

# Supporting Credibility of Single Cell Thermal Battery Modeling through V&V/UQ Activities

**Benjamin B. Schroeder\***, Eric Allcorn, John C. Hewson, Harry K. Moffat, Edward S. Piekos, Bradley L. Trembacki, Tyler G. Voskuilen, and Scott A. Roberts

Sandia National Laboratories, PO Box 5800, MS 0828, Albuquerque, NM, 87185-0828,

\*Corresponding Author: bbschro@sandia.gov

**Abstract:** *When computational models are used for design, qualification, or product acceptance purposes, assessing and communicating the model's credibility to the end users is essential. Verification, validation, and uncertainty quantification (V&V/UQ) practices are used to monitor code reliability and pedigree, estimate uncertainties present in model predictions, and quantify the impact of model form errors through comparisons with experimental data. Previously, similar V&V/UQ practices have been used to establish the credibility of a thermal-only model of a molten salt battery. The current work now applies V&V/UQ practices including code verification, solution verification, uncertainty quantification, and model validation to a multi-physics model, consisting of thermal, electrochemical reactions, mechanical deformation, and fluid flow physics, of a single cell from a molten salt battery. Applying this process to establish model credibility can result in the identification of either modeling or experimental data gaps that need to be addressed.*

*Following the identification of a gap in the model's electrochemical model parameterization and calibration, a mitigation plan was formulated. Through a new experimental campaign aligned with the modeling effort, single cell discharge data was gathered for a range of temperature and electrical load conditions, enabling calibration of thermodynamic and kinetic model parameters. Comparing the calibrated model with validation datasets allows the model's credibility story to be solidified, providing customers with a structured basis for understanding the model's utility.*

**Keywords:** Thermal battery; molten salt electrolyte; single cell; calibration; validation; credibility

## Introduction

A multi-physics modeling capability for thermally activated molten salt batteries has been developed over the last decade [1–3]. The current model variant includes capabilities to capture the coupling of thermal transport, electrochemical reactions, mechanical deformation, and fluid flow for single battery cells [4]. Motivating this capability development is the overarching goal of providing battery designers with a desktop tool that allows for exploration of battery design parameters and performance optimization; the Thermally Activated Battery Simulator

(TABS) v5 is the graphical user interface version of this tool being distributed [5].

Previously, simulation predictions of engineering applications were presented as analysis results and it was acknowledged that significant modeling assumptions and simplifications were necessary when developing the simulations. The current paradigm of engineering simulations has begun to include both qualitative analysis of and quantification of the impact of such modeling simplifications and assumptions. To provide this type of information to the users of TABS, approaches and methods from the Verification, Validation, and Uncertainty Quantification (V&V/UQ) field were incorporated into the tool development process. A V&V/UQ study of a full battery setup of TABS v3, exercising only thermal physics, was previously completed [6]. Within that full battery study, prediction sensitivity and uncertainty caused by common geometric variabilities and uncertainty in material properties, as well as error caused by numerical discretization were quantified. Now, V&V/UQ processes are applied to a single cell model containing coupled multi-physics, such that the credibility of the product and resulting predictions can be provided to TABS users, enabling greater confidence in battery designs prior to physical builds.

## Model Credibility

When establishing the credibility of the single cell modeling tool, elements of the Predictive Capability Maturity Model (PCMM) [7] process provide guidance as to what aspects of the simulation process should be addressed. The elements of PCMM are 1) ensure the code implementation of the math equations and numerical methods are tested (*code verification*), 2) establish the impact of simplifications used when describing the physical phenomena (*physics and material model fidelity*), 3) determine the impact of simplifications used when describing the physical system (*representation and geometric fidelity*), 4) evaluate the impact of numerical methods on the predictions of interest (*solution verification*), 5) consider the system's sensitivity to input uncertainty (*uncertainty quantification*), and 6) compare model predictions with experimental data to establish predictive capabilities (*validation*). Greater detail of how each element was applied to the TABS v4-v5 single cell model follow.

*Code Verification:* Regression tests were implemented to ensure that the impact of capability developments and refinements on prediction quantities of interest were understood when implemented. Version control was also used to transparently track code changes during development.

