IV.C.5-Mechanistic Modeling Framework for Predicting Extreme Battery Response (SNL)

Tony Geller (Sandia Program Manager)
Sandia National Labs (1)
Albuquerque, NM 87185-0836
Phone: (505) 844-7795; Fax: (505) 844-4523
E-mail: asgelle@sandia.gov

Harry Moffat (PI)
Phone: (505) 844-6912; Fax: (505) 844-9297
E-mail: hkmoffa@sandia.gov

Subcontractor:
S. Pannala, Oak Ridge National Labs, TE
R. Kee, Colorado School of Mines, CO

Start Date: Oct 2013
Projected End Date: September 2015

Objectives

- Address root cause and implications of thermal runaway of Li-ion batteries by delivering a software architecture solution that can lead to the development of predictive mechanisms that are based on identification of species.
- .

Technical Barriers

Key technical risks associated with the proposal involve the lack of mechanistic understanding of interfacial layers associated with electrodes in the Li-ion system.

Additionally barriers involving the development of mechanistic understanding of degradation mechanisms and detailed kinetics of solid phase processes and liquid phase secondary reactions abound with the Li-ion battery community. We will develop software for these mechanisms to be addressed and then make that software available as open source. Future collaborations using the software we hope will help to fill these gaps.

Additionally we will pursue upscaling of microstructure parameters to the macrohomogeneous scale. This approach addresses some of the uncertainty.

Technical Targets

- Implement 1DElectrode capability within CAEBAT and verify.
- Implement partially saturated porous flow and solid mechanics modeling within 1Delectrode.
- Develop consistent thermodynamic/transport models of the entire cell using CANTERA. Add partial saturation and solid mechanics models to CAEBAT. Build SEI Models that can predict the autocatalytic temperature behavior experimentally observed
- Implement upscaling ideas from microstructure models within CAEBAT using both averaged results and perhaps statistical distributions.
- Exercise new capability by developing new models for thermal runaway processes with 1DElectrode / CAEBAT

Accomplishments

- Linked 1Delectrode model into CAEBAT architecture, running thermal and electrical simulations using AMPERES/1Delectrode.
- Validated models against Dualfoil model within 1DElectrode/CAEBAT.
- Developed microstructural electrode models from experimental FIB-SEM and X-ray tomography reconstructions.
- Effective electrode properties are extracted from microscale models, which can be used in CAEBAT cell-scale models.
- 1Delectrode model improvements include real thermodynamics based chemistry (activities, …), Stefan-Maxwell nondilute diffusion, and consistent enthalpy-based, multi-species energy conservation. This is new to battery modeling software.
- A formulation for two-phase, multispecies electrochemical transport in porous electrodes has been developed, for subsequent implementation into 1Delectrode.This is also new to the battery modeling community.
- Successfully reconstructed 3D microscale digital models of Li-ion cathodes from FIB-SEM images and developed electrochemical transport

(1) Sandia National Laboratories

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

models with Faradaic and Ohmic internal heat generation.

- Successfully simulated a 1C discharge rate in a cathode using the reconstructed 3D microscale model showing reasonable cell potential and Joule heating curves over full discharge cycle.

Introduction

We are expanding the functionality of the CAEBAT-I architecture developed at Oak Ridge National Laboratory by incorporating advanced speciation models. These models are built on the Cantera open-source software library for elementary thermodynamic, transport and kinetic processes. We will be implementing this modeling capability to address two key aspects of Li-Ion battery chemistry that will support the existing CAEBAT-I program.

1) Modeling the processes that transform chemical energy to thermal energy in abusive scenarios and the associated heat release for both normal operation and abusive conditions. In doing this we focus on interactions between electrode-particle scale physics present within our Cantera-based approach and the cell-level physics already present within the CAEBAT framework. . We will add models that can capture the autocatalytic temperature rise observed at elevated temperatures, fitting data from Sandia's BATLab program.

2) Modeling thermo-electro-mechanical interactions within porous materials that determine the heat, mass and electrical transport processes, addressing cell-level structural evolution under normal operation and abusive conditions. This will include modeling gasification mechanisms by adding partial saturated flow to battery models so that mechanisms for gasification may be envisioned and applied in at least a 1D context.

