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Multiphysics Modelling, Parameter Sensitivity Analysis, and Optimization of a Lithium Polymer Battery

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Batteries have been a forefront energy storage solution owing to their flexibility to supply power to a broad range of applications. Lithium-polymer (LiPo) batteries, a subcategory of the widely adopted lithium-ion batteries, exhibit heightened safety properties due to the utilization of a solid or gel polymer that acts as a separator and electrolyte. In this study, a pseudo-2D electrochemical coupled thermal multiphysics model of lithium cobalt oxide (LCO) cathode, graphite anode, and poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) polymer electrolyte LiPo battery was developed using COMSOL Multiphysics®. To improve the model accuracy and battery performance, ten parameters for energy density optimization were screened via sensitivity analysis, and the five most sensitive parameters were selected for optimization. Simultaneous optimization of these parameters through the Constrained Optimization By Linear Approximation (COBYLA) optimization algorithm resulted in a ~25 % increase in energy density and a ~21 % increase in power density for both 1 C and 0.5 C discharge rates without significantly increasing heat generation during discharge. These increases are attributed to the maximization of anode active material and the minimization of electrode and separator thicknesses. The developed model can be integrated into the experimental design of batteries to improve target performance applications such as energy and power. It can be further employed to optimize various battery chemistries and configurations.

1. Introduction

Lithium polymer (LiPo) batteries utilize gel polymer electrolytes, improving the resistance to volume variations, increasing thermal stability, and making the battery safer overall (Long et al., 2016). Due to the complexity of the definition of performance, energy and power densities become major indicators of battery efficiency (Grazioli et al., 2016). Energy density describes the battery capacity, while power density describes the output power capabilities of the battery. These performance indicators are primarily affected by battery chemistry parameters (Domalanta et al., 2022). To simulate battery behavior with different parameters and operating conditions without the need for time-consuming experiments, the numerical modeling of batteries raised interest. A well-established model would entail insights into battery performance optimization by adjusting specific battery parameters. Sensitivity analysis of lithium-ion battery models has been the subject of previous studies to provide valuable insight into the effects of varying battery design parameters on performance (Jin et al., 2018). Optimizing such parameters would entail improving battery capacity, performance, and efficiency, which in turn will have knock-on effects on battery manufacturing and usage as more energy can be stored more safely, efficiently, and with less material (Pan et al., 2022).

At present, relatively few studies have tackled the modeling of LiPo batteries (Golmon et al., 2009). Although common among lithium-ion batteries, LiPo battery parameter optimization, and sensitivity analyses are relatively unexplored territory in research. As such, this study bridges the gap by proposing an electrochemical-thermal one-dimensional multiphysics model for LiPo batteries, integrating sensitivity analysis and a subsequent parameter optimization algorithm to propose better battery design and optimize performance for energy or power use cases.

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2. Methodology

The methodology is divided into four parts. The first part is developing the multiphysics model. The second is validating the model and determining significant parameters; the third is analyzing its sensitivity, and finally, optimizing the parameters for battery energy density.

2.1 Multiphysics model

The electrochemical model used was based on the pseudo-2-dimensional (P2D) model of Doyle and Newman (1995). It uses a one-dimensional geometry with a combination of porous electrode theory, concentrated solution theory for electrolyte mass and charge transfer, Butler-Volmer kinetics, Ohm's law for solid phase current density, and Fick's law for solid phase mass transfer. The one-dimensional thermal model was based on the model developed by Gu and Wang (2002) described in Eq(1). The heat generation term q is dependent on several phenomena shown in Eq(2), where the first and second terms on the right-hand side represent the reversible and irreversible heat generation. The third term describes the Joule heating that occurs because of resistance to current flow through the electrode. The physical parameters of the base model were adapted from the study of Domalanta et al. (2023). The coupled P2D electrochemical-thermal model described was implemented using COMSOL Multiphysics™ 5.5.