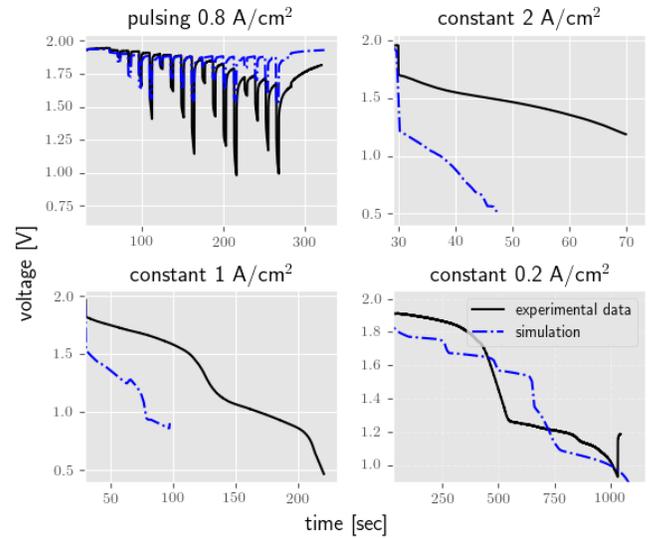
*Physics and Material Model Fidelity:* Impact of the fidelity of physics and material models included within simulations was studied and became an adjustable feature of the tool with documented impact on prediction quantities [4].

*Representation and Geometric Fidelity:* The single cell model uses a 2D axisymmetric representation. This simplification of a 3D object is perceived to be a good approximation due to the minimal expected axial variation and significant reduction in computational cost.

*Solution Verification:* Second order convergence of the spatial discretization (a 2<sup>nd</sup> order FEM scheme) was found for a user identified set of prediction quantities of interest. Relative error values due to the predictor-corrector tolerance used for the adaptive time-stepping scheme were also identified. Quantifying these numerical error sources allowed for informed default values to be set in the tool as well as guidance provided in the tool's documentation.

*Uncertainty Quantification:* Through a combination of expert elicitation and literature search, probabilistic uncertainties were derived for physical model parameters and material properties. Those uncertainties were then propagated through the single cell model using the stratified random sampling approach Latin Hypercube sampling, producing uncertainty estimates for single cell performance characteristics of interest. Sensitivity of the model responses to uncertain model inputs was characterized using global sensitivity measures, Sobol indices.

*Validation:* To test the predictive capability of the single cell model, single cell test data for a variety of load conditions was compared with corresponding model predictions. Multiple battery chemistries are supported by TABS, but the FeS<sub>2</sub>/LiSi cathode/anode with LiCl–KCl electrolyte configuration is common and was used for current validation activities. Figure 1 shows how the model predictions using nominal parameter values compared with an experimental dataset at 500°C, that included data under constant loads (2, 1, and 0.5 A/cm<sup>2</sup>) as well as a pulsing load with a base load of 0.8 A/cm<sup>2</sup>. For the constant load cases, significant under-prediction of the voltage, potentially attributed to incorrect parameterization of physics models resulting in loss mechanisms, is evident in all three cases and appears to be a function of load. The 0.2 A/cm<sup>2</sup> load case also indicates that the capacity of the experimental battery is significantly lower than predicted. Capacity loss could be



**Figure 1.** Validation comparisons of nominal simulation results with experimental data.

caused by unreacted FeS<sub>2</sub>, which the model predicts to be completely consumed during the battery life.

Resulting from this V&V/UQ analysis was the identification of a gap in the model credibility. While five of the six aspects of model credibility considered were explored, analyzed, reported, and deemed to be acceptable for the customer, model validation illuminated a significant limitation with the tool's credibility. Parameter used for many of the important physics models within the single cell simulations, used values with limited physical derivation. To mitigate the gap in the tool's credibility, an experimental campaign was leveraged to provide a calibration basis for many of the model's important parameters. Once the model calibration has updated parameter values, the single cell model can be validated against additional datasets, solidifying its credibility.

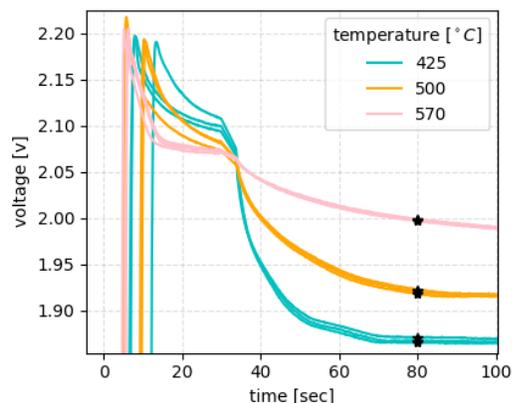
### Calibration

When approaching calibration of the multi-physics contained within the single cell framework, we took the approach of tackling the phenomena in the approximate order of impact on the prediction of interest, voltage traces. This approach was justified by the hierarchical relation among the physical phenomena, i.e., if the thermodynamics under-predict open circuit voltage, no reaction or diffusion process can force the voltage higher. Following that philosophy, thermodynamic open circuit predictions of the FeS<sub>2</sub>/LiSi system are first considered, followed by reaction rates of the first cathode and anode plateaus. Simultaneous with the reaction rates, capacity loss mechanisms such as solid state diffusion rates must also be considered.

