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Multiphysics Model Incorporating Shuttling-Induced Capacity Loss and Cost Analysis of Lithium-Sulfur Batteries

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With the growing popularity of electric vehicles, longer lasting batteries are necessary for better mileage. Battery chemistries with larger energy densities compared to Lithium-Ion Batteries (LIB) need to be developed. Lithium-Sulfur Battery (LSB) is a good alternative due to its high theoretical and practical energy densities. However, commercialization of LSBs has yet to be realized due to shorter lifetimes caused by non-ideal battery processes such as polysulfide shuttling. Through multiphysics modeling, the effects of shuttling can be observed. Additionally, cost analysis can determine the feasibility of LSBs for mass production and its competitiveness against LIBs. In this work, energy density optimization and LSB cost estimation were done using combined multiphysics modeling and cost modeling approaches. Using COMSOL Multiphysics®, the energy densities of the batteries with and without shuttling were optimized by changing the thickness and porosity of the cathode and separator. Then, a bottom-up cost analysis of the optimized battery cell was conducted using the BatPaC model. It was observed that shuttling leads to a lower optimized energy density. To compensate for the shuttling-induced capacity loss, the model's optimized battery dimensions had a separator porosity increase by 22.08 % and a cathode thickness and porosity decrease by 23.72 % and 16.21 %. Additionally, shuttling increases battery material costs by 13.35 % because of the larger and more expensive current collectors must compensate for the size of the smaller electrodes. Future works may explore various C-rates and use cases to identify optimal battery parameters for each.

1. Introduction

Lithium-ion batteries have been the most popular battery chemistry due to their high energy density, superior safety, and other properties (Kamyab, 2020). However, this chemistry is reaching its practical energy density limits (Fotouhi et al., 2016), and with electric vehicles needing better mileage at the same vehicle weight and size (Kamyab, 2020), there is a need to develop an alternative battery chemistry with a larger energy density. One of the alternatives currently being developed is the lithium-sulfur battery (LSB) because of its comparatively higher theoretical energy density of 400 to 600 Wh/kg (Li et al., 2019). Recent research on LSBs highlights its limitation of having a shorter battery lifetime of 200 to 300 cycles (Kamyab, 2020). This is a factor in why there is currently no commercial production of this promising battery chemistry. This is due to permanent capacity losses introduced by non-ideal processes such as polysulfide shuttling, which is the diffusion of soluble polysulfide anions from the cathode to the anode. Without considering non-ideal processes and understanding the complex mechanism of LSBs, current models are unable to accurately determine the cause of the LSB performance issues (Kamyab, 2020). Further research on polysulfide shuttling in LSBs is needed for energy density optimization and cost minimization.

Multiphysics modeling is an effective and cost-efficient way of determining the effects of various design parameters and operating conditions on the battery performance. An accurate simulation of battery characteristics contributes to the development of more energy-dense batteries and more efficient battery

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management systems (Tamilselvi et al., 2021). Kumaresan et al. (2008) created a multiphysics model that could predict transient LSB behavior through changing variables such as separator and cathode porosity. These variables are related to the amount of electrolyte solution and active materials in the system, which could affect the cell's capacity (Taleghani et al., 2017). This model was used by Kamyab et al. (2020) in studying the polysulfide shuttling process and its effect on the active material loss and continuous decrease of volume fractions of Li2S on the cathode surface. The relationships of energy density with other parameters have been explored in other battery chemistries but not yet in LSBs. For example, cathode and anode thicknesses demonstrate a direct relationship with energy density in sodium-ion batteries along with low porosities (Domalanta et al., 2022). With the model of Kumersan et al. (2008) and its derivatives, several other factors that may affect LSB energy density can be explored.

Aside from multiphysics modeling, bottom-up cost modeling can be utilized to estimate the cost of production. This method calculates the cost based on the materials and processes that are present in the manufacturing of the battery. The Battery Performance and Cost (BatPaC) model of Argonne National Laboratory allows users to estimate the performance and cost of any battery based on the effects of its materials, design, and manufacturing process (Nelson et al., 2022). Although it was originally designed for LIBs, this has been adapted to study the environmental impact (Deng et al., 2017) and the potential material demand (Xu et al., 2022) of LSBs for automotive applications. Combined multiphysics modeling and bottom-up cost modeling have also been done to investigate the impact of the battery application on the overall cost of sodium-ion batteries (Domalanta et al., 2022). However, these adapted models have yet to account for non-ideal processes such as polysulfide shuttling. Thus, an opportunity is presented for these two modeling techniques to provide a more comprehensive analysis of LSBs.

