

A Reduced Order Thermal Model for Lithium Ion Batteries Derived from the Cahn-Hilliard Equation

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INTRODUCTION-Lithium iron phosphate (LiFePO_4) is the most commonly used phosphate-based cathode material for Li-ion batteries. Traditionally mathematical models of intercalation dynamics in LiFePO_4 cathodes were based on a spherical diffusion or a shrinking core concept. However, recent experimental and theoretical advances indicate a more realistic single particle (SP) model must account for phase equilibrium and nonequilibrium solid-solution transformations. The reduced order model (ROM) presented below is a bulk scale thermal model statistically derived from SP Cahn Hilliard COMSOL simulations of the LiFePO_4 cathode. The ROM was developed and validated based on experimental electrical and thermal data and property data for an A123 Systems 26650, 2.3 Ah cylindrical battery.

THEORY/COMPUTATIONAL METHODS The Cahn-Hilliard SP model is a fourth-order partial differential equation in concentration, so casting it directly in the weak form results in second order spatial derivatives in the weak formulation. Our model resolves this by rephrasing the problem in COMSOL Multiphysics' standard PDF format as a system of two coupled second order PDEs in ion concentration and chemical potential respectively.

$$\bar{\mu} = -k_b T \ln\left[\frac{\bar{c}}{1-\bar{c}_m}\right] + \frac{\bar{\Omega}(c_m - \bar{c})}{c_m} - \frac{KV_s}{cm} \bar{\nabla}^2 \bar{c}$$

The basic evolution equation for mass conservation is,

$$\frac{\partial \bar{c}}{\partial \bar{t}} = -\bar{\nabla} \cdot \bar{F}$$

where \bar{c} is the ion concentration and F is the ion flux. The ion flux is driven by the gradient of the diffusional chemical potential $\bar{\mu}$ as,

$$\bar{F} = \frac{-D_O(c_m - \bar{c})}{k_m T c_m} \bar{\nabla} \bar{\mu}$$

where D_O is the ion diffusivity and c_m is the maximum ion concentration, T is the absolute temperature, k_b is Boltzmann's constant, $\bar{\Omega}$ is the enthalpy of mixing per site, K is the gradient energy penalty coefficient and $V_s = 1/c_m$. Parameter studies were conducted for conditions producing enthalpies of mixing ($\bar{\Omega}$) resulting in repulsive and attractive forces between Li^+ ions and vacancies.