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + q \tag{1}$$

$$q = -\sum_j a_{sj} \bar{\imath}_{nj} \left(U_j - \frac{T \partial U_j}{\partial T} \right) + \sum_j a_{sj} \bar{\imath}_{nj} (\bar{\eta}_j) - \sum_{k=e\&s} (\langle i_k \rangle \cdot \nabla \langle \phi_k \rangle^k) \tag{2}$$

2.2 Model validation and parameter estimation

The developed multiphysics model was validated by comparing the root mean square error (RMSE) of the model's discharge data against the experimental data of Domalanta et al. (2023). To closely match the experimental data, modification of the model's transport and kinetic parameters was performed using the parameter estimation function of COMSOL Multiphysics Optimization Module, which minimizes the deviations between two discrete data sets by varying one or more model parameters. In this study, the Levenberg-Marquardt method for parameter estimation was selected as proposed by Santhanagopalan et al. (2007).

2.3 Sensitivity analysis

The parameter sensitivity was calculated using a Multiparametric Sensitivity Analysis (MPSA) derived from the work of Jiang et al. (2020) described in Eq(3). For this study, the sensitivity of energy and power densities to variations in battery design parameters are the basis of assessment. Each parameter will be assessed for two objective functions. This study used ten generated values for each parameter. The average of the results will then be used to assess the overall sensitivity of energy and power densities to the tested parameter. The five most sensitive parameters for energy density at 1 C and 0.5 C discharge rates were considered sensitive and subjected to parameter optimization.

$$M_i = \sqrt{\frac{1}{m} \sum_{n=1}^{m} \left[\frac{\left(\frac{g_i(x_0) - g_i(x_n)}{g_i(x_0)} \right)}{\left(\frac{x_0 - x_n}{x_0} \right)} \right]^2} \tag{3}$$

2.4 Parameter optimization

This study utilized the built-in COBYLA module for optimization in COMSOL Multiphysics as illustrated in Figure 1. This applies to nonlinear systems and does not require the derivative of the objective function to be known (Mei et al., 2018). This algorithm employs iterative linear approximations to optimize the objective function, energy density optimization, within given constraints. First, the power density of the modeled battery must not fall by more than 10 % in the optimization result to avoid solving with a significantly reduced rate capability. Second, the discharge time is limited to the maximum theoretical value for a given C-rate. For instance, the maximum discharge time is limited to 3,600 s at 1 C, while the discharge time is limited to 7,200 s at 0.5 C. The result of this constraint is that the optimization algorithm will minimize the battery mass such that the battery capacity is still 2,000 mAh. Third, the heat generation and the average heat generation rate should not increase by more than 20 % to avoid excessive heat generation, which may lead to unsafe battery operation.

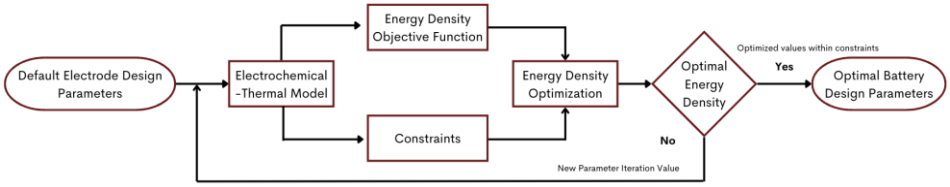

Figure 1: LiPo battery optimization procedure flowchart

3. Results and discussion

3.1 Parameter estimation

Simultaneous estimation of the rate constants and diffusion coefficients in the anode and cathode via the Levenberg-Marquardt method yielded different values depending on the discharge rate, as shown in Table 1.

Table 1: Estimated parameter values from the Levenberg-Marquardt method

Parameter	Initial	Estimated	
		1 C Discharge	0.5 C Discharge
$k_{cathode}$ ($mol^{2.5}/mol^{0.5}•s$)	6.67 x 10^{-11}	9.60 x 10^{-13}	9.59 x 10^{-13}
k_{anode} ($mol^{2.5}/mol^{0.5}•s$)	1.76 x 10^{-11}	9.48 x 10^{-13}	9.38 x 10^{-13}
$D_{Li.s,cathode}$ (m^2/s)	1.00 x 10^{-11}	1.00 x 10^{-13}	1.07 x 10^{-13}
$D_{Li.s,anode}$ (m^2/s)	5.50 x 10^{-14}	3.90 x 10^{-14}	1.93 x 10^{-14}

