Abstract: Prior modeling of LiSi/FeS$_2$ molten salt batteries used a multi-plateau approach for the anode reactions but used a reaction-extent model for the cathode. This required an assumption as to which reaction mechanism/interface is currently reacting and prevented multiple simultaneous reactions during high current discharge.

We present an update to the previously presented multi-plateau model [1–3] for the cathode reactions with calibration against experimental data over a wide range of discharge currents using a 1D isothermal model. We then couple this new model with electrolyte phase-change and transport for single-cell simulations. Using this model, we present results from 2D axisymmetric single-cell coupled thermal-electrochemical simulations of start-up and freeze-out at varying load resistances.

Keywords: thermal battery; primary lithium cell; molten salt electrolyte; iron disulfide; computational modeling

Introduction
Predictive modeling of thermal batteries requires coupling between several key physical phenomena. A robust electrochemical model for the active components along with electrical transport is required to predict start-up times and operational performance, but this alone is not sufficient. The electrochemistry must be coupled with thermal transport, phase change, and porous flow in order to capture the relevant transport processes. The development of predictive models in order to guide battery design and enable efficient design optimization is a primary goal of this and our previous work [1–5]. In this work, we present a more robust multi-plateau electrochemical model for the FeS$_2$ cathode and compare isothermal 1D results with this model against experimental constant-current discharge data over a range of currents. Next, we couple this model with our 2D axisymmetric single cell model and show how thermal sources, such as Joule heating and phase change latent heat, influence the lifetime electrical performance. We also examine the effect that a partially saturated cell has on electrical startup performance.

Model
The electrochemical model described in previous work by Hewson et al. [1–3] used a concentric sphere multi-plateau model for the anode reactions and a reaction-extent model for the cathode reactions. The second aspect of this work is the integration of this new model into the multi-physics simulation capability described in [4] with necessary additional physics to allow simulation of battery start-up and freeze-out.

Multi-plateau model: In this work we present a graph-based model for phase change in the electrodes with an arbitrary number of volume phases and interconnecting reacting surfaces. The full cathode reaction pathway described by Hewson et al. [1] is

\[
\text{FeS}_2 \leftrightarrow \text{Li}_2\text{Fe}_2\text{S}_4 \leftrightarrow \text{Li}_{2+x}\text{Fe}_{1-x}\text{S}_2 + \text{Fe}_{1-x}\text{S} \leftrightarrow \text{Li}_2\text{FeS}_2 \leftrightarrow \text{Li}_2\text{S} + \text{Fe}.
\]

Experimental and thermodynamic analysis shows that the Li$_3$FeS$_2$ plateau is small relative to the overall cathode capacity so it can be safely neglected. The non-stoichiometric plateau involving Li$_{2+x}$Fe$_{1-x}$S$_2$ and Fe$_{1-x}$S is another source of numerical instability, since the equilibrium chemistry between the different species in that system is numerically much stiffer than the other reactions. Fortunately, at the temperatures of interest for thermal battery operation that equilibrium strongly favors the formation of Li$_{7/3}$Fe$_{2/3}$S$_2$ and FeS. This leads to a reduced reaction set of

\[
\text{FeS}_2 \leftrightarrow \text{Li}_2\text{Fe}_2\text{S}_4 \leftrightarrow \text{Li}_{7/3}\text{Fe}_{2/3}\text{S}_2 + \text{FeS} \leftrightarrow \text{Li}_2\text{S} + \text{Fe}.
\]

To represent these reactions generally, and allow for inclusion of self-discharge reactions and other side reactions, we construct a graph representation of the mechanism whose vertices consist of volume phases and surfaces, an example of which is shown in Figure 1. This assumes that solid-phase diffusion to the reacting surface is not the rate-limiting step. The graph can be constructed completely from the reaction definitions at each surface, however the orientation (which phase is the inner phase) must also be specified for surface area calculations.

The three reactions for the reduced mechanism above are applied on three surface vertices, and with an appropriately selected electrode particle morphology model the surface area of each surface vertex can be constructed using its connectivity and the volume of its interior volume vertices. For the results shown in this work, we use a spherical morphology although a platelet morphology could be used with the same technique. This graph-based approach makes it easy to extend our implementation to alternate chemistries (e.g. CoS$_2$) or to add different self-discharge pathways.

The production and consumption rates for the individual phases in this system can also be discontinuous in time. If the reaction is not limited by its surface area going to zero, as is the case for reactions in the outer phases with a spherical mor-
The basic components of the multi-physics thermal battery model we use have been described in our prior publications [4, 5, 7]. These include thermal transport, porous flow, and species transport in the electrolyte. These equations are applied on the axisymmetric domain shown in Figure 2, where thermal transport is solved on all regions, porous flow and species transport are solved in the anode, cathode, and separator, and electrical transport is solved in the anode, cathode, separator, and collectors. The level set burn front approach described in our prior publications is used to model the burn front movement in the two heat pellets. This burn front moves at a prescribed velocity, so we can use this velocity and the cell radius to calculate a non-dimensional time to compare the electrochemical startup against. For the electrical transport equations, we apply a constant 0.5 Ω resistive load boundary condition at the outer edge of the collectors.

