Transient Studies of a Sodium Sulfur Cell

Sarah Caprio

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Transient Studies of a Sodium Sulfur Cell

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Thesis submitted to the
Statler College of Engineering and Mineral Resources
at West Virginia University

in partial fulfillment of the requirements for the degree of

Master of Science in Chemical Engineering

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ABSTRACT

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Sarah Caprio

Modern grids will include input from fossil-fueled power generation facilities as well as renewable energy sources, and these are expected to work together actively. One major problem with this integrated power production is that most renewable energy sources are intermittent and variable, and thus introduce a very challenging situation with regard to grid stability and reliability. Also, fossil-fueled power generation facilities have load cycles based on expected usage. A non-reliable power source cannot feasibly be used to supply the grid with proper amounts of energy needed in peak times. A solution to this dilemma is power storage. The sodium-sulfur battery has high potential for electrical storage at the grid level due to its high energy density, low cost of the reactants, and high open-circuit voltage. However, the use of sodium-sulfur batteries at the grid level requires high current density operation that can cause cell deterioration, leading to lower sulfur utilization and lower energy efficiency. In addition, it can result in undesired thermal runaway leading to potentially hazardous situations. A rigorous, dynamic model of a sodium-sulfur battery can be used to study these phenomena, design the battery for optimal transient performance, and develop mitigation strategies.

Most literature on sodium-sulfur batteries is concerned the dynamics of the sulfur electrode (a sodium-polysulfide melt). There is limited data in the open literature for dynamics of an entire cell. With this motivation, a first-principles dynamic model of a sodium-sulfur cell (with beta”-alumina electrolyte) has been developed.

The state of discharge (SOD) of a sodium-sulfur cell significantly affects the heat generation rate, rates of electrochemical reactions, and internal resistance. To capture these
phenomena correctly, a fully coupled thermal-electrochemical model has been developed. The thermal model considers heat generation due to Ohmic loss, Peltier heat, and heat due to the entropy change. Species conservation equations are written in the sulfur electrode by considering the phase transition and change in the composition depending on the SOD. The electrochemical reactions are modeled by using Arrhenius-type rate equations with temperature-dependent terms and varying species concentration depending on the SOD. Species conservation equations are written in the beta”-alumina electrolyte for the ionic species by considering the change in composition due to diffusion and migration. In addition, the potential distribution, and the cell resistance for this spatially distributed system has been modeled. The physicochemical properties are considered to be temperature-dependent. The model is used to study both charging and discharging characteristics of the cell at varying current densities.

The PDE-based model is solved in Aspen Custom Modeler by using method of lines. Our work shows that an appropriate thermal management strategy is necessary for high current-density operation, especially in the case of high penetration of the renewable energy into the grid.
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1. Introduction

The sodium sulfur battery is an advanced secondary battery, which can be used for various power systems applications. Secondary batteries are able to be discharged and charged repeatedly, as opposed to a primary battery which cannot be recharged. Sodium sulfur batteries are ideal candidates for load-following applications, such as large-scale power storage for the smart grid, due to their high energy density, low cost of the reactants, and high open-circuit voltage. [1]

There are several appealing attributes for using sodium sulfur batteries for large energy storage at the grid level. Since many cells can be connected to produce several MW battery systems, sodium sulfur batteries can be applied to large capacity needs. Sodium sulfur batteries can also be made to fit custom storage requirements. These batteries are appealing for their compactness as well: the required area for installation is approximately one third of that for a lead acid battery.

The life expectancy of a typical sodium sulfur battery is about 15 years. These batteries produce no pollution gases, vibration, or noise pollution, which
makes them an appealing energy storage option to the environmentally conscious. [2]

The use of sodium sulfur batteries at the grid level benefits both the electricity generating companies and the electricity consumers. For the companies that produce energy for the power grid, more efficient electricity generation would mean less costly operation and less waste. In addition, due to lesser variation in the load, equipment life can be improved. For the consumers of energy from the power grid, better storage systems could mean reduced electricity bills and electricity that is more reliable from their providers.

1.1. Background

The design for sodium sulfur batteries was first proposed by Ford Motor Company in 1968. [3] The sodium sulfur battery consists of a central molten sodium electrode and outer molten sulfur/sodium-polysulfide electrode, separated by a solid ceramic beta”-alumina electrolyte (often represented by $\beta''-Al_2O_3$). See Figure 1 for a representation of the configuration of a central sodium sulfur cell.

The sodium electrode contains the liquid sodium in a stainless steel wick. The sulfur electrode contains the liquid sulfur in a graphite matrix (for better electronic conduction).
The half-cell reactions that take place in the sodium and sulfur electrodes, respectively, are given by

\[ 2Na \leftrightarrow 2Na^+ + 2e^- \]  

(1)
The overall cell reaction is given by

$$2Na^+ + xS + 2e^- \leftrightarrow Na_2S_x$$  \hspace{1cm} (2)

The reaction proceeds forward during cell discharge, and the reverse reaction occurs during charge. During discharge, the potential difference between the cathode and anode drives the flow of positive sodium ions across the electrolyte. The beta”-alumina electrolyte is mostly impermeable to electrons, practically a perfect insulator. When the sodium ions cross the electrolyte/sulfur electrode boundary, they react with the liquid sulfur in the sulfur electrode to produce sodium polysulfides.

The sulfur electrode changes in composition based on the amount of sodium that crosses the electrolyte separator. The concentration of sodium polysulfide in the melt is indicated by the subscript $x$. The phase of the melt changes depending on the state of discharge (SOD) of the cell. This is due to the change in $x$ during discharge. As the sodium ions cross the electrolyte and react with the sulfur, the concentration of sulfur decreases (i.e. the subscript $x$ gets smaller).
Figure 2 shows the phase diagram of the sodium polysulfide melt. [4] It is desirable to stay in the liquid phase for proper operation of the cell. For example, for the sodium polysulfide melt to stay liquid at all sulfur compositions, the cell would have to operate above 900°C, which is not realistic or necessary. The sodium sulfur battery usually operates at a temperature between 300°C and 400°C, at which the sodium, sulfur, and polysulfides for this system exist in liquid phase.

![Phase diagram of \( \text{Na}_2\text{S}_x \) (sodium polysulfide).]
During discharge of the cell, operation is terminated when the polysulfide $Na_2S_3$ is formed to avoid precipitation of solids in the sulfur electrode due to formation of $Na_2S_2$. The open circuit voltage of the cell at 350 °C is 2.075 V. The specific energy density of the battery reaches 760 Wh/kg at 350°C, nearly three times of that for a lead acid battery.

