

A Multi-scale Thermo-Electrochemical LiFePO₄ Battery Model Based on the Domino-Cascade Mechanism

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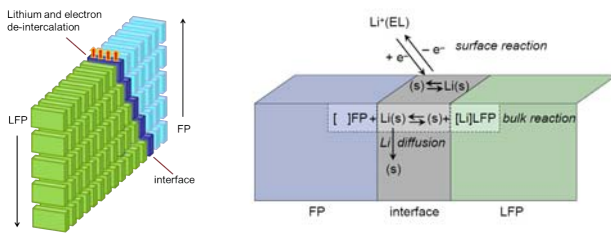
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Abstract

Here we present a multi-scale model for batteries based on physico-chemical properties. LiFePO₄ (LFP) as cathode material offers high power characteristics and thermal stability. The two-phase behavior of LFP is described using elementary kinetics based on the domino-cascade model proposed by Delmas et. al. [1]. Due to the importance of heat transport and safety issues an application to thermal runaway is shown using global kinetics.

Domino-Cascade Model

The **domino-cascade mechanism** describes the phase change from LiFePO₄ (LFP) to FePO₄ (FP). We assume the presence of an interface existing between LFP and FP. Along this **interface diffusion of Li-ions** is considered while charge transfer reaction is assumed to take place at the tree-phase boundary of LFP, FP and liquid electrolyte.



This mechanism is calculated through CANTERA [2] based on elementary reaction equations drafted above. The heat source and reaction rate are coupled with DENIS.

Multi-scale Model

Transport

The model includes three transports in three different scales. Each scale has 1D. Heat source is calculated in coarse mesh. Solved in DENIS.

~20 mm scale
Heat transport

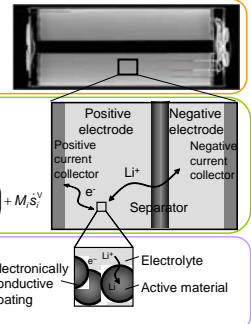
$$\frac{\partial(\rho C_p T)}{\partial t} = \frac{\partial}{\partial y} \left(\lambda \frac{\partial T}{\partial y} \right) + \dot{Q}_{\text{chem}} + \dot{Q}_{\text{ohm}}$$

~100 μm scale
Lithium ion charge transport in electrolyte

$$\frac{\partial(c_i)}{\partial t} = \frac{\partial}{\partial y} \left(D_i(c_i, T) \frac{\partial c_i}{\partial y} \right) + \frac{z_i F}{RT} \frac{\partial}{\partial y} \left(D_i(c_i, T) c_i \frac{\partial \phi}{\partial y} \right) + M_i s_i^v$$

~100-1000 nm scale
Lithium ion transport

$$\frac{\partial \rho_{Li}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D \frac{\partial \rho_{Li}}{\partial r} \right) - \frac{M_{Li}}{zF} j$$



Kinetics

In addition to transports, kinetics of electrochemistry is considered in the model. Solved in DENIS.

Butler-Volmer equation

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

Overpotential

$$\left\{ \begin{array}{l} \text{Activation} \quad \eta_{\text{act}} = \Delta \phi(t) - \Delta \phi_{\text{eq}}(c_{Li}) - \eta_{\text{conc}} \\ \text{Concentration} \quad \eta_{\text{conc}} = \frac{RT}{zF} \ln \left(\frac{c_0}{c(t)} \right) \end{array} \right.$$

Validation of Domino-Cascade Model

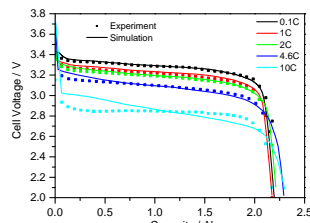


Fig. 1

Discharge curves show **good agreement** with experiment at 293 K in different C-rates. For higher C-rates (2C, 4.6C, 10C) the active surface-area of the interface has to be adjusted to higher values to reach full capacity. (Fig. 1)

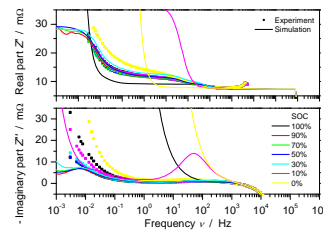


Fig. 2

EIS (electrochemical impedance spectroscopy): **phase-transfer process** dominates at low frequencies. Diffusion within bulk phase is not a limiting factor. Deviation at boundary values of SOC is due to thermodynamics. (Fig. 2)

Application of Multi-scale Model to Thermal Runaway

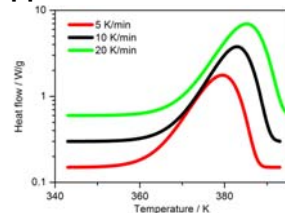


Fig. 3

DSC simulations are conducted and compared with a result by Spotnitz et al. [3] (Fig. 3 and Fig. 4).

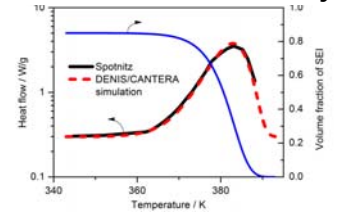


Fig. 4

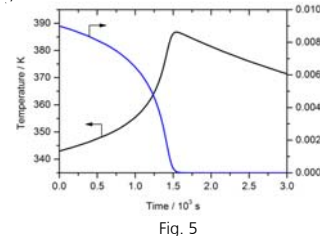


Fig. 5

Thermal runaway is successfully observed at extreme condition under low heat transfer coefficient and thermal conductivity (Fig. 5).

Conclusion

- Good agreement with experiments in discharge curves
- Impedance spectra shows good agreement for wide range of SOC

- Conducted first thermal runaway simulation
- Simulated a DSC curve of SEI decomposition and successfully reproduce curve by Spotnitz et al.