In this work, multiphysics modeling and cost modeling approaches were used to determine the effect of shuttling on the LSB cell dimensions and mass production cost. An optimized cell for energy applications was configured by varying the thickness and porosity of both the cathode and separator, where the maximum energy density is obtained. The cost was calculated based on the amount of each cell component needed to obtain a battery cell set targeted rate power of 120 kW, in line with the values of Deng et al. (2017).

2. Methodology

The methodology (Figure 1) is divided into two parts. First was the multiphysics modeling of a lithium-sulfur battery with and without the shuttling-induced capacity loss, optimizing their energy density by varying the cathode and separator dimensions. Second, the generated multiphysics models' optimized parameters (separator and cathode porosity and thickness) were translated to the BatPaC model, where the results (USD/kWh of the LSB) for each model were benchmarked and compared to each other.

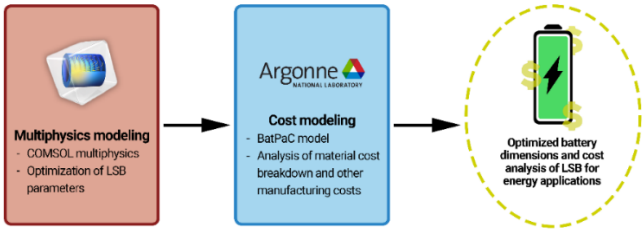

Figure 1: Schematic diagram of the methodology from LSB multiphysics modeling and optimization followed by cost analysis

2.1 Multiphysics modeling of Lithium-Sulfur Battery cell

The LSB considered in this work employs a metallic lithium anode foil and a porous carbon-sulfur cathode separated by a porous polymeric separator with LiTFSI ((Lithium bis(trifluoromethanesulfonyl)imide) electrolyte, as described in Kumaresan et al. (2008). The battery was modeled based on the porous electrode theory framework, whose material balance includes both the matrix phase and solution phase transports of the lithium and polysulfide ions (Newman and Tiedemann, 1975). Additionally, the material balance was coupled with polarization relations so that the electrolytic processes included in the equations were homogeneous (Newman and Thomas-Alyea, 2012). The time and spatial dependent variables, including concentration, potential, and energy density, were calculated by solving the material and charge balance equations while satisfying other nonlinear partial differential equations that govern the geometry of the cell, such as thermodynamic kinetics, porosity change, precipitation equations, and shuttling approximation. The one-dimensional model (Figure 2)

has two domains, the porous separator and the cathode, while the anode was modeled as a boundary at the edge of the separator opposite the cathode.

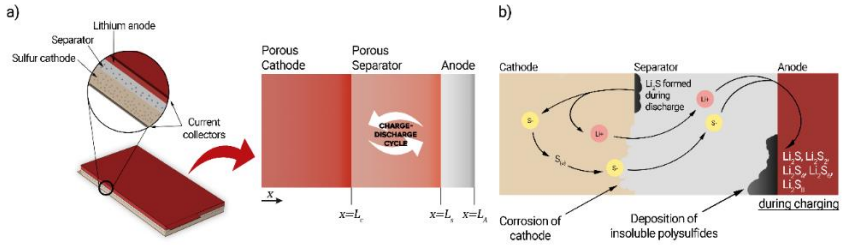

Figure 2: (a) Schematic diagram of the lithium-sulfur battery model (b) Polysulfide shuttling during charging

Two multiphysics models were created to represent LSBs with or without the shuttling approximation. Like the model by Kamyab et al. (2020), the shuttling currents were not included in the kinetic expressions to simplify the model. Instead, the shuttling-induced capacity loss was approximated by including a loss of active material as a result of the shuttling back and forth of the polysulfide anions. The derivations of the mathematical equations of the model and the input model parameters are detailed in the work of Kumaresan et al. (2020). For the shuttling approximation derivations these were detailed in the work of Kamyab et al. (2020).
The models were then replicated in COMSOL Multiphysics® using an existing model by Zhang et al. (2016), which used similar equations. The model was modified to include the shuttling equations by Kamyab et al. (2020). After, the Nelder-Mead algorithm (Singer and Nelder, 2009) was used to optimize the thickness and porosity of both the cathode and separator. This algorithm is an iterative method where these four parameters were continuously improved to calculate a maximum energy density. The models were set to run for three charge-discharge cycles to standardize the endpoint of each optimization trial. The C-rate for both models was set at 0.1 C to validate the model equations used and since it is the appropriate rate for energy storage applications (Kamyab et al., 2020). The total calculation time for all trials lasted approximately 6 h.