Figure 3 shows the relationship between phase change and SOD for the sodium-polysulfide melt in the sulfur electrode. [5] Before discharge operations begin, the sulfur electrode contains mostly sulfur. Then the sulfur electrode transitions to a two-phase mixture of sulfur and polysulfide. As the reaction progresses, more sodium ions react with the sulfur and the mole fraction of total sulfur decreases. At a mole fraction of approximately 0.729, the sulfur electrode becomes single-phase polysulfide until the melt reaches 0.571 mole fraction sulfur. At this point, the solid polysulfide $Na_2S_2$ begins to form and proper operation of the cell is no longer possible.
Figure 3: Idealized EMF/phase relationships for the sodium sulfur cell.

Most literature defines state of discharge with regard to $Na_2S_3$. Therefore, the cell is considered “100%” discharged when the sulfur electrode composition reaches $Na_2S_3$. The same convention is used in this work.
1.2. Literature Review

Previous work developing these batteries began with Ford Motor Company in the 1960s and 1970s for electric vehicle applications. This work was halted in the 1990s with the emergence of other battery technologies such as Ni-metal hydride and Li-ion. More recent studies have been conducted by collaborations of Tokyo Electric Power Company (TEPCO) and NGK Insulator, Ltd., (NGK) to develop sodium sulfur technology for utility energy storage. By the late 1990s, a number of systems up to the MWh scale had been developed and demonstrated on the electrical grid.

cell. Then, Kawamoto [11] developed a more accurate model for just the sulfur electrode concerning the cell voltage and sodium ion concentration profile.

The most extensive reference for sodium sulfur batteries is “The Sodium Sulfur Battery” by J.L. Sudworth and A.R. Tilley. [1] This book presents a critical review of the literature (up to 1985) concerning sodium sulfur batteries. In particular, it describes the development of sodium sulfur batteries, principles of operation, design and manufacture, performance and safety, and prototype demonstrations.

There are an abundance of thermal studies or models concerning the cell, and extensive work has been done to understand the dynamics of the sodium-polysulfide melt. Resistance and impedance studies have also been conducted for sodium sulfur cells. [12], [13]

1.4. Problem Statement

The use of sodium sulfur batteries for grid-level storage requires large numbers of cells operating at high current density in order to achieve the large storage capacity. The operation of sodium sulfur batteries at high current density can cause cell deterioration, leading to lower sulfur utilization and lower energy efficiency. In addition, high current density operation can result in undesired
thermal runaway leading to potentially hazardous situations. Therefore, there is a need for understanding the processes that occur in the cell during operation.

The purpose of this research is to create a dynamic model of a sodium sulfur cell during charge and discharge, which improves and adds to existing literature on the subject. It will consider:

- the total cell (sodium and sulfur electrodes, electrolyte, and metal case)
- non-isothermal operation
- transient operation
- sodium ion concentration in each part of the cell during operation
- potential/resistance in each part of the cell
- voltage of the cell at different load requirements

A greater understanding of the thermal and electrochemical processes that occur in the battery during discharge and charge is necessary in order to optimize the operating conditions for the use of this battery, as well as develop proper thermal management systems. A rigorous, dynamic model can eventually help to develop strategies for the safe and efficient operation of sodium sulfur battery modules at the grid level.
2. Model Development

For this research, a simplified version of the cell will be considered. The model considers the cell to be a perfectly symmetric cylinder and covers the length of the electrolyte, $L$, as shown in Figure 4. End effects are neglected.

Figure 4: Simple representation of a sodium sulfur cell.
The model considers heat generation due to Ohmic loss within the cell, Peltier heat at the electrolyte boundaries, and heat due to entropy change. The radiative and convective heat transfer at the outside surface of the metal cell container is also considered as heat loss.

For the electrochemical phenomena, the model considers species conservation equations in the sulfur electrode for the chemical and ionic species by considering the phase transition and change in the species concentration depending on the SOD. The physicochemical properties in the sulfur electrode are modeled by using Arrhenius-type equations with temperature-dependent terms.

Species conservation equations are written in the beta”-alumina electrolyte for the ionic species by considering the change in composition due to diffusion and migration via a potential gradient driving force.

The sodium ions present in the sodium electrode are assumed to never be depleted, as there is a sodium reservoir to replenish the sodium electrode during operation.

2.1. Approach and Objectives

The sodium electrode contains a stainless steel wick that is in direct contact with the inner side of the beta”-alumina electrolyte, allowing for complete wetting
of the electrolyte surface with liquid sodium. As long as the wick is in contact with reserve sodium, the electrolyte surface will never lack liquid sodium needed for the half-cell reaction that occurs at the sodium electrode/beta”-alumina electrolyte interface. The beta”-alumina electrolyte is a transporter of sodium ions only: no electrons or sulfur ions permeate the electrolyte. The sulfur/sodium polysulfide melt is sustained in a graphite matrix for better electron conduction in the sulfur electrode. The dimensions and several other parameters for the sodium sulfur cell being modeled are the same as those of the experimental cell used by Kawamoto. [10]

Relations for the temperature, potential, and concentration were formed from first principles. The sulfur electrode is the most important component of a sodium sulfur cell, as the rate limiting mechanisms take place here. Therefore, the model of the sulfur electrode was developed first, followed by the model of the beta”-alumina electrolyte and the model of the sodium electrode, to complete the dynamic model of a single sodium sulfur cell.

The current literature does not present a model that considers the thermal, electrochemical, and potential changes for an entire sodium sulfur cell. The simulations that do exist in literature are generally concerned with the sulfur electrode only, or if they consider the entire cell, they are isothermal models. The final goal for this work is to develop a complete PDE-based model in Aspen
Custom Modeler by using method of lines for the operation of a sodium sulfur cell which accurately models the thermal, electrochemical, and potential gradients within each section of the cell during both charge and discharge.

2.2. Governing Equations

The following assumptions are used to simplify the model:

- the cell potential, temperature, and concentration gradients are assumed to be one-dimensional in the $r$-direction (radius)
- convection of the reactants within each cell compartment is neglected since they are each sustained in a solid matrix
- the supply of sodium in the sodium electrode is never depleted during operation
- the sodium electrode/beta”-alumina electrolyte interface is always completely wetted.

With these simplifications assumed valid, the following model was developed.

2.2.1. Sulfur Electrode

An energy balance on the sulfur electrode yields the following equation
\[ r \rho(S) c_p(S) \frac{\partial T(S)}{\partial t} - \frac{\partial}{\partial r} \left( r \lambda(S) \frac{\partial T(S)}{\partial r} \right) = r q(S) \] (4)

where \( r, \rho, c_p, \lambda, T, t, \) and \( q \) are the radius, density, specific heat, thermal conductivity, temperature (°C, unless otherwise specified), time, and the heat source per unit volume for the sulfur electrode, respectively.

