Multi-scale Simulation of Thermo/Electrochemical Mechanism in Li-ion Cells at Elevated Temperature

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Thermal runway of lithium ion cells is one of critical issues for practical operation of large-scale cells [1].

As a pilot study preliminary to building an early-alert heat management system for Li-ion cells, we present 1D multi-scale simulation of a single cell with calculation of side reactions occurred at elevated temperature in addition to simulation of normal operating conditions. The thermo-electrochemical model used in this work is designed to understand electrochemical and thermochemical kinetics in range from micro to macro scales [2]. Lithium insertion and extraction through active materials are assumed to follow Butler-Volmer kinetics.

Two different kinds of cells are compared to investigate contributions to temperature rises by thermodynamic potentials of each type of cathode: lithium iron phosphate ($LiFePO_4$, LFP) and blends of lithium manganese oxide ($LiMn_2O_4$, LMO) spinel with lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$, LNCA). Thermodynamic potentials, entropy and enthalpy of lithiation, of LFP are referred from work done by Dodd [3]. The potentials for the blends are obtained by applying weighting factors to potentials of pure LMO and LNCA based on experiments by Tran et al. [4]. The thermodynamic potentials and kinetic of the blend cell are validated by comparison with experimental discharge curves in 0.1, 1, 5 and 10 C rate at 303, 313 and 333K (Fig. 1).

As for thermochemical side reactions at elevated temperature, we include exothermic decomposition mechanisms of solid electrolyte interface (SEI) [5,6] and solvent (ethylene carbonate, EC) [7,8] as well as oxidation mechanisms of released gas from the decomposition reactions and cathode. Reaction rates are assumed to follow Arrhenius form and Tafel-like expression for non-charge transfer reactions and charge transfer reaction, respectively. Fig. 2 shows prognosis of cell average temperature and heat flow of anode by self-heating due to decompositions of SEI and EC at constant ambient temperature of 400K in non-operational condition. A sharp peak represents rapid decomposition of SEI inducing simultaneous reactions of both decomposition of SEI and EC (e.g. formation of SEI).

Furthermore, predictions of temperature and kinetic behavior in case of external short circuits are presented comparing with experimental measurement of cell surface temperature.

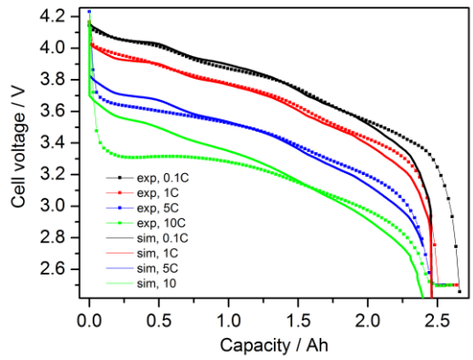

Fig. 1. Comparison between simulation and experiment of discharge curves for LMO spinel/LNCA mixture cathode/MCMB anode in various C rates at room temperature.

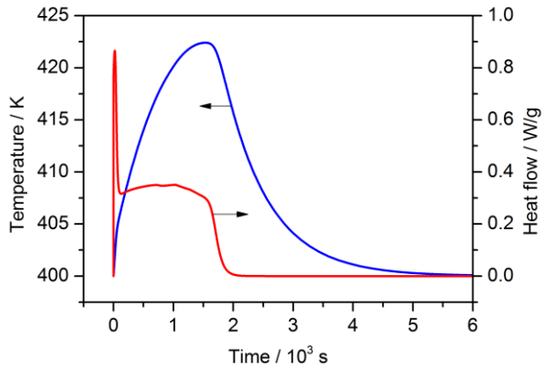

Fig. 2. Cell average temperature profile and heat flow from anode of self-heating by SEI formation and decomposition with full cell model at constant ambient temperature of 400K.

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