2.2 Cost analysis

The optimized LSB design derived through modeling in COMSOL Multiphysics® formed the basis for the battery cost analysis in Battery Performance and Cost (BatPaC) model v5.0. The BatPaC model was modified to accommodate the optimized battery dimensions in COMSOL. In addition, the material usage was also modified in BatPaC to account for the optimal porosity and thickness of both the cathode and separator. Other optimized parameters affecting the cost of the battery were obtained from the models, which are presented in Table 1.

Table 1: Optimized parameters from the multiphysics model translated to the BatPaC model

Parameter	Model without Shuttling Approximation	Model with Shuttling Approximation
C-rate where parameters were optimized	0.10	0.10
Cathode void fraction (vol%)	37.00	31.00
Cathode specific area (cm^2/cm^3)	1,328	1,328
Cathode active material exchange current (mA/cm^2)	0.20	0.20
Anode active material exchange current (mA/cm^2)	0.50	0.50
Separator thickness (µm)	1.00	1.00
Separator void fraction (vol%)	34.60	42.24
Open circuit voltage at 20 % SOC (V)	2.03	2.04
Open circuit voltage at 50 % SOC (V)	2.05	2.05

Additional parameters which are intrinsic to the battery materials were adapted from the study of Deng et al. (2017) for BatPaC calculations. The costs of the individual components of the battery (Table 2) were acquired from the study of Yang et al. (2020). Then, the calculated material costs and specific energy densities for the LSB models were compared to literature values for LSBs from Yang et al. (2020). In addition, the costs and specific energies of the two models were compared to determine the effect of shuttling on the specific energy and cost of the battery pack. Finally, the cost distribution of individual cell components was obtained to determine which component greatly affects the price due to shuttling.

Table 2: Price per unit of each battery component (in US$)

Component	Price	Component	Price	Component	Price
Sulfur	0.13 US$ kg^{-1}	Lithium foil	100.00 US$ kg^{-1}	Copper Foil	13.00 US$ kg^{-1}
Carbon	3.00 US$ kg^{-1}	Electrolyte	60.40 US$ kg^{-1}	Aluminum Foil	3.60 US$ kg^{-1}
PVDF Binder	7.00 US$ kg^{-1}	Separator	0.30 US$ m^{-2}	NMP	2.00 US$ kg^{-1}

3. Results and discussions

3.1 Optimization of Lithium-Sulfur Battery cell

The optimized thickness and porosities of both the cathode and separator, along with the cell energy densities of both models, are summarized in Table 3. The model with the shuttling approximation provided a lower optimized energy density, which is consistent with the claim that capacity losses are caused by these polysulfides deposited in the anode side. To compensate for this capacity loss and increase the energy density of the cell, the model with shuttling had adjusted optimized battery dimensions.

The model considering polysulfide shuttling had a thinner cathode. To compensate for the capacity loss, the cathode thickness was decreased to lower the internal resistance along with the shorter electron diffusion distance across the cathode. Next, shuttling-induced capacity loss led to a battery with a larger separator porosity. This allowed the increase in the electrolyte volume in the separator, which enhanced the ion transport. In contrast, the cathode porosity of the model with shuttling approximation was lower. This helped increase the energy density of the battery since reducing the porosity of the cathode increases the amount of active material available at the beginning of the battery's life. Unlike the previous battery dimensions, the optimized separator thicknesses of the two models are equal. The value of the optimized separator thickness is relatively lower than the cathode thickness. This means that to maximize the energy density, the separator should be thin to allow the fast diffusion of the ions to each electrode. No further adjustments to the separator thickness were made, even with the addition of the shuttling approximation.

Table 3: Optimized thickness and porosities of both the cathode and separator and the cell energy densities.

Parameter	Model without Shuttling Approximation	Model with Shuttling Approximation
Cathode thickness [µm]	31.20	23.80
Separator thickness [µm]	1.00	1.00
Cathode porosity	0.37	0.31
Separator porosity	0.35	0.42
Cell Energy Density (1 cycle) [Wh/kg]	2,391.70	2,338.50

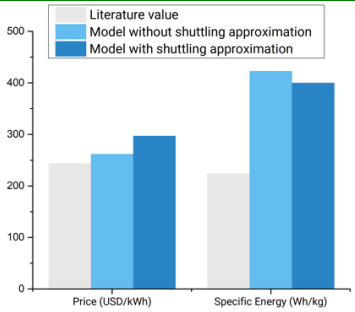

Figure 3: Comparison of calculated battery cost and practical specific energies with literature values obtained from Yang et al. (2020)