The key additions to this model in the present work are the inclusion of the new electrochemical models, a modified form of the porous flow equation that is compatible with our melting and capillary flow models, and the addition of Joule heating and reaction heating.

In the porous flow system outlined previously, we use the van Genuchten model [8] to provide closure between saturation and pressure, providing two additional governing equations for the liquid and gas phases. This results in a different initial liquid pressure in each section of the cell (cathode, anode, and separator) that produces a large pressure gradient at their interface. In addition, we treat the solid electrolyte as a liquid with an artificially high viscosity and evaluate the liquid velocity using Darcy’s law,

\[
v = -\frac{\kappa}{\mu} (\nabla P - \rho g). \tag{1}
\]

As a result of this combination, the large pressure gradient between the cell components results in a non-negligible velocity, even when the electrolyte is solid and \( \mu \) is large. To compensate for this, we modify the Darcy flow equation to include the capillary pressure, \( P_c \), as

\[
v = -\frac{\kappa}{\mu} (\nabla P + C \nabla P_c - \rho g), \tag{2}
\]

where \( C \) is a smoothly transitioning scalar at the melt temper-
Cell Voltage

\[ C = \frac{1}{2} \left( \tanh \left( \frac{T_m - T}{\Delta T} \right) + 1 \right). \]  

(3)

Since the capillary pressure gradient is opposite the liquid pressure gradient prior to melting and \( C = 1 \) below the melt temperature, these terms cancel below the melt temperature and there is no artificial flow of the solid electrolyte.

An additional change is that we calculate the effective density and specific heat using the porosity and saturation to combine the solid, liquid, and gas properties. This is different from the prior work, which neglected the gas when determining effective thermal properties. The effect of this is a higher thermal diffusivity during the heat-up period, which has a significant effect on the battery’s electrochemical startup delay.

**Results and Discussion**

In this section, we demonstrate simulations of two separate physics models. First we show the results of the one-dimensional electrochemical model using the new multi-plateau model compared with data over a range of discharge currents. Second, we include this model in the 2D axisymmetric model of battery startup and show how different phenomena influence startup behavior.

**One-dimensional electrochemical model:** The results from the calibrated model are shown in Figure 3 at three currents, although the total data set used for the calibration included more intermediate currents between the high and low data sets shown here. There are a few interesting features to notice in this comparison. First, for the medium current case our model captures the change in slope that occurs at about 40% discharged but still includes a plateau from the third cathode reaction, which is not observed experimentally. This could be indicative of a transport limitation, such as changing electrical conductivity, which our model does not capture. Second, the phase transitions happen more sharply in the low current simulation than in the corresponding experiment. This could be due to a number of factors, including non-uniform particle sizes and the greater importance at low reaction rates of the non-stoichiometric phase we neglected in our initial simplifications of the FeS\(_2\) mechanism or the omission of solid state diffusion limits as the reaction proceeds to secondary plateaus.

**Two-dimensional multi-physics model:** For comparisons of startup behavior we use the non-dimensional time, \( \tau \), which is the ratio of the physical time to the time it takes for the heat pellet to burn across the radius of the cell,

\[ \tau = \frac{t_{\text{vb}}}{r_{\text{cell}}}. \]  

(4)

The thermal diffusivity of the partially saturated materials is higher than the fully saturated materials in these simulations because the thermal conductivity is not treated as a function of the saturation but the thermal mass is. While this assumption may require further examination, its effect here is that the partially saturated system starts up at \( \tau \approx 1.1 \) while the fully saturated system starts at \( \tau \approx 1.75 \) (Figure 4).

Changing time scales, the behavior of the cell during the solidification phase change is strongly influenced by insulation properties and internal heat sources. Inclusion of sources such as Joule heating, while small compared to the heat pellet release, can be influential when analyzing the full life of the cell. For example, in Figure 5, the effects of different heat sources and sinks on the percentage of the battery capacity that can be discharged with a constant 0.5 \( \Omega \) load are apparent. Omitting Joule heating results in a 9% reduction in operating time (defined here as the time to fall to 1 V), while omitting the melting latent heat of the electrolyte increased the operating time by 15% and changed the voltage response considerably. Obviously, using a higher discharge current or different thermal insulation will change the amount discharged, but the key here is the relative importance of the thermal source terms.

**Summary**

In this work we have shown a new graph-based multi-plateau electrochemical reaction model that is robust over the range of currents tested and does not exhibit the oscillatory behavior seen in the previous models. We have shown that this model can reasonably match the experimental voltage profiles over a
wide range of currents. We have also demonstrated the utility of this model in a fully coupled simulation that successfully captures the effects of both small and large thermal sources and transport limitations on the electrochemical response.

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References