The density, specific heat, and thermal conductivity are taken as functions of temperature in the model. These properties of sodium polysulfides for 300-375°C are based on the data given by Sudworth and Tilley [1] and properties of liquid sulfur. See the Appendix for the development of these correlations.

The heat source term (W/m³) is defined in the following way

\[ q(S) = Q_{Ohmic} + Q_{Entropy} \] (5)

\[ Q_{Ohmic} = \frac{1}{\sigma_e(S)} \left( \frac{l}{2\pi r L} \right)^2 \] (6)

\[ Q_{Entropy} = \frac{a_s}{K_p} \left( \varphi_e(S) - \varphi_i(S) - \mu \right) \left( T \frac{dE}{dT} \right) \] (7)

Here, \( \sigma_e, a_s, K_p, \varphi_e, \varphi_i, \mu, \) and \( dE/dT \) are the electronic conductivity of the melt, surface area per unit volume of graphite matrix, the surface polarization resistance coefficient, electronic and ionic potential, local potential, and temperature dependence of open circuit voltage, respectively.
The electronic conductivity, surface area per unit volume, and polarization coefficient are constant values reported by Kawamoto. [11] The term $T(dE/dT)$ is called the entropy term, and depends on SOD as determined by Knoedler’s experimental data. [8] See the Appendix for the description of the SOD function as well as the correlation for the entropy term resulting from a fit to Knoedler’s data.

The local potential is given by the following equation

$$
\mu = \begin{cases} 
2.05, & M \geq 0.710286 \\
\alpha_1 + \beta_1 X_e, & M < 0.710286 
\end{cases}
$$

(8)

Here, $\alpha_1$ and $\beta_1$ are overpotential coefficients from Cleaver and Davies’ experimental cells [14], $M$ is the mole fraction sulfur, and $X_e$ is the mole fraction ‘electrolyte’ ($Na_2S$) in the sulfur electrode, as defined by Cleaver and Davies [15].

The overpotential coefficients are functions of temperature. Their correlations are shown in the Appendix. The mole fraction sulfur is related to the mole fraction electrolyte as $X_e = 1/X_S$ and $M = X_S/(2 + X_S)$, where $X_S$ is the value of the subscript $x$ in $Na_2S_x$.

The conservation of sodium ions in the sulfur electrode is given by [11]:

$$
\frac{\partial C_{+}(S)}{\partial t} = - \frac{1}{F K_p} a_s \left( \varphi_{e(S)} - \varphi_{i(S)} - \mu \right)
$$

(9)

where $C_{+}$ and $F$ are the concentration of sodium ions and Faraday’s constant. The potential relations for the sulfur electrode are given by [11]:

16
Here, \( \sigma_{i(S)} \), \( D \), and \( t_+ \) are the ionic conductivity, diffusion coefficient of sodium ions, and the transference number of sodium ions in the sulfur electrode, respectively.

The ionic conductivity of the sodium polysulfide melt is a function of the mole fraction of sulfur in the melt. [16] The diffusion coefficient for sodium ions in the melt is defined by Thompson and Newman in reference [17] as a function of temperature and mole fraction electrolyte (\( \text{Na}_2\text{S} \)) in the melt. The transference number of sodium ions is based on the experimental cells of Cleaver and Davies. [14] See the Appendix for supplemental descriptions of these relations.

### 2.2.2. Beta”-Alumina Electrolyte

The energy conservation equation in the beta”-alumina solid electrolyte is given by:

\[
\frac{\partial T_{(el)}}{\partial t} = \frac{1}{\rho_{(el)}c_{p(el)}} \left( q_{(el)} r + \frac{\partial}{\partial r} \left( r \lambda_{(el)} \frac{\partial T_{(el)}}{\partial r} \right) \right) \tag{12}
\]
where $\rho$ and $c_p$ are the density and specific heat capacity of the electrolyte. The density is determined based on the thermal expansion coefficient given by Sudworth and Tilley. [1] The derivation for the density is shown in the Appendix. The specific heat capacity and thermal conductivity of the electrolyte are functions of temperature, as obtained from reference [18], shown in Table 1.

The heat source term $q_{(el)}$ (W/m$^3$) in the electrolyte consists of Ohmic heat loss,

$$q_{(el)} = \frac{J^2}{\sigma_i}$$

(13)

where $J$ is the current density. The means of proton transfer in the sodium ion conducting beta”-alumina is dominated by the ionic conductance and ion migration. The sodium ion conservation in the electrolyte is given by:

$$\frac{\partial C_{+(el)}}{\partial t} = \frac{D_{(el)}}{\rho_{(el)}} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{+(el)}}{\partial r} \right)$$

(14)

where $\rho$ is the porosity of the beta”-alumina electrolyte. This porosity is based on the theoretical and calculated density of sodium beta”-alumina, and is a function of temperature. See the Appendix for this derivation.

Conservation of positive ions in the electrolytes is shown below, considering both diffusion and migration:

$$-\sigma_{i_{(el)}} \frac{\partial \varphi_{i_{(el)}}}{\partial r} - FD_{(el)} \frac{\partial C_{+(el)}}{\partial r} = J$$

(15)
The ionic conductivity, $\sigma_i$, and diffusion coefficient, $D$, are functions of temperature, as shown in Table 1. See the Appendix for the derivation of their relations.

### 2.2.3. Sodium Electrode

Since the half-cell reaction occurs at the sodium electrode/electrolyte interface only, the sodium electrode model considers only this interface. The equations in this section are the boundary conditions at $r = r_{el,i}$. The energy balance for the sodium electrode takes the following form

$$m_{ss}c_{p,ss} \frac{\partial T_{(Na)}}{\partial t} + m_{Na}c_{p,Na} \frac{\partial T_{(Na)}}{\partial t} = q_{(Na)} + 2\pi r_{el,i} L \lambda_{(el)} \frac{\partial T_{(el)}}{\partial r} \bigg|_{r=r_{el,i}}$$

where $m$ is the mass with subscripts $ss$ and $Na$ denoting the stainless steel wick and the liquid sodium within in the sodium electrode. The heat source term, $q_{(Na)}$ (W), for the sodium electrode considers the Ohmic heat loss at the interface of the electrolyte,

$$q_{(Na)} = \frac{l^2 \rho_{l(Na)} r_{el,i}}{2\pi (r_{el,i}/2)L}$$

where $\rho_{l(Na)}$ is the resistivity of liquid sodium. This is an approximation for the sodium electrode contribution to the Ohmic loss in the cell. The resistivity of
liquid sodium is a function of temperature, as defined in *The Sodium Sulfur Battery*. [1] This expression is shown in Table 1.