3.2 Cost analysis

A side-by-side comparison between the prices and energy densities of the two battery models, as well as the literature values obtained from Yang et al. (2020), are presented in Figure 3. For the analysis, the literature values were used as the baseline value for the LSB, with a cost of 243.70 USD/kWh and a practical specific energy of 224 Wh/kg. The projected price increase for the batteries is 7.51 % (18.3 USD/kWh) and 21.87 % (53.30 USD/kWh), and the projected specific energy increase for the batteries is 88.84 % (199 Wh/kg) and

78.57 % (176 Wh/kg) for the battery model with shuttling and the battery without shuttling approximation. In this regard, the specific energy for the optimized batteries increased with respect to the baseline.
When comparing the prices for the two optimized batteries, a price increase of 13.35 % was observed when shuttling was considered. The price breakdown for both optimized models is presented in Figure 4. From the cost breakdown, the component with the largest relative difference in price is the electrolyte. Comparing the two models, the electrolyte for the battery without shuttling was 33.64 % more costly than the battery with shuttling. This stems from the thicker and more porous cathode of the model without shuttling approximation, leading to an increase in the electrolyte volume. The price of the battery with shuttling approximation was higher due to the large contribution of the current collectors, as shown in Figure 4. The thickness of the cathode for the model with shuttling is less than the one without. To compensate for the smaller component size, larger current collectors are needed in order to allow the battery to output the set target voltage. Finally, it can be noted that the optimized battery parts, separator, and cathode, had a low contribution to the overall cost per pack of the two models. A similar trend was observed in the cost breakdown of a lithium-sulfur pouch cell by Yang et al. (2020), where the weight and cost of the electrode and separator materials were significantly lower than the other parts of the battery. Still, the dimensions of the separator and cathode influence the size of the other parts of the battery, indirectly affecting the cost.

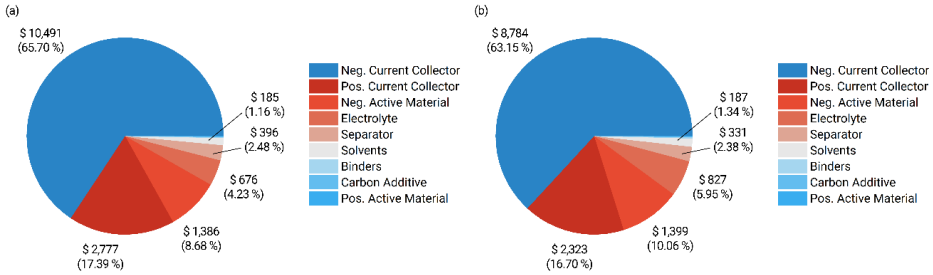

Figure 4: Cost breakdown (in USD/pack) for an optimized battery (a) with polysulfide shuttling, (b) and without polysulfide shuttling

4. Conclusions

Lithium-sulfur batteries are gaining interest due to their high practical energy densities with the potential to replace current lithium-ion batteries in the market. This study combines multiphysics modeling and cost modeling approaches to determine the effect of shuttling-induced capacity loss, which is the main hindrance to the development and commercialization of LSBs. Through the study, the following findings were obtained:

- Shuttling-induced capacity loss leads to lower energy density. To compensate for the shuttling-induced capacity loss and achieve a higher energy density, LSB designs should have a more porous separator and a thinner and less porous cathode. The models showed that the separator porosity increased by 22.08 %, while the cathode thickness and porosity decreased by 23.72 % and 16.21 % when the shuttling-induced capacity loss was considered. Higher separator porosity enhances ion transport, while lower cathode porosity allows an increase in the active material. Similarly, the thinner cathode results in a lower internal resistance due to a shorter diffusion distance.
- Due to the adjustments in the battery dimensions, the model with shuttling showed an increase in cell cost per kWh by 13.35 %. In addition, it was determined that the part of the battery that caused the largest price increase was the current collectors.

This study provides insights into the effect of shuttling-induced capacity loss, energy density, and cell design of 0.1C batteries. In the future, various applications and parameters may be considered. They may explore various C-rates to identify optimal battery dimensions for the different applications of LSBs. It is necessary to discuss strategies on how to reduce or control the capacity loss induced by polysulfide shuttling. This analysis gives additional insight on the feasibility of LSBs for mass production and as a viable alternative to LIBs.

Nomenclature

BatPaC - Battery Performance and Cost, -
L_c - cathode length, µm
LIB – Lithium-ion battery, -
LSB – Lithium sulfur battery, -
LiTFSI - Lithium bis(trifluoromethanesulfonyl)im-ide, -
L_s - separator length, µm
SOC – state of charge, %

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