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Toward Modeling Thermal Runaway of Li-ion Batteries

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Introduction and motivation

Thermal runaway of lithium batteries is major issue for development of high-power cells. We present preliminary numerical study of the runaway extreme event in **$LiFePO_4$/graphite cells** initiated via thermal decomposition of the solid elecctrolyte interface (SEI) layer. The approach is based on a multi-scale model from nano-scale to macro-scale and includes global electrochemical and thermochemical kinetics as implemented into the in-house software DENIS.

Multi-scale model

Transport

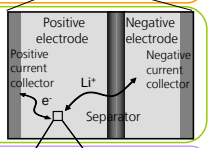
The model includes three transport regimes at three different scales. Each scale is modeled in 1D. Solved in DENIS. [1],[2]

~20 mm scale
Heat transport

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

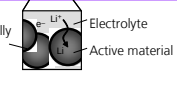
~100 µm scale
Lithium ion charge transport in electrolyte

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



~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 transport, electrochemical kinetics is considered in the model. Solved in DENIS.

Butler-Volmer equation

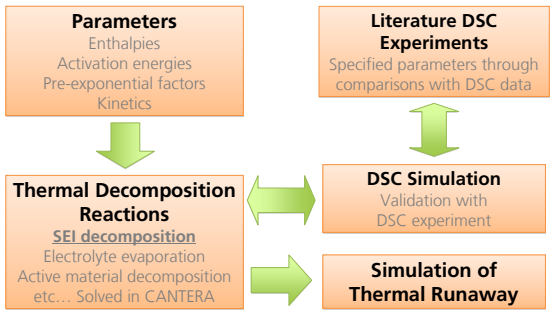
$$i = i_0\left(\exp\left(\frac{\alpha F}{RT}(\eta_{act} - R_{SEI}\cdot i)\right) - \exp\left(-\frac{(1-\alpha)F}{RT}(\eta_{act} - R_{SEI}\cdot i)\right)\right)$$

Overpotential

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

Thermal decomposition model

Modeling Procedure



SEI decomposition

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + 0.5\ O_2$$

The exothermic SEI decomposition reaction is calculated based on the above reaction equation through CANTERA [3].

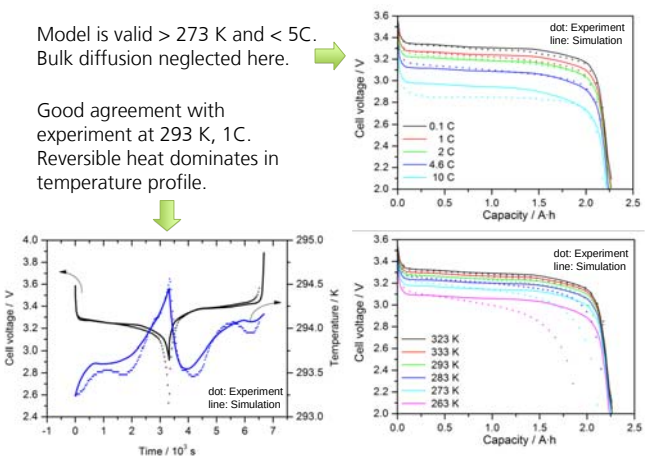
Parameters [4]

Pre-exponential factor [s^{-1}]	7.88×10^{36}
Activation energy [J/mol]	2.81×10^{5}
Heat of reaction [J/g]	257

Validation of heat transport model

Model is valid > 273 K and < 5C. Bulk diffusion neglected here.

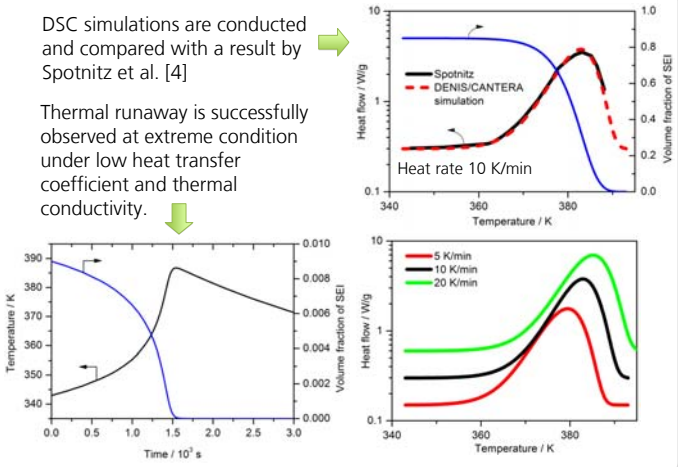
Good agreement with experiment at 293 K, 1C. Reversible heat dominates in temperature profile.



Thermal runaway simulation

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

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



Conclusion

- Developed multi-scale thermal battery model
- The heat transport model is validated in wide range of operating conditions
- Simulated a DSC curve of SEI decomposition and successfully reproduce curve by Spotnitz et al.
- Conducted first thermal runaway simulation

[1] W. G. Bessler, S. Gewies and M. Vogler, Electrochimica Acta 53 (2007) 1782 - 1800
[2] J. Neidhardt, Jouranl of Electrochemical Society (2012) submitted
[3] D. G. Goodwin, http://code.google.com/p/cantera (2001-2010)
[4] R. Spotnitz and J. Franklin, Journal of Power Sources 113 (2003) 81-100