The concentration of sodium ions at the beta”-alumina interface is defined in the following way

\[
\frac{\partial C_{+(Na)}}{\partial \tau} = -\frac{I}{FV_{(Na)}}
\]  

(18)

where \( V \) is the volume of the sodium electrode, including the molten sodium, the wick, and the reservoir. The ionic potential drop from the sodium electrode to the beta”-alumina electrolyte interface is given by

\[
\varphi_{i(Na)} = -\eta_{(Na)}
\]  

(19)

where \( \eta_{(Na)} \) is the linear current potential relationship derived from Butler-Volmer kinetics, shown in Table 1. No electronic potential change is considered in the sodium electrode.

See the Appendix for additional correlation information regarding the resistivity of liquid sodium and the specific heats of sodium and stainless steel.

Table 1 lists the additional expressions used for model variables. See Table 2 for values and references for other parameters used in the model.
### Table 1: Additional Model Expressions

<table>
<thead>
<tr>
<th>Expression</th>
<th>Reference/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J = 1/(r\pi Lr_{el,0}) )</td>
<td></td>
</tr>
<tr>
<td>Sodium Electrode:</td>
<td></td>
</tr>
<tr>
<td>( \rho_{l(\text{Na})} = 6.87 \times 10^{-8} + 2.44 \times 10^{-10}T_{(\text{Na})} + 2.67 \times 10^{-13}T_{(\text{Na})}^{2} + 1.07 \times 10^{-15}T_{(\text{Na})}^{3} - 2.67 \times 10^{-18}T_{(\text{Na})}^{4} )</td>
<td>[1]</td>
</tr>
<tr>
<td>( c_{p,ss} = -4.591 \times 10^{-4}T_{(\text{Na})}^{2} + 0.4813T_{(\text{Na})} + 444.99 )</td>
<td>[1]</td>
</tr>
<tr>
<td>( c_{p,\text{Na}} = 1437.08 - 0.58063T_{(\text{Na})} + 4.624 \times 10^{-4}T_{(\text{Na})}^{2} )</td>
<td>[1]</td>
</tr>
<tr>
<td>( \eta_{(\text{Na})} = (IRT_{(\text{Na})})/(2\pi r_{el,0}L_{0}F) )</td>
<td></td>
</tr>
<tr>
<td>Beta”-Alumina Electrolyte:</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{(el)} = 2.451 + 2.456 \times 10^{-4}T_{(el)} - 6.178 \times 10^{-7}T_{(el)}^{2} + 4.275 \times 10^{-10}T_{(el)}^{3} - 6.993 \times 10^{-14}T_{(el)}^{4} )</td>
<td></td>
</tr>
<tr>
<td>( \rho_{(el)} = 3220 \exp\left(-3\alpha_{T}(T_{(el)} - 25)\right) )</td>
<td></td>
</tr>
<tr>
<td>( c_{p,(el)} = 0.7321 + 5.006 \times 10^{-4}T - 2.151 \times 10^{-7}T^{2} )</td>
<td></td>
</tr>
<tr>
<td>( P_{(el)} = (3220 - \rho_{(el)})/3220 )</td>
<td></td>
</tr>
<tr>
<td>( D_{(el)} = D_{0}\exp[-H/(RT_{(el)})] )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{i(\text{el})} = (\sigma_{0(\text{el})}/T_{(\text{el})})\exp[-H/(RT_{(\text{el})})] )</td>
<td></td>
</tr>
<tr>
<td>Sulfur Electrode:</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{(S)} = 0.4813 - 1.8648 \times 10^{-3}T_{(S)} + 2.4844T_{(S)}^{2} )</td>
<td>[19], Liquid sulfur dominates melt</td>
</tr>
<tr>
<td>( D_{(S)} = (1.53 \times 10^{-6})\exp\left(-8590/T_{(S)}\right)\exp\left(5.30X_{e}\right) )</td>
<td>[17], T in Kelvin</td>
</tr>
<tr>
<td>( \alpha_{1} = -8.1667 \times 10^{-5}(T_{(S)} + 2.5087) )</td>
<td>[14], [15], T in Kelvin</td>
</tr>
<tr>
<td>( \beta_{1} = -7.350 \times 10^{-4}(T_{(S)} - 1.5600) )</td>
<td>[14], [15], T in Kelvin</td>
</tr>
<tr>
<td>( \beta_{2} = (3.0783 \times 10^{-5})(T_{(S)}) + 0.0472 )</td>
<td>[14], [15], T in Kelvin</td>
</tr>
<tr>
<td>( t_s = (-\beta_{2}/\beta_{1} - X_{e})/(1 - X_{e}) )</td>
<td>[14], [15], [11], [20]</td>
</tr>
<tr>
<td>Linear fit [16], [11]</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{i(S)} = \sigma_{i0(S)}(1 - p_{(S)}) )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{i0(S)} = \begin{cases} -457.04M + 657.04, &amp; M \geq 0.72 \ -242.99M + 207.75, &amp; 0.60 &gt; M &gt; 0.72 \ 61.956, &amp; M \leq 0.60 \end{cases} )</td>
<td>[11]</td>
</tr>
<tr>
<td>( X_{e} = (2/C_{e})(W_{S}/32)(1/V_{(S)}) )</td>
<td>[11]</td>
</tr>
<tr>
<td>( X_{e} = 1/X_{S} )</td>
<td></td>
</tr>
<tr>
<td>( M = X_{e}/(2 + X_{e}) )</td>
<td></td>
</tr>
<tr>
<td>( a_{s} = a_{50}(1 - p_{(S)})\times 1, \quad X_{S} &lt; 5.24 )</td>
<td>[11], [20]</td>
</tr>
<tr>
<td>( a_{s} = a_{50}(1 - p_{(S)})\times (5.24/X_{S}), \quad X_{S} &gt; 5.24 )</td>
<td></td>
</tr>
<tr>
<td>( SOD = \begin{cases} -343.55M + 304.82, &amp; \text{single phase polysulfide} \ -202.43M + 202.23, &amp; \text{two phase sulfur/polysulfide} \end{cases} )</td>
<td>See Appendix</td>
</tr>
<tr>
<td>( \frac{dE}{dT} = \begin{cases} -15.536SOD^{5} + 32.652SOD^{4} - 22.969SOD^{3} + 6.0576SOD^{2} - 0.5629SOD - 0.0362 \end{cases} )</td>
<td>See Appendix</td>
</tr>
</tbody>
</table>
Table 2: Values of Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Reference/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>30</td>
<td>W/m²K</td>
<td>[1], based on stainless steel container/air</td>
</tr>
<tr>
<td>$\alpha_L$</td>
<td>7.5×10⁻⁶</td>
<td>K⁻¹</td>
<td>[1]</td>
</tr>
<tr>
<td>$c$</td>
<td>0.066</td>
<td>-</td>
<td>[10], [21]</td>
</tr>
<tr>
<td>$\delta$</td>
<td>5.67×10⁻⁹</td>
<td>W/m³K⁴</td>
<td>Stefan-Boltzmann constant</td>
</tr>
<tr>
<td>$L$</td>
<td>0.18</td>
<td>m</td>
<td>[11]</td>
</tr>
<tr>
<td>$r_{el,i}$</td>
<td>0.0069375</td>
<td>m</td>
<td>[11]</td>
</tr>
<tr>
<td>$r_{el,o}$</td>
<td>0.0075</td>
<td>m</td>
<td>[11]</td>
</tr>
<tr>
<td>$r_o$</td>
<td>0.015</td>
<td>m</td>
<td>[11]</td>
</tr>
<tr>
<td>$T_{air}$</td>
<td>330</td>
<td>°C</td>
<td>[8]</td>
</tr>
<tr>
<td>$p_t$</td>
<td>1.8×10⁻⁴</td>
<td>V/K</td>
<td>[22]</td>
</tr>
<tr>
<td>$K_p$</td>
<td>1×10⁻⁴</td>
<td>Ω/m²</td>
<td>[11]</td>
</tr>
<tr>
<td>$F$</td>
<td>9.6487×10⁷</td>
<td>C/kmol</td>
<td>Faraday's constant</td>
</tr>
<tr>
<td>$\sigma_{e(S)}$</td>
<td>50</td>
<td>A/V</td>
<td>[11]</td>
</tr>
<tr>
<td>$\rho(S)$</td>
<td>0.35</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>1×10⁴</td>
<td>m²/m³</td>
<td>[11]</td>
</tr>
<tr>
<td>$W_s$</td>
<td>0.1</td>
<td>kg</td>
<td>[11]</td>
</tr>
<tr>
<td>$D_o$</td>
<td>3.98×10⁻⁸</td>
<td>m²/s</td>
<td>[23]</td>
</tr>
<tr>
<td>$H$</td>
<td>5.497</td>
<td>kcal/mol</td>
<td>[23], [24]</td>
</tr>
<tr>
<td>$\sigma_{0(el)}$</td>
<td>1.49×10⁶</td>
<td>K/Ωm</td>
<td>[23], [24]</td>
</tr>
<tr>
<td>$m_{Na}$</td>
<td>0.057</td>
<td>kg</td>
<td>[11]</td>
</tr>
<tr>
<td>$m_{ss}$</td>
<td>20.3</td>
<td>kg</td>
<td>[1], linearly scaled to cell dimensions</td>
</tr>
<tr>
<td>$i_0$</td>
<td>5×10⁴</td>
<td>A/m²</td>
<td>[25]</td>
</tr>
<tr>
<td>$V_{(Na)}$</td>
<td>2×10⁻³</td>
<td>m³</td>
<td>Cell from [11]</td>
</tr>
<tr>
<td>$V_{(S)}$</td>
<td>9.5425×10⁻⁵</td>
<td>m³</td>
<td>-</td>
</tr>
<tr>
<td>$\rho(S)$</td>
<td>1880</td>
<td>kg/m³</td>
<td>[1], less than 1% variation</td>
</tr>
<tr>
<td>$c_{p(S)}$</td>
<td>1315</td>
<td>J/kgK</td>
<td>[1], less than 1% variation</td>
</tr>
</tbody>
</table>