Our modular approach will emphasize hierarchical approaches to modeling the detailed chemistry system and onset of thermal abuse from a species-specific point of view. These represent a natural extension to the current CAEBAT architecture currently developed at ORNL. We will also develop upscaling algorithms to bring information from subgrid variations in microstructure developed by Prof. Bob Kee at the Colorado School of Mines to the macrohomogeneous scale. This approach to incorporating detailed chemistry and fundamental processes into the CAEBAT OAS is based on the open-source program Cantera. Our first goal is to advance the state of the art in modeling chemical processes within the battery community using open software standards. Because the battery community has lacked such an infrastructure, fundamental quantitative comparisons of chemistry have not occurred to a significant extent within the community. We expect to emulate what has occurred within the combustion community with programs such as Chemkin, which brought together experimentalists and computational scientists to create an infrastructure, which was then used to quantitatively understand and predict mechanistic details.

Approach

We have two complimentary goals within this project. The first goal is to advance the state of the art in modeling chemical processes within the battery community using open software standards. This is an important and often misunderstood goal. Because the battery community has lacked such an infrastructure, fundamental quantitative comparisons of chemistry have not occurred to a significant extent within the community. *We hope to emulate what has occurred within the combustion community with programs such as Chemkin,* which *brought together experimentalists and computational scientists to create an infrastructure which was then used to elucidate mechanistic details.*

The second goal of the project is to start populating this infrastructure with models of various levels of fidelity that may address the thermal runaway process observed to occur within Li-ion batteries. Ideally this would involve understanding the formation of the SEI layer and its evolution as a function of temperature. Although the mechanistic details of this process as well as inputs for constitutive models that would make a model for this just are not available for engineering-level capabilities. We will propose starting with those models and then refine them using the experimental data from Sandia's BATLab program to interpret the thermal runaway process from an engineering perspective. Furthermore, we will expand the engineering details into more sophisticated level that will track individual species in mechanisms that closely resembles the corrosion processes based on our current understanding of the stability of the passivating layers. This would necessarily involve determining the stability and thermodynamics of components of the SEI layer as a function of temperature and pressure.

An unappreciated feature of batteries is the need to understand the thermo-mechanical interactions of the porous materials as a function of the state of discharge and as a function of the number of cycles. We at Sandia have started to address this issue within our codes and would like to transfer some of the technology to the CAEBAT architecture with collaboration from ORNL. This involves solving the partially saturated flow equations, which are important for some battery systems, and represent failure mechanisms in others. And we also propose to include the poroelastic stress constitutive equations using the effective stress principles. This concept is essentially new to batteries, though we have extensively used it in other contexts with Sandia codes such as Goma, which can model the mechanical environments found in drying porous media or porous media in contact with continuum fluids that undergo external stresses.

Key technical risks associated with the proposal involve the lack of mechanistic understanding of interfacial layers associated with electrodes in the Li-ion system. We will pursue upscaling of information from DFT or ab-initio, or MD atomistic calculations to the continuum level to address this area where absolutely needed and the sensitivity to model parameters is very high.

The impact of this project will be far-reaching. By the end of the project we will have created infrastructure for the inclusion of detailed mechanistic models for thermochemical processes that are important to battery performance and safety. Additionally, the mechanistic understanding of thermal runaway processes in Li-ion batteries will be advanced. This capability can be linked to existing cell, module and pack-level capabilities being developed under CAEBAT-I.

Results

Model Development

We have expande d the list of electrode objects that can be used with 1DElectrode to include diffusional objects with and without the total arbitrary Lagrangian Eulerian (TALE) capability.

We have added the capability to employ arbitrary fitted OCV curves into the electrode object (which is the industry norm) in order to compare against dualfoil, which uses this method exclusively. The default method for specification of the OCV within 1Delectrode is to calculate the OCV from the specification of the electrochemical potentials of all of the species involved in the interfacial kinetics reaction, and this is the method that will eventually lead to the greatest progress in understanding degradation methods.

