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A Multi-scale Thermo-Electrochemical $LiFePO_4$ Battery Model Based on the Domino-Cascade Mechanism

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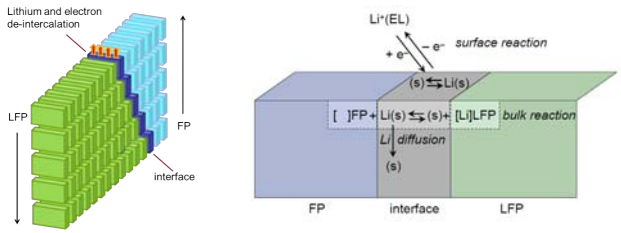
Abstract

Here we present a multi-scale model for batteries based on physico-chemical properties. $LiFePO_4$ (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 $LiFePO_4$ (LFP) to $FePO_4$ (FP). We assume the presence of an interface existing between LFP and FP. Along this **interface diffusion of Li-atoms** 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

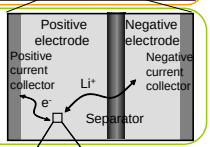
The model includes three transports in three different scales. Each scale has 1D. Heat source is calculated in coarse mesh. Solved in DENIS.

~20 mm scale
Heat transport

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

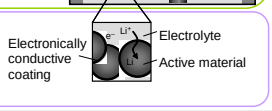
~100 µm scale
Lithium ion charge transport in electrolyte

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



~100-1000 nm scale
Lithium ion transport

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



Kinetics

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

Butler-Volmer equation

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

Overpotential

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

Validation of Domino-Cascade Model

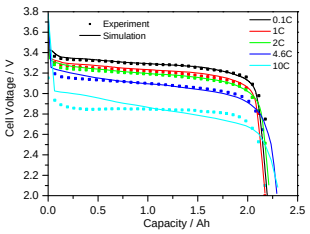


Fig. 1

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)

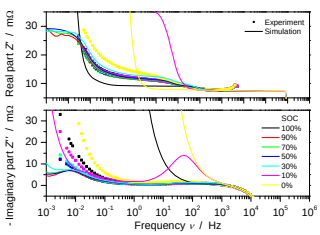


Fig. 2

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

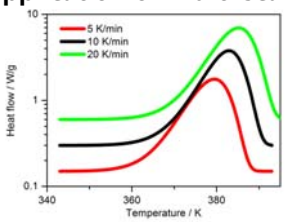


Fig. 3

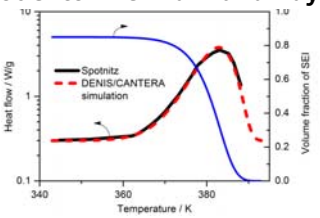


Fig. 4

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

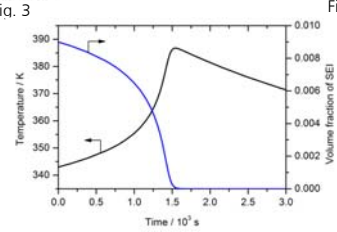


Fig. 5

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.

[1] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, F. Weill, Nature Materials, 7 (2008) 665-671
[2] D. G. Goodwin, http://code.google.com/p/cantera (2001-2010)
[3] R. Spotnitz, J. Franklin, Journal of Power Sources 113 (2003) 81-100