2.3. Boundary Conditions

The boundaries of this system include the sodium electrode/beta”-alumina electrolyte interface, the beta”-alumina electrolyte/sulfur electrode interface, and the outer metal container of the cell. The sodium electrode half-cell reaction only occurs on the electrolyte interface via the stainless steel wick; therefore, this
boundary is the only sodium electrode boundary considered. It is also assumed that the Peltier heat loss occurs at the sulfur electrode interface of the electrolyte. Temperature continuity is assumed at both of the electrolyte interfaces. There is no ionic flux or ionic potential flux at the outer container boundary of the cell. Heat is lost to the surroundings (air) at the outer metal container.

Table 3 lists the boundary condition equations for this system during charge and discharge.
Table 3: Boundary Conditions

<table>
<thead>
<tr>
<th>Number</th>
<th>Location</th>
<th>Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC1</td>
<td>$r = r_{el,i}$</td>
<td>$C_{+(Na)} = C_{+(el)}$</td>
</tr>
<tr>
<td>BC2</td>
<td>$r = r_{el,i}$</td>
<td>$T_{(el)} = T_{(Na)}$</td>
</tr>
<tr>
<td>BC3</td>
<td>$r = r_{el,i}$</td>
<td>$\varphi_{i(el)} = -\eta_{Na}$</td>
</tr>
</tbody>
</table>

Beta”-Alumina Electrolyte ($el$) / Sulfur Electrode ($S$):

<table>
<thead>
<tr>
<th>Number</th>
<th>Location</th>
<th>Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC4</td>
<td>$r = r_{el,o}$</td>
<td>$C_{+(el)} = C_{+(S)}$</td>
</tr>
<tr>
<td>BC5</td>
<td>$r = r_{el,o}$</td>
<td>$T_{(el)} = T_{(S)}$</td>
</tr>
<tr>
<td>BC6</td>
<td>$r = r_{el,o}$</td>
<td>$-\lambda_{(el)} 2\pi r_{el,o} L \frac{\partial T_{(el)}}{\partial r} = -\lambda_{(S)} 2\pi r_{el,o} L \frac{\partial T_{(S)}}{\partial r} \pm Ip_{e} T_{(S)}$</td>
</tr>
<tr>
<td>BC7</td>
<td>$r = r_{el,o}$</td>
<td>$-\sigma_{i(el)} \frac{\partial \varphi_{i(el)}}{\partial r} - FD_{(el)} \frac{\partial C_{+(el)}}{\partial r} = J$</td>
</tr>
<tr>
<td>BC8</td>
<td>$r = r_{el,o}$</td>
<td>$-\sigma_{i(S)} \frac{\partial \varphi_{i(S)}}{\partial r} - FD_{(S)} \frac{\partial C_{+(S)}}{\partial r} = J$</td>
</tr>
<tr>
<td>BC9</td>
<td>$r = r_{el,o}$</td>
<td>$\varphi_{i(el)} = \varphi_{i(S)}$</td>
</tr>
<tr>
<td>BC10</td>
<td>$r = r_{el,o}$</td>
<td>$\frac{\partial \varphi_{e(S)}}{\partial r} = 0$</td>
</tr>
</tbody>
</table>

Sulfur Electrode ($S$) / Metal Container:

<table>
<thead>
<tr>
<th>Number</th>
<th>Location</th>
<th>Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC11</td>
<td>$r = r_{o}$</td>
<td>$\frac{\partial C_{+(S)}}{\partial r} = 0$</td>
</tr>
<tr>
<td>BC12</td>
<td>$r = r_{o}$</td>
<td>$\frac{\partial T_{(S)}}{\partial r} + \left(\frac{\alpha}{\lambda_{(S)}}\right)(T_{(S)} - T_{air}) + \left(\frac{c_{s}}{\lambda_{(S)}}\right)(T_{(S)}^{4} - T_{air}^{4}) = 0$</td>
</tr>
<tr>
<td>BC13</td>
<td>$r = r_{o}$</td>
<td>$\frac{\partial \varphi_{i(S)}}{\partial r} = 0$</td>
</tr>
<tr>
<td>BC14</td>
<td>$r = r_{o}$</td>
<td>$\varphi_{e(S)} = \varphi_{o} \text{ so as to satisfy:}$</td>
</tr>
</tbody>
</table>

\[ l = -2\pi L \int_{r_{el,o}}^{r_{o}} \frac{\alpha_{s}}{K_{p}} (\varphi_{e(S)} - \varphi_{i(S)} - \mu) r \, dr \]
3. Dynamic Simulation

This system of equations was solved using Aspen Custom Modeler and the method of lines. Several transient profiles were produced using the model for the sodium sulfur cell. The model is validated at various currents and states of discharge and charge by comparing to the experimental results of Kawamoto. [11]

4. Results and Discussion

The following sections contain results of the dynamic simulation developed in Aspen Custom Modeler using method of lines to solve the PDE-based model.

4.1. Voltage and Resistance

Figures 5 and 6 show the cell voltage as a function of state of discharge for the 80Wh experimental cell used by Kawamoto, for 3, 6, and 9 A charge and discharge. The calculated trends were generated with the model, and the measured data on these figures are experimental data.
Figure 5: Cell voltage vs SOD during discharge/charge at +/-3A.

The model-generated curves for discharging and charging the cell closely match the measured discharge/charge voltage curves. These results are representative of typical charge and discharge characteristics, since cell performance is generally stable for more than 1500 cycles. [11]
Figure 6: Cell voltage vs SOD during discharge/charge at +/-6A.

During discharge, the cell voltage is nearly level in the two-phase region of operation (<55% SOD), and then tapers off for the remaining discharge. The charging cell begins in the single-phase region of the sulfur electrode composition, and the voltage continues to increase and level out once the melt is two-phase again.
Figure 7: Cell voltage vs SOD during discharge/charge at +/-9A.

Figures 8, 9, and 10 show the total cell, sodium electrode, beta”-alumina electrolyte, and sulfur electrode resistances for charging and discharging at 3, 6, and 9 A. The sodium electrode adds a negligible resistance to the total cell resistance. The beta”-alumina electrolyte consistently adds about 0.0024 Ω to the overall resistance.
Figure 8: Cell resistance vs SOD during discharge/charge at +/-3A.

The sulfur electrode is the largest contributor to the resistance of the cell during both charge and discharge. These results match the values reported in literature for this cell. [11]
Figure 9: Cell resistance vs SOD during discharge/charge at +/-6A.

The calculated values of beta”'-alumina electrolyte and sodium electrode resistances are in agreement with Kawamoto’s approximations. [11]
Figure 10: Cell resistance vs SOD during discharge/charge at +/-9A.

It can be seen from these results that the sodium electrode contributes a negligible amount to the cell resistance, which puts more emphasis on the importance of optimizing the sulfur electrode design.
4.2. Temperature

Figures 11 and 12 show the temperature profile within the cell at 60% SOD during discharge and charge. Operating at higher current/current density results in higher temperatures within the cell.

Figure 11: Temperature profile over cell during discharge at 60% SOD.

The dashed line represents the beta”-alumina electrolyte/sulfur electrode interface (at \( r = r_{el,o} \)). The position (radius) goes from the sodium electrode/beta”-alumina electrolyte interface (\( r = r_{el,i} \)) to the outer sulfur electrode radius (\( r = r_o \)).
The temperature across the beta”-alumina electrolyte is nearly constant, and then the temperature decreases across the sulfur electrode.

Figure 12: Temperature profile over cell during charge at 60% SOD.

There is a greater temperature increase during discharge than charge. This is due to the reactions that take place in the sulfur electrode, which are exothermic during discharge and endothermic during charge.
Figure 13 shows the temperature in the cell (at the sodium electrode, the center of the beta”-alumina electrolyte, and the center of the sulfur electrode) while the cell is discharging and charging at +/- 6 A.

![Graph showing temperature vs SOD during discharge/charge at +/-6A.]

Figure 13: Temperature vs SOD during discharge/charge at +/-6A.

It is observed here that as the cell discharges, the exothermic reactions in the sulfur electrode lead to the increase in cell temperature. During charge, the temperature initially decreases and then returns to the starting temperature.
4.3. Sodium Ion Concentration

The distribution of sodium ion concentration during discharge and charge are shown in Figures 14 and 15, for +/- 6 A operation.

Figure 14: Sodium ion concentration profile from sodium/electrolyte interface to sulfur electrode during discharge at +6A.

The dashed line represents the beta”-alumina electrolyte/sulfur electrode interface (at \( r = r_{el,o} \)). The concentration of sodium ions in the beta”-alumina
electrolyte and sulfur electrode increases as the cell discharges. The sodium ions in the beta’”-alumina electrolyte increase as expected during charge, when the ions are returning to the sodium electrode.

Figure 15: Sodium ion concentration profile from sodium/electrolyte interface to sulfur electrode during charge at -6A.

The concentration profiles seen in these results are similar to those developed by Kawamoto for the same experimental cell. [11]
4.4. Potential Gradients

Distributions of the ionic and electronic potentials during discharge (+6 A) are shown in Figures 16 and 17.

Figure 16: Ionic potential over cell during discharge at +6A.

The dashed line represents the beta”-alumina electrolyte/sulfur electrode interface (at \( r = r_{el,o} \)). As the cell discharges, the ionic and electronic potential
trends decrease. This is consistent with the results of Kawamoto for the ionic and electronic potentials in the sulfur electrode during discharge operation. [11]

Figure 17: Electronic potential over cell during discharge at +6A.

Figures 18 and 19 show the ionic and electronic potential distribution in the cell during charge (-6 A).
Figure 18: Ionic potential over cell during charge at -6A.

The distribution of ionic potential in the cell shows a similar trend to the ionic potential in the sulfur electrode for Kawamoto’s charging model. [11]
The electronic potential distribution in the sulfur electrode increases with charging operation, as expected.

4.5. Sensitivity Studies

The following sections contain sensitivity studies which test the integrity of the dynamic model. The first section tests the model at different furnace air temperatures, and the second tests the model under different load requirements.
4.5.1. Temperature

The temperature of the furnace air (surrounding the experimental cell) is controlled by the user. This temperature is kept constant by means of an insulated and heated furnace wall, which is not considered in the scope of this model. Figure 20 shows the cell voltage during discharge and charge (+/- 6 A) for an air temperature of 300, 315, and 330°C.