The values of $k_{cathode}$, k_{anode}, and $D_{Li.s,cathode}$ changed proportionally regardless of the C-rate, describing that the C-rate value does not hold a substantial effect on the estimation of the mentioned parameters. Additionally, the aforementioned parameters decreased by two orders of magnitude. The $k_{cathode}$, k_{anode}, and $D_{Li.s,cathode}$ decreased by 70-, 18-, and 100-fold in both C-rates. Only the estimated $D_{Li.s,anode}$ value changed with respect to the C-rate, decreasing at 60 % of its original value at 1 C and 35 % of its initial value at 0.5 C. The deviation stems from the experimental data; two different batteries with the same battery chemistry were used to obtain the discharge data at 1 C and 0.5 C to ensure fresh and uncycled batteries and to circumvent degradation and capacity fade effects. As such, these two batteries may not be accurately identical in terms of anode structure and solid-electrolyte interface thickness, affecting the estimated diffusion coefficient.

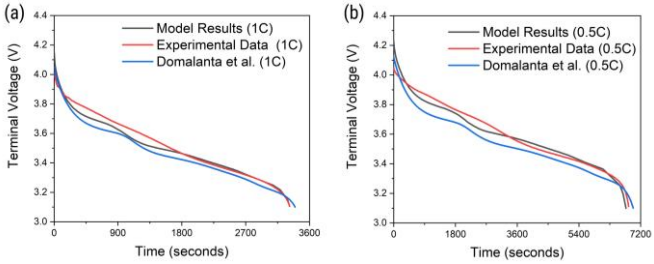

Figure 2: Comparison between fitted model results (black lines), experimental data (red lines), and reference literature model results (blue lines) for (a) 1 C and (b) 0.5 C discharge rates

Figure 2 displays parameter adjustments' effects during discharge at 1 C and 0.5 C. For both discharge rates, significant deviations are observed at the start of the discharge process. Near the end of the discharge, the model results almost mirror the experimental data. It was found that the maximum deviation was observed at the start of the discharge process for both C-rates having a minimal RMSE of only 35 mV for both C-rates. This accuracy has shown significant improvement from the reference base model of Domalanta et al. (2023), which had an RMSE of 60 mV and 70 mV, for 1 C and 0.5 C. Improvement was attributed to the fitted parameter values in Table 1 that may have a closer resemblance to the actual property values unlike that of the base model reference that relied on literature-reported values.

3.2 Sensitivity analysis

Each selected design battery parameter was analyzed for each discharge rate. Energy density sensitivity (M_{ED}) reveals the two most sensitive parameters are similar for both discharge rates, which are the anode active material fraction ($\varepsilon_{s,anode}$) and length (L_{anode}) in order. This suggests that the anode properties are integral to the

optimization of energy density. It is critical to note that their M_{ED} sensitivity values are several magnitudes higher than other values, with 0.985 for $\varepsilon_{s,anode}$, and 0.632 for $L_{anode,}$ (both at 1 C). The next most sensitive parameter is $L_{cathode}$ with a M_{ED} value of 0.256 at 1 C, which is around four times less than that of $\varepsilon_{s,anode}$, emphasizing their impact on optimization. Sensitivity values vary with C-rates due to transport limitations at higher C-rates and thermodynamic limitations at lower C-rates.

Power density sensitivity (M_{PD}) values are lower compared to M_{ED} values on average, around five times, and there are no notable values from M_{PD} values since they are generally in line with prominent parameters for M_{ED} in which L_{anode}, and $L_{cathode}$ are the most sensitive with an average M_{PD} value of 0.291 at 1 C. Results from this sensitivity analysis are aligned with the findings of Hosseinzadeh et al. (2017), where the lengths and the active material fraction were determined to be sensitive for both densities; while particle size is more sensitive to energy density. The top four parameters in each discharge rate are chosen for optimization. Given that the sensitivity of $\varepsilon_{s,anode}$, L_{anode}, and $L_{cathode}$ overlap for both discharge rates, only L_{sep} and $R_{p,anode}$ were added.

3.3 Parameter optimization

The five selected parameters were optimized to maximize energy density using the COBYLA optimization algorithm with the parameter range, and optimized values are presented in Table 2.

