Physically based modeling and simulation of a LiFePO₄-based lithium-ion battery

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Goal and approach

Goal: Impedance-based SOC diagnostics of LiFePO₄ cells

Multi-scale modeling

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

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

Model

Parameters:
- LiPF₆ Concentration: 1.5 mol l⁻¹
- Li⁺ and PF₆⁻ - diffusion coefficients: 1·10⁻¹⁰ m² s⁻¹
- Thickness (anode / separator / cathode): 40 µm / 20 µm / 80 µm
- Bulk diffusion coefficients (LiC₀ / LiFePO₄): 1·10⁻¹⁴ m² s⁻¹ / 1·10⁻¹⁶ m² s⁻¹
- Exchange current density: 3·10⁻⁶ A m⁻³
- Particle radius (anode / cathode): 1 µm / 0.1 µm

Thermodynamic data:
- Separation in enthalpy and entropy
- LiFePO₄: J. L. Dodd, PhD thesis, California Institute of Technology, 2007

Electrochemical modeling

Discharge curves

- Discharge curves starting from 100 % SOC at different discharge rates
- Flat discharge curve, voltage variation mainly from Cₑ 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

Thermodynamics

- Empirical half-cell enthalpy, entropy

Kinetics

- Butler-Volmer kinetics
- Concentration overpotential

Solid-state transport

- Mass conservation
- Spherical diffusion in particle

Electrolyte transport

- Nerst-Planck equation
- Charge neutrality

Heat transport

- Ohmic, chemical heat production
- Heat conduction and convection

Cell voltage

Electrochemical behavior

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 (5x 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