Figure 20: Cell voltage vs SOD during discharge/charge at varying air temperature.
The cell voltage is only slightly affected by the furnace air temperature during operation. It might become an issue if the air was at too low a temperature however, since the reactants must be kept in the molten state for proper operation of the cell (above 98°C for elemental sodium, above 110°C for elemental sulfur).

Figure 21 shows how the internal cell temperature is affected by the air temperature in the furnace.

Figure 21: Temperature profile over cell during discharge at 60% SOD for varying air temperature.
The dashed line represents the beta”-alumina electrolyte/sulfur electrode interface (at $r = r_{el,o}$). It can be seen that the cell temperature increases with increased furnace air temperature, as expected.

Figure 22 shows how the sodium ion concentration (at 60% SOD) is affected by changes to the air temperature.

Figure 22: Sodium ion concentration profile from sodium/electrolyte interface to sulfur electrode at 60% SOD for varying air temperature.

The distribution of sodium ion concentration in the beta”-alumina electrolyte and sulfur electrode shows a steeper trend when the air temperature is lower.
Figures 23 and 24 show the ionic and electronic potential distributions across the cell for 60% SOD at different furnace air temperatures.

Figure 23: Ionic potential over cell during discharge at 60% SOD for varying air temperature.

The ionic potential in the cell increases at increased temperatures of the furnace air. The same is observed for the electronic potential in the cell.
Figure 24: Electronic potential over cell during discharge at 60% SOD for varying air temperature.

The temperature within the cell under high current density operation is considered in Figure 25. At high current density operation, the cell temperature gradient increases significantly. This can cause unsafe conditions and is of major concern for cell design and optimization.
The temperature of the air was a constant 335°C here. This result is in good agreement with the thermal behavior reported by Kawamoto and Kusakabe for the same experimental cell. [10]
4.5.1. Current

In the previous results, the cell was modeled for constant current operation. This section shows the cell operating with a changing current. Figure 26 shows the cell discharging at 3 A, and then stepping to 6 A, 3 A, and 9 A. The charging is also shown for -3 A, then to -6 A, -3 A, and -9 A.

Figure 26: Cell voltage vs SOD during discharge and charge with current step changes.
The cell voltage steps up or down with increased or decreased current requirements, respectively. The voltage of the cell during discharge begins to slope downward when the sodium polysulfide melt composition becomes single phase. It is observed that the voltage of the cell decreases more rapidly as a higher current is being drawn from it. Similarly for charging the cell, towards the end of charge, the cell voltage increases slowly for lower current and increases more rapidly for higher current. Figure 27 shows the cell resistance during the same step changes to current as explained above.

Figure 27: Cell resistance vs SOD during discharge and charge with current step changes.
The cell resistance behaves as expected during the discharging and charging of the cell. Figure 28 shows the cell power during the current step changes described above.

![Figure 28: Cell power vs SOD during discharge and charge with current step changes.](image)

The power of the cell changes with each step change of current as expected.
5. Conclusions

The dynamic behavior of a sodium sulfur cell (with beta”-alumina electrolyte) was modeled using Aspen Custom Modeler. The present model captures the heat generation, electrochemical reactions, and internal resistance of the cell. The model is non-isothermal, transient, and considers each part of the cell. Though the present method of simulation is based on the assumptions that it is a simple one-dimensional system with no end effects, the results of our calculations agree well with those of the experiment.

Our work shows that the temperature in the cell rises drastically with increased current density, and an appropriate thermal management system is necessary for high current density operation, especially if sodium sulfur batteries are to be incorporated into the energy grid as a smart storage option.
6. Suggestions for Future Work

The current scope of this research includes a single cell that is at the lab scale. The sodium sulfur batteries used in industry could vary in size. Therefore, the dynamic model of a single sodium sulfur cell should be enhanced to incorporate multiple cells in a battery module, which would have a larger storage capacity for applications such as smart grid energy load leveling. A thermal management approach will be needed so that the temperature of the cells can be controlled, since thermal runaway is a major safety concern with large-scale energy storage. This will mitigate many hazards associated with large-scale energy storage, specifically thermal runaway. A thermal management system could also utilize the generated heat elsewhere.

6.1. Applications of Technology

Electricity storage has the potential benefit of promoting renewable energy technology penetration into the market, such as wind, solar, and hydroelectricity. The addition of large storage systems will improve the ability to use these intermittent sources of energy. Some of the key applications of electric energy storage systems include load leveling, regulation, and power quality. Load leveling uses the stored electricity generated during off-peak demand times for on-peak
dispatch at the system level. Figure 29 shows the typical energy demand times and how additional energy storage can level the required power supply. [2]

Figure 29: Load leveling application of sodium sulfur batteries.

Energy regulation provides voltage and frequency support at the transmission and distribution level to ensure there are no spikes or drops that might adversely affect the system, therefore avoiding equipment damage. Power quality applications aid in smoothing fluctuations at the distribution level.

NGK Insulators has several sodium sulfur battery storage systems in place in Japan and the United States. The batteries are installed in block modules, as seen in Figure 30, alongside power generation facilities. [2]
Figure 30: Example of installed sodium sulfur battery system (by NGK Insulators).
### 7. Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_s)</td>
<td>Surface area of graphite matrix per unit volume sulfur electrode</td>
</tr>
<tr>
<td>(a_{s0})</td>
<td>Net surface area of graphite matrix per unit volume sulfur electrode</td>
</tr>
<tr>
<td>(c_p)</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>(C_+)</td>
<td>Concentration of sodium ions</td>
</tr>
<tr>
<td>(D)</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>(D_0)</td>
<td>Arrhenius constant for electrolyte diffusion coefficient</td>
</tr>
<tr>
<td>(dE/dT)</td>
<td>Temperature dependence of open circuit voltage</td>
</tr>
<tr>
<td>(e^-)</td>
<td>Electron</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>(H)</td>
<td>Activation energy for sodium ion movement in electrolyte</td>
</tr>
<tr>
<td>(I)</td>
<td>Current</td>
</tr>
<tr>
<td>(i_0)</td>
<td>Exchange current density of sodium electrode</td>
</tr>
<tr>
<td>(J)</td>
<td>Current density</td>
</tr>
<tr>
<td>(K_p)</td>
<td>Polarization coefficient</td>
</tr>
<tr>
<td>(L)</td>
<td>Length of electrolyte</td>
</tr>
<tr>
<td>(M)</td>
<td>Mole fraction elemental sulfur in sulfur electrode</td>
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<td>(m)</td>
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<td>Molecular weight</td>
</tr>
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<td>(p)</td>
<td>Porosity</td>
</tr>
<tr>
<td>(p_t)</td>
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<tr>
<td>(Q_{\text{Ohmic}})</td>
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</tr>
<tr>
<td>(Q_{\text{Entropy}})</td>
<td>Heat due to reaction</td>
</tr>
<tr>
<td>(R)</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>(r)</td>
<td>Radius</td>
</tr>
</tbody>
</table>
\( r_{el,i} \)  Radius of inner electrolyte
\( r_{el,o} \)  Radius of outer electrolyte
\( r_o \)  Radius of outer cell container
\( SOD \)  State of discharge (with respect to \( Na_2S_3 \))
\( T \)  Temperature
\( T_{air} \)  Temperature of ambient air
\( t \)  Time
\( t^+ \)  Transference number of sodium ions
\( V \)  Volume
\( W_s \)  Weight of initially charged sulfur
\( x \)  Subscript in polysulfide, \( Na_2S_x \)
\( X_e \)  Mole fraction electrolyte (\( Na_2S \))
\( X_s \)  Value of \( x \) in polysulfide, \( Na_2S_x \)

