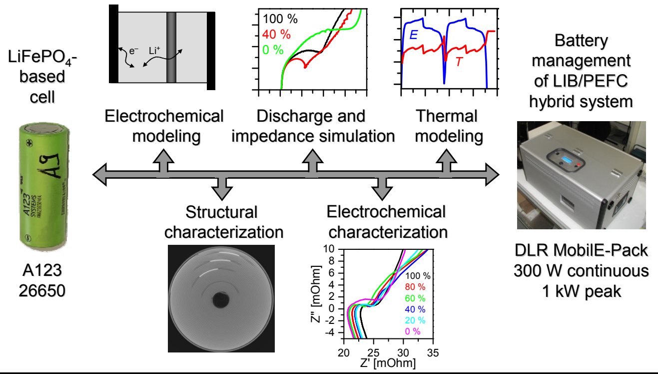
Physically based modeling and simulation of a $LiFePO_4$-based lithium-ion battery

C. Hellwig, D. N. Fronczek*, Ş. Sörgel and W. G. Bessler
German Aerospace Center (DLR), Institute of Technical Thermodynamics, Stuttgart, Germany
*E-mail: david.fronczek@dlr.de

Goal and approach

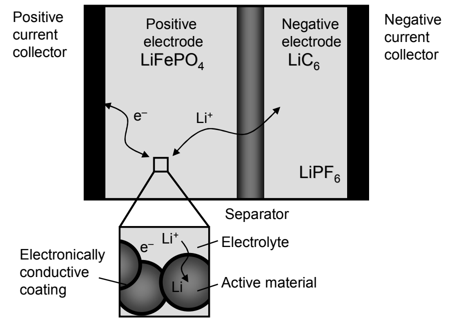
Goal: Impedance-based SOC diagnostics of $LiFePO_4$ cells



Multi-scale modeling

Mass and charge transport is modeled on particle and repeat unit scale.

- Li^+ charge transport in electrolyte: 100 µm scale
- Li transport in solid phase: ~100–1000 nm scale



Model

Parameters:

- $LiPF_6$ Concentration: 1.5 mol l^{-1}
- Li^+ and PF_6^- - diffusion coefficient: $1\cdot10^{-10}$ m² s^{-1}
- Thickness (anode / separator / cathode): 40 µm / 20 µm / 80 µm
- Bulk diffusion coefficients (LiC_6 / $LiFePO_4$): $1\cdot10^{-14}$ m² s^{-1} / $1\cdot10^{-16}$ m² s^{-1}
- Exchange current density: $3\cdot10^5$ A m^{-3}
- Particle radius (anode / cathode): 1 µm / 0.1 µm

Thermodynamic data:

- Separation in enthalpy and entropy
- LiC_6: Y. Reynier, R. Yazami, B. Fultz, Journal of Power Sources 119–121 (2003) 850–855
- $LiFePO_4$: J. L. Dodd, PhD thesis, California Institute of Technology, 2007

Thermodynamics
- Empirical half-cell enthalpy, entropy

$$\Delta\phi_{eq}(c_{Li}) = -\frac{\Delta G}{zF} = -\frac{\Delta H(c_{Li}) - T\Delta S(c_{Li})}{zF}$$

Kinetics
- Butler-Volmer kinetics
- Concentration overpotential

$$i = i_0\left(\exp\left(\frac{\alpha F}{RT}\eta_{act}\right) - \exp\left(-\frac{(1-\alpha)F}{RT}\eta_{act}\right)\right)$$

$$\eta_{conc} = \frac{RT}{zF}\ln\left(\frac{c_0}{c(t)}\right) \qquad \eta_{act} = \Delta\phi(t) - \Delta\phi_{eq}(c_{Li}) - \eta_{conc}$$

Solid-state transport
- Mass conservation
- Spherical diffusion in particle

$$\frac{\partial \rho_{Li}}{\partial t} = \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D \frac{\partial \rho_{Li}}{\partial r}\right)}_{\text{Diffusion}} - \underbrace{\frac{M_{Li}}{zF}i}_{\text{Chemistry}}$$