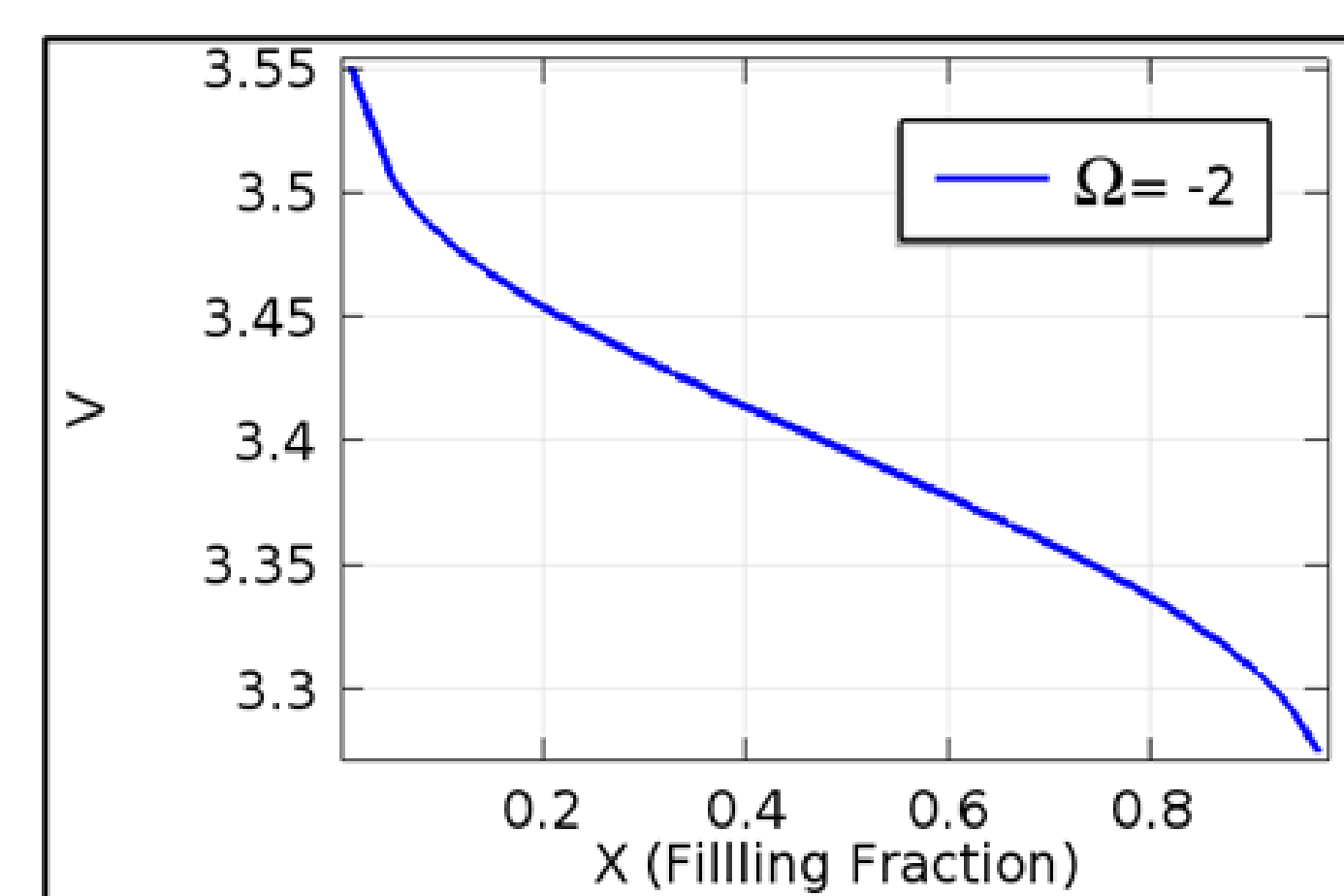


Figure 1. SP Battery voltage profiles for repulsive behavior.

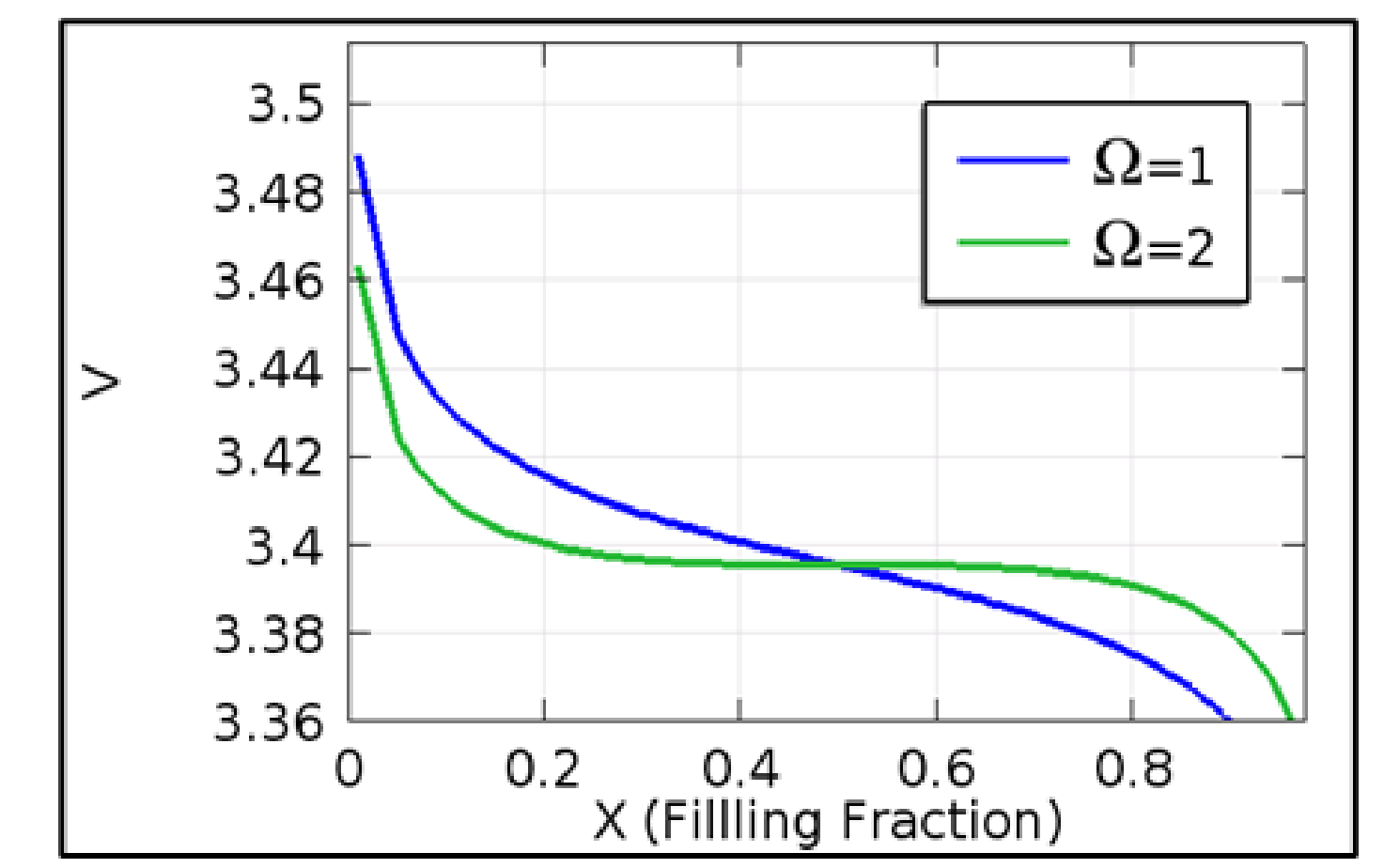


Figure 2. SP Battery voltage profiles for attractive behavior.