**Greek Letters**
\( \alpha \)  Heat transfer coefficient between the cell container and the air
\( \alpha_1 \)  Overpotential coefficient (Cleaver & Davies [15])
\( \alpha_L \)  Linear coefficient of thermal expansion for electrolyte
\( \beta_1 \)  Overpotential coefficient (Cleaver & Davies [15])
\( \beta_3 \)  Overpotential coefficient (Cleaver & Davies [15])
\( \delta \)  Stefan-Boltzmann constant
\( \epsilon \)  Effective emissivity
\( \eta_{(Na)} \)  Overpotential of sodium electrode
\( \lambda \)  Thermal conductivity
\( \mu \)  Local potential
\( \rho \)  Density
\( \rho_{l(Na)} \)  Resistivity of liquid sodium
\( \sigma_0 \)  Arrhenius constant for electrolyte ionic conductivity
\(\sigma_e\)  Electronic conductivity

\(\sigma_i\)  Ionic conductivity

\(\sigma_{i0}\)  Net ionic conductivity of polysulfide melt

\(\phi_0\)  Cell potential (voltage)

\(\phi_e\)  Electronic potential

\(\phi_i\)  Ionic potential

**Subscripts**

\(air\)  Air in the furnace, surrounding sodium sulfur cell

\((el)\)  Denotes variable within the beta”-alumina electrolyte

\((Na)\)  Denotes variable within the beta sodium electrode

\(Na\)  Liquid sodium in the sodium electrode

\((S)\)  Denotes variable within the beta sulfur electrode

\(ss\)  Stainless steel wick in the sodium electrode
8. Appendix

This appendix contains explanations for parameter correlations that were developed by fitting to experimental data in the open literature.

8.1. Sulfur Electrode

The thermal conductivity of the sodium polysulfide melt in the sulfur electrode is assumed to be dominated by the sulfur present in the melt. With this assumption, the thermal conductivity of the melt takes the form of the equation shown in Figure 31. This relation for thermal conductivity, as a function of temperature, comes from Kaye and Higgins. [19]
The density of the melt is based on the experimental data for sodium polysulfides given in *The Sodium Sulfur Battery*. [1] For this cell, the operating temperature range is 300°C to 400°C. Therefore, a constant density is valid for this model.

The specific heat of the sodium polysulfide melt is based on the data given by Sudworth and Tilley for polysulfides, in the Appendix of *The Sodium Sulfur Battery*. [1] The data given related the melt specific heat to the mole fraction of
sulfur in the melt. This value is taken to be constant over the operating range for this model. There is less than one percent variation in the value of the specific heat.

The entropy term, which accounts for the reaction in the sulfur electrode, is a function of state of discharge. The data gathered by Knoedler involved experiments on sodium sulfur cells and their heat generation rates. [8] A line of best fit was found for the experimental data relating the entropy term to the discharge (Ah). This discharge was then normalized so that it could be applied to any cell. Figure 32 shows the fit equation for the entropy term as a function of state of discharge.

Figure 32: The entropy term correlation for the sodium sulfur cell.
The state of discharge is a function of the melt composition. This is determined by looking at the cell voltage plot (see Figure 3) as well as comparing to data in the Appendix of *The Sodium Sulfur Battery* for the sodium polysulfide melt. [1] The equation for SOD as a function of melt composition takes the following form:

\[
\text{SOD} = \begin{cases} 
-343.55M + 304.82, & \text{single phase polysulfide} \\
-202.43M + 202.23, & \text{two phase sulfur/polysulfide} 
\end{cases} \quad (20)
\]

The overpotential coefficients in Equation (8) are shown in Figure 33. These data points are the experimental data from Cleaver and Davies’ experiments with sodium sulfur cells. [14], [15]
8.2. Beta”-Alumina Electrolyte

The bulk theoretical density of the electrolyte is assumed to be 3220 kg/m$^3$, based on the work of Ryan et al. concerning the properties of beta”-alumina. [18]

The density of the solid electrolyte is calculated based on the linear coefficient of thermal expansion for beta”-alumina ($\alpha_L$, from Sudworth and Tilley [1]).

$$\rho_{(el)} = 3220 \exp \left( -3\alpha_L (T_{(el)} - 25) \right)$$

(21)
The porosity of the solid electrolyte is approximated using the following relation

\[ p_{(el)} = \frac{(3220 - \rho_{(el)})}{3220} \]  \hspace{1cm} (22)

where 3220 kg/m\(^3\) is the theoretical density of the electrolyte and \(\rho_{(el)}\) is the actual density of the electrolyte. The actual density changes with temperature, therefore making the porosity a function of temperature as well.

The ionic conductivity and diffusion coefficient of sodium ions in the beta”-alumina electrolyte take Arrhenius forms (see Table 1). These equations are from Whittingham and Huggins. [23] The values presented in this reference for the Arrhenius constant for ionic conductivity \(\sigma_{0(\text{el})}\) and the activation energy for sodium ion movement \(H\) were tuned to match the experimental data produced by Virkar et al. [24]

8.3. Sodium Electrode

The specific heat capacity for the liquid sodium and stainless steel wick in the sodium electrode are shown in Figure 34. The relation for sodium was given in the Appendix of *The Sodium Sulfur Battery* for the properties of liquid sodium. [1] Experimental measurements of the specific heat of stainless steel were also given, and a best fit was obtained from this data.
Figure 34: Specific heat of liquid sodium and stainless steel wick in sodium electrode.

\[
c_{p(\text{Na})} = 4.624 \times 10^{-4} T^2 - 0.58063 T + 1437.08
\]

\[
c_{p(\text{SS})} = -4.591 \times 10^{-4} T^2 + 0.4813 T + 444.99
\]

\[R^2 = 0.994846\]
9. References