To calibrate the thermodynamic and kinetic mechanisms for the single cell chemistry of interest, a data gathering

campaign in sync with those objectives was needed. This experimental campaign was designed to aid model calibration by holding open circuit for prolonged periods at the beginning of the cells' activation and testing cell performance over a range of temperatures to decouple reaction pre-exponential factors and activation energies. Single cells were loaded between hot platens, fixed at the temperature of interest; a programed current load profile was applied with sheets of mica and then stainless steel collectors sandwiching the cell. 3 kilograms of compression was placed on the cells for testing. Replicates of each load and temperature condition were collected and pellet geometries were consistent across all experiments. The replicates were meant to enable characterization of unit to unit variability and measurement uncertainty.

The first model aspect investigated was the thermodynamic modeling of open circuit voltage (OCV). Thermodynamics using NASA 9 parameter and Shomate polynomials, previously described in [1], have been used to describe the  $\text{FeS}_2/\text{LiSi}$  single cell systems throughout the reaction process to equilibrium. When attempting to use the new datasets to observe OCV, issues arose due to physical phenomena not previously considered. Figure 2 shows voltage traces for three temperatures, where no load was applied until 30 seconds. The initial voltage spikes and

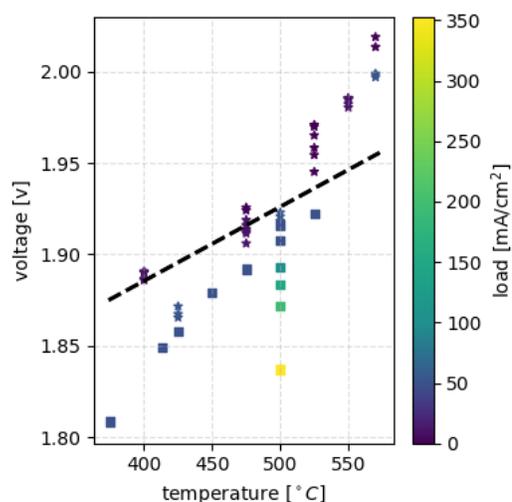


**Figure 2.** Experimental voltage data traces where the current was held at open circuit for 30 seconds, followed by a 50  $\text{mA}/\text{cm}^2$  load. Stars indicate where data for estimating the cell's initial OCV was extracted.

subsequent exponential behaviors are not fully understood and hypothesized to be a result of reactions with oxidized electrode materials that are not included within the current chemistry models. Lithiated cathodes have previously been found to reduce the initial voltage spiking behavior [? ], but was not an aspect measured in the current campaign. Alternative reactions for the system involving oxidation products  $\text{FeSO}_4$  and  $\text{Li}_5\text{Fe}_2\text{S}_4(\text{s})$  [? ] have been hypothesized, but have not been experimentally found [? ]. Then, once a low (50  $\text{mA}/\text{cm}^2$ ) load is applied, a

new equilibrium voltage is not immediately reached, but transitioned to in a temperature dependent, exponential behavior. Due to the unaccounted for initial reactions, the system's initial OCV could not be extracted during the initial non-loaded period, but was instead extracted after an equilibrium voltage was approximately reached for the low loading condition (shown as stars in the figure).

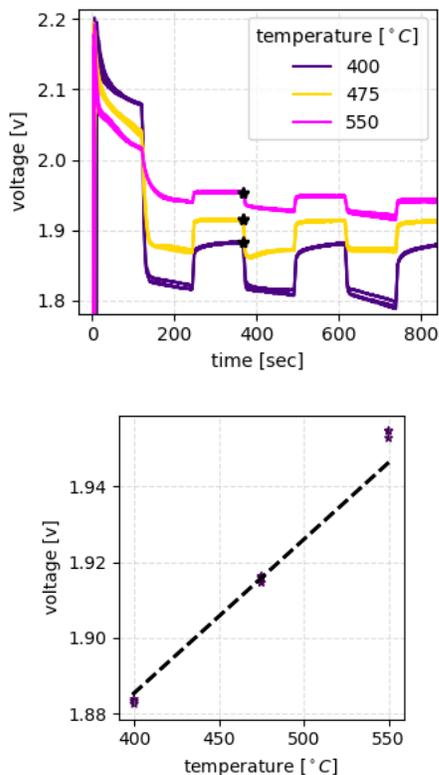
To validate the thermodynamic model, OCV estimates from the new dataset (★) as well as other legacy datasets of lesser characterized derivation (□), are compared with the model over a range of applicable temperatures, as shown in Figure 3. The load associated with each data point