We have added to Cantera the ability to combine the concepts of a generalized Butler-Volmer formulation for charge-transfer reactions at interfaces with an affinity formulation, , which is used extensively in the geochemistry community and which with the addition of the voltage-dependent modification of the activity energy can be made to look like a generalization of the B-V reaction..

Comparison To Dualfoil (

In order to validate our model we have carried out a validation exercise against Dualfoil.Fig. 1 demonstratest that we can duplicate Dualfoil calculations fairly well when the problem statement is specified. Additional work on the transport formulation within 1Delectrode was pointed out to be demonstrated by this exercise.

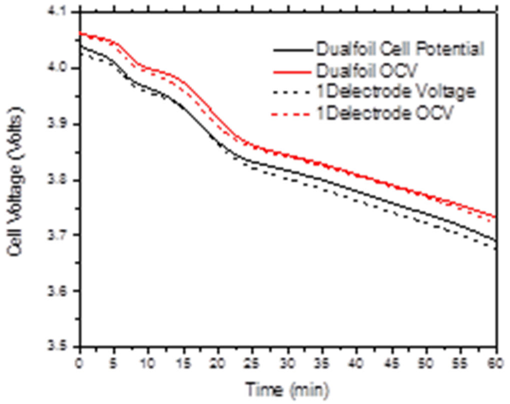


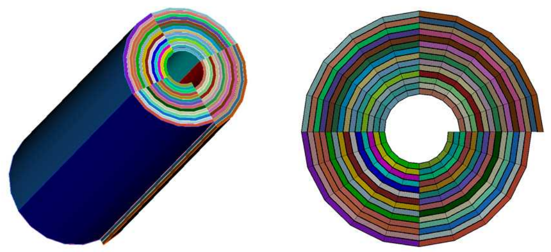
Figure 1 Comparisons of Dualfoil to 1Delectrode using the OCV fitting capability and recently installed generalized Butler-Voler implementation within Cantera.

CAEBAT development

One of the primary tasks is to integrate the 1D electrode model based on cantera into Virtual Integrated Battery Environment (VIBE). We have successfully integrated this new software into the suite of components for modeling electro-chemistry inside VIBE. Below we show an existing example to demonstrate the capability to swap the dualfoil with the 1D electrode component and perform a coupled electrochemical, electrical and thermal simulation. In FY15, we will perform some detailed validation and comparison of the cell level simulations.

Example: Cylindrical Cell (Electrochemical-Electrical-Thermal)

This example contains the electro-chemistry, electrical and thermal transport components in a rolled cylindrical cell. Fig. 2-a shows the geometry and the finite element mesh used to resolve the geometry of the cylindrical cell and the current collectors. The top hierarchy model has 168 (56 each for the cell-sandwich and positive and negative current collectors) zones in 4 quadrants. The zones describe different current collector and cell sandwich regions. The simulation uses 56 concurrent 1D Electrode simulations for different cell-sandwich zones. Typical results are



shown in Fig. 2b. The maximum temperature occurs at the cell core as expected.

Figure 2-a: Geometry and mesh of the simulated cylindrical cell

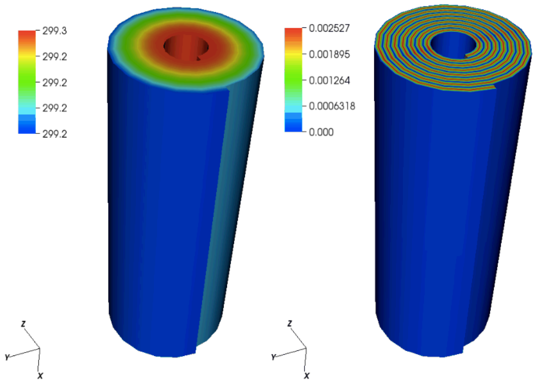


Figure 2-b: Sample results for cylindrical cell (temperature on the left and the electrical potential on the right)

Effective Properties from microscale electrode calculations

Accurately predicting electrical and thermal performance of lithium-ion batteries and pack assemblies is of great importance. By understanding fundamental electrochemical and thermal behaviors at the electrode microscale, and upscaling the results, macroscale models can be improved. Many previously published models approximate the electrode microstructures as packed spheres. However, actual electrode microstructures can differ significantly from the spherical approximation. Figure 3 illustrates a small segment of a graphite anode that has been reconstructed using X-ray tomography.