Electrolyte transport
- Nernst-Planck equation
- Charge neutrality

$$\frac{\partial(\varepsilon c_i)}{\partial t} = \underbrace{\frac{\partial}{\partial y}\left(D_i\frac{\partial c_i}{\partial y}\right)}_{\text{Diffusion}} + \underbrace{\frac{z_i F}{RT}\frac{\partial}{\partial y}\left(D_i c_i \frac{\partial \phi}{\partial y}\right)}_{\text{Migration}} + \underbrace{M_i \dot{s}_i^V}_{\text{Chemistry}}$$

$$\sum_i (c_i z_i) = 0$$

Heat transport
- Ohmic, chemical heat production
- Heat conduction and convection

$$\frac{\partial(\rho c_p T)}{\partial t} = \underbrace{\frac{\partial}{\partial y}\left(\lambda\frac{\partial T}{\partial y}\right)}_{\text{Conduction}} + \underbrace{\dot{Q}_{chem} + \dot{Q}_{ohm}}_{\text{Sources}} - \underbrace{\alpha(T_{cell} - T_{env})}_{\text{Losses}}$$

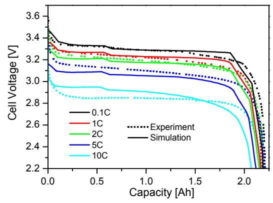
Cell voltage

$$E = \phi_{cathode} - \phi_{anode}$$

Electrochemical behavior

Discharge curves

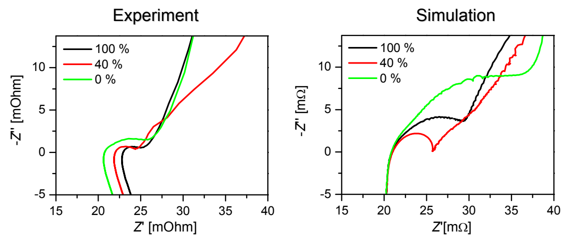
- Discharge curves starting from 100 % SOC at different discharge rates



- Flat discharge curve, voltage variation mainly from C_6 electrode
- Voltage losses at higher discharge rates due to transport limitations in electrodes

Electrochemical impedance spectra

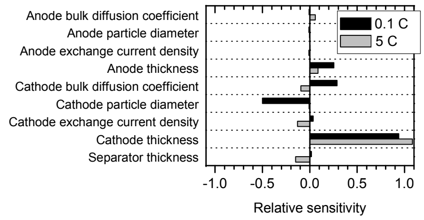
- Impedance spectra of an unpolarized cell at different SOC



- Considerable influence of SOC on impedance spectrum
- Impedance simulations are feasible, so far only qualitative agreement

Sensitivity analysis

- Sensitivity of cell parameters on discharge capacity



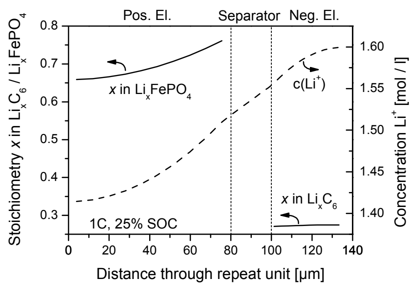
- Allows detailed insight into rate-limiting processes.
- Cathode is limiting component

Spatial concentration variations

Concentration variation at SOC 25 % with 1C discharge rate:

Electrolyte:
- S-curve behavior of Li^+-concentration in electrolyte
- No interaction with separator assumed

Bulk:
- Stoichiometry change during discharging in dependence on diffusion limitations in electrolyte



Outlook: Lithium-sulfur batteries

- Promising system for high-energy batteries (5× specific energy)
- Major challenge today: Limited cycle life
- New model will account for side reactions and other degradation mechanisms, allowing the study of cell aging