**Figure 3.** Comparison of experimental data used to approximate open circuit voltage with thermodynamic model (line) over a range of temperatures. Data with less known derivation shown as squares.

is shown as the color of the marker due to limitations in extracting OCV data previously mentioned. Comparing the available OCV data with the thermodynamic model shows that the data agrees well with the model between  $450^\circ\text{C}$  and  $500^\circ\text{C}$ , but a significant discrepancy between the model and the data exists for temperature  $550^\circ\text{C}$  and above. Less concern was placed on the model's performance at temperatures  $550^\circ\text{C}$  and above, because it is believed that the cathode material starts to degrade in this temperature range, which the thermodynamic model does not capture.

To reduce the aforementioned problems with extracting OCV data, a final experimental dataset was designed to provide insight into the OCV trends of the single cells throughout the active lifetime. To accomplish this, 120 second periods without load and with 100  $\text{mA}/\text{cm}^2$  load are alternated, as shown in Figure 4. The initial spiking behavior followed by slow decay is still present, but now OCV values closely matching the thermodynamic model



**Figure 4.** (Top) Experimental voltage traces over time with alternating open circuit and  $100 \text{ mA/cm}^2$  every 120 seconds. (Bottom) Comparison of initial open circuit voltages (★) extracted from top plot with thermodynamic model over a range of temperatures.

are observed during the first two periods of open circuit after a load has been applied. This dataset shows close agreement with the thermodynamic model, with slight deviation at the higher temperature conditions that are known to possibly be beyond the physics described by the thermodynamic theory currently considered.

### Summary

Credibility of the single cell thermal battery simulation tool TABS is being supported by V&V/UQ processes. Due to a gap in the model's predictive capabilities found during model validation, an experimental campaign was aligned with the calibration of thermodynamic and kinetic aspects of the single cell model. Following the validation of the thermodynamic model, kinetic reaction rates can now be calibrated to a subset of the datasets and the full single cell model can then be validated against the remaining datasets.

### Acknowledgments

The authors gratefully acknowledge funding from the Joint Department of Defense/Department of Energy Munitions

Technology Development Program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Unclassified Unlimited Release SAND2018-4408 C

### References

1. Hewson, J., H. Moffat, C. Leuth, and D. Ingersoll. "Predicting Electrochemical Phenomena in Lithium Molten Salt Thermal Batteries." Proceedings of the 44th Power Sources Conference, Las Vegas, 2010.
2. Hewson, J., H. Moffat, and V. Brunini. "Model Parameterization for Electrochemical Predictions of LiSi/FeS<sub>2</sub> Batteries." Proceedings of the 46th Power Sources Conference, Las Vegas, 2014.
3. Voskuilen, T., J. Hewson, H. Moffat, and S. Roberts. "Multi-Physics, Multi-Plateau Reaction Model for LiSi/FeS<sub>2</sub> Batteries." Proceedings of the 47th Power Sources Conference, Orlando, 2016.
4. Voskuilen, T., C. Jove-Colon, H. Moffat, B. Schroeder, B. Trembacki, and S. Roberts. "Multi-Physics Cost and Complexity Reduction Strategies for Modeling Thermally Activated Batteries." Proceedings of the 48th Power Sources Conference, Denver, 2018.
5. Roberts, S., C. Jove-Colon, H. Moffat, M. Neilsen, E. Piekos, B. Schroeder, B. Trembacki, and T. Voskuilen. "TABS : A Thermal Battery Desktop Design Tool." Proceedings of the 48th Power Sources Conference, Denver, 2018.
6. Trembacki, B., S. Harris, E. Piekos, and S. Roberts. "Uncertainty Quantification, Verification, and Validation of a Thermal Simulation Tool for Molten Salt Batteries." Proceedings of the 47th Power Sources Conference, Orlando, 2016.
7. Oberkampf, W. L., M. Pilch, and T. G. Trucano. "Predictive Capability Maturity Model for Computational Modeling and Simulation." SAND2007-5948, Sandia National Laboratories, 2007.