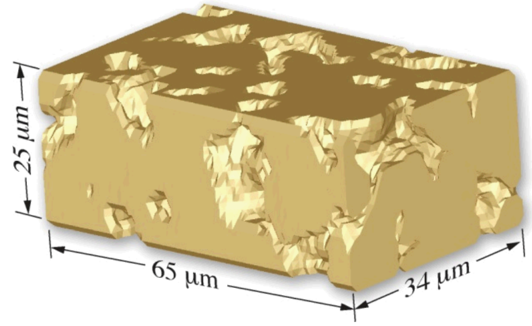


Figure 3: Reconstructed anode microstructure from an X-ray tomography experiment (X-ray data courtesy of Prof. Scott Barnett, Northwestern University).

Models developed at CSM predict the electrochemical and thermal behaviors at the electrode microscale. These models are based upon microstructural geometries that are reconstructed from either FIB-SEM or X-ray tomography experiments. The modeling itself is implemented with extensions of the ANSYS FLUENT software.

To date, the microstructural modeling has focused on the cathode, assuming an ideal anode. Both the electrode and electrolyte phases are resolved in three dimensions, using millions of finite control volumes. The models solve conservation equations for lithium concentrations and electrostatic potentials within the electrode and electrolyte phases. Electrochemical charge transfer at the phase interfaces is represented in Butler-Volmer form. The thermal models represent both Faradaic and Ohmic contributions. A new algorithm has been developed to model accurately the Ohmic heating, which is very sensitive to computational noise in evaluating the local electrostatic-potential gradients.

The microscale models are being extended to fully couple the full anode-separator-cathode assembly at the microscale. Additionally, the binder phases are being incorporated into the electrode models.

Upscaling ideas -Microstructurally Derived Heat-Generation Tables

Upscaling is important aspect of the microscale modeling. Extracting effective physical properties, such as mass density, heat capacity, and thermal conductivity, is relatively straightforward. However, evaluating the local heat-release rates is much more challenging. One objective of the microscale effort is to predict and communicate effective properties into cell- and module-scale models using the CAEBAT architecture. Fig. 4 is an example of a heat generation table idea. The heat generation values will override the native heat-generation functions where necessary within the macrohomogeneous representation of the material. The tables will be parameterized as a function of internal state variables such as local temperature, SOC, and C-rate.

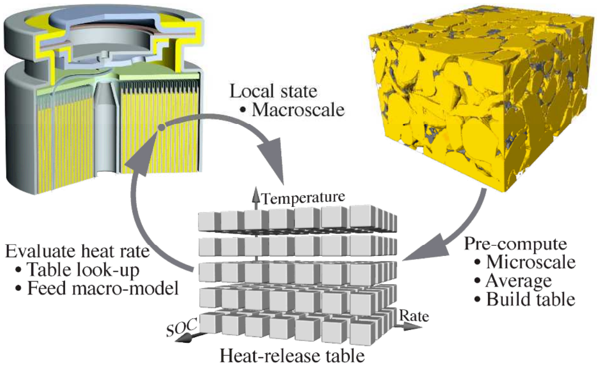


Figure 4: Methods of upscaling of heat generation tables are being evaluated

Conclusions and Future Directions

In addition to the partially saturated porous flow and solid mechanics modeling efforts which we have planned, we have started to design new models for the SEI layers based on analogs to corrosion system, whose formulation reactions are thermodynamically reversible, so that they may be designed to dissipate under some conditions. Combining these models with traditional thermal models for thermal runaway, we will then attempt to fit these against Sandia's Batlab data.

FY 2013 Publications/Presentations

1. 2014 DOE Annual Peer Review Meeting Presentation
2. 89th Lithium Battery Technical/Safety Group Meeting, Sandia Labs, Sept 2014.

(1) Sandia National Laboratories

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation,
a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's
National Nuclear Security Administration under contract DE-AC04-94AL85000