For repulsive behavior shown in Figure 1 the voltage response was similar to simple diffusion or shrinking core model behavior. For attractive forces shown in Figure 2 there is significant plateauing and increasing $\bar{\Omega}$ results in a "rotation" of the voltage response about the half-filled particle concentration.

RESULTS: Singular value decomposition and principal component regression on the simulation data showed that there was no significant improvement of the model fit for retaining more than two singular values (temperatures). To generalize the model for any temperature over the batteries operating range the resulting rank 2 vector solution was decomposed into the product of a diagonal matrix and a 2D rotation matrix. The solution parameters were fitted to the A123 Systems 26650 battery by second order polynomials in temperature and the model fit is shown in Figure 3.

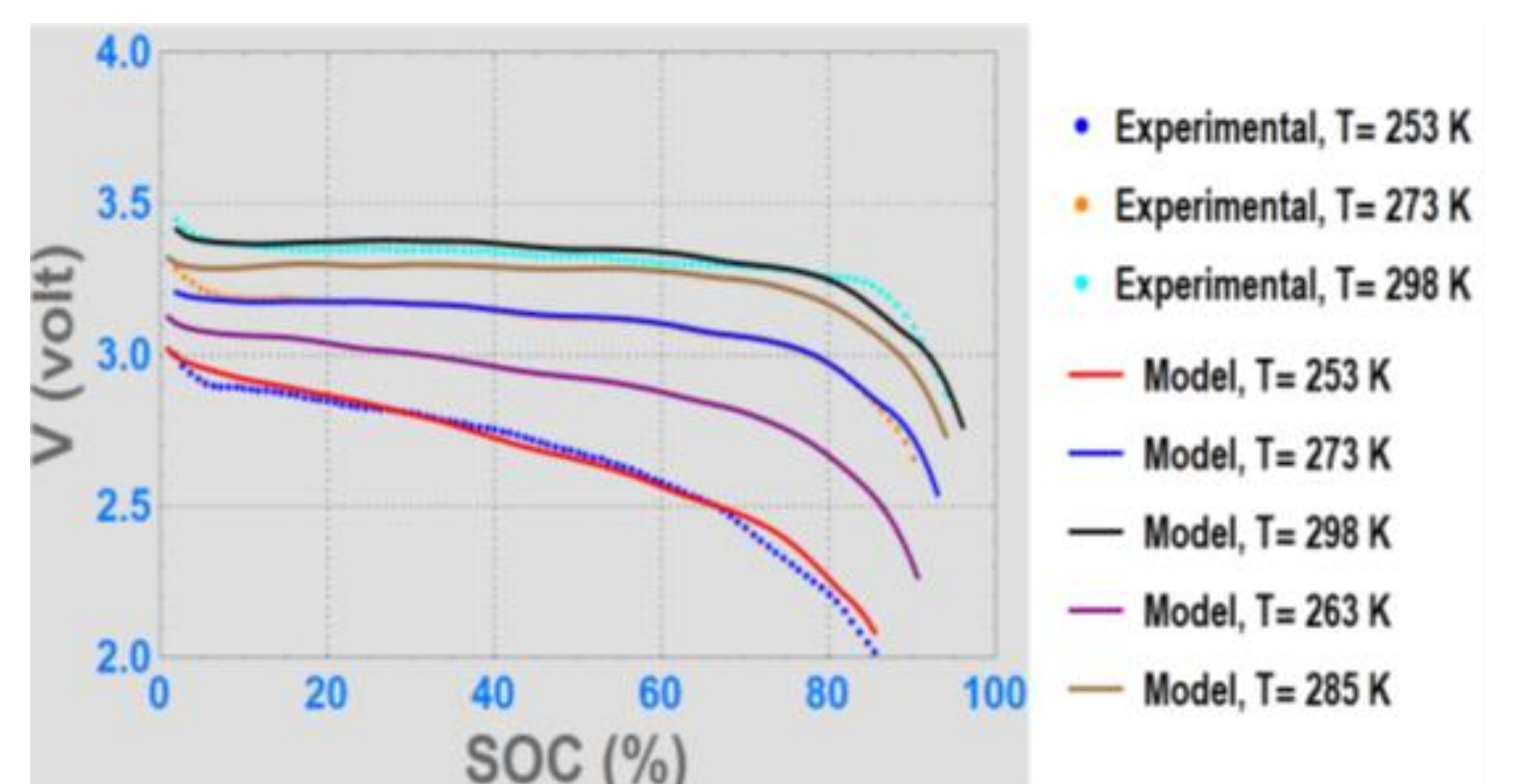


Figure 3. Voltage SOC Response for the ROM Thermal Model

REFERENCES:

1. Bazant, M. Theory of Chemical Kinetics and Charge Transfer Based on Nonequilibrium Thermodynamics. *Accounts of Chemical Research* 2013, 46, 1144-1160.
2. Guo, M.; Sikha, G.; White, R. Publisher'S Note: Single-Particle Model for A Lithium-Ion Cell: Thermal Behavior [J. Electrochem. Soc., 158, A122 (2011)]. *Journal of The Electrochemical Society* 2011, 158, S11.