Table 2: Optimized parameters for the five most sensitive parameters

Parameter	Range	1 C Discharge Rate			0.5 C Discharge Rate		
		Initial	Optimized Value	% Change	Initial	Optimized Value	% Change
$\varepsilon_{s,anode}$	0.4–0.7	0.5052	0.7	+38.6 %	0.5052	0.69645	+37.9 %
L_{anode} (µm)	35–105	73.5	55.559	-24.4 %	73.5	55.068	-25.1 %
$L_{cathode}$ (µm)	35–105	70	50.134	-28.4 %	70	53.169	-24.0 %
L_{sep} (µm)	20–40	25	20	-20.0 %	25	20	-20.0 %
$R_{p,anode}$ (µm)	5–20	12.5	12.45	-0.4 %	12.5	12.417	-0.7 %

From the sensitivity analysis, it can be determined that the anode material fraction greatly influences the battery's energy density and increases in value after optimization. Increasing anode material enhances lithium-ion density, improving the energy density. The optimized anode material fraction for 1 C discharge lies at the upper boundary (0.7) of the parameter constraint. This upper boundary value was selected based on related literature detailing the maximum experimentally obtainable values of anode active material fraction. As such, the “true” optimal value may lie beyond the constraints but may be physically limited by the manufacturing of porous anode materials. The anode material fraction can be increased by using stable graphite with low-capacity fade and higher purity that could be achieved from optimized carbonization of a high carbon source (Du et al., 2017). Additionally, the anode’s thickness was minimized to provide enough lithium ions to meet the specified battery capacity, while the cathode’s thickness was optimized to maximize its saturation with lithium ions by the end of the discharge process. The thickness of the separator was minimized to the boundary value of 20 µm, the lowest in related literature (Deimede and Elmasides, 2015). Because the separator acts to prevent short-circuiting, it is recommended to minimize its thickness to a safe value to reduce the proportion of its mass to other battery components. Specific thickness can be achieved by carefully selecting physical parameters during battery coating/lamination and calendering.

Table 3: Battery performance indicators of the optimized model

Parameter	1 C Discharge Rate			0.5 C Discharge Rate		
	Initial	Optimized Value	% Change	Initial	Optimized Value	% Change
Energy Density (Wh/kg)	137.4	171.12	+24.5 %	142.06	176.81	+24.5 %
Power Density (W/kg)	145.83	178.49	+22.4 %	75.088	90.642	+20.7 %
Discharge Time (s)	3,391.7	3,451.3	+1.8 %	6,810.7	7,022.4	+3.1 %
Q_{gen} (kJ)	7.2819	7.3813	+1.4 %	5.808	6.5171	+12.2 %
Avg. Q (W)	2.147	2.139	-0.4 %	0.9280	0.9280	+8.8 %

From Table 3, it was found that when the objective function is energy density, it also significantly improved the battery's power density. This result stems from the applied constraints to the optimization algorithm, specifically, the discharge time. Since these parameters cannot be adjusted to increase the discharge time and, by extension, the total capacity of the battery, the only course that the optimization algorithm can take is to minimize the mass of the battery. Given that the discharge rate is also fixed, this inevitably increases power density as well. This also explains the lack of change in the anode active particle radius, as sensitivity analysis revealed

that adjusting this parameter affects the battery model's discharge time rather than power density. Finally, similar energy density improvements were obtained by a similar optimization study from Lee et al. (2020), lending credence to the magnitude of improvement obtained in this study.

The critical difference between the results at 1 C and 0.5 C is the relative increase in heat generation observed in the optimized 0.5 C model. In the 1 C optimization, there was barely any change in heat generation, while the optimized 0.5 C model yielded an 8.8 % increase in average heat generation. This deviation is attributed to the significantly different values of the anode diffusion coefficient obtained during the parameter estimation step. Since the estimated 0.5 C anode diffusion coefficient is about half the value of the diffusion coefficient estimated at 1 C, the optimized 0.5 C model has significantly greater polarization within its anode because of the concentration gradients within the solid particles and between the particles and electrolytes. Consequently, this increased resistance increases the ohmic heat generation in the optimized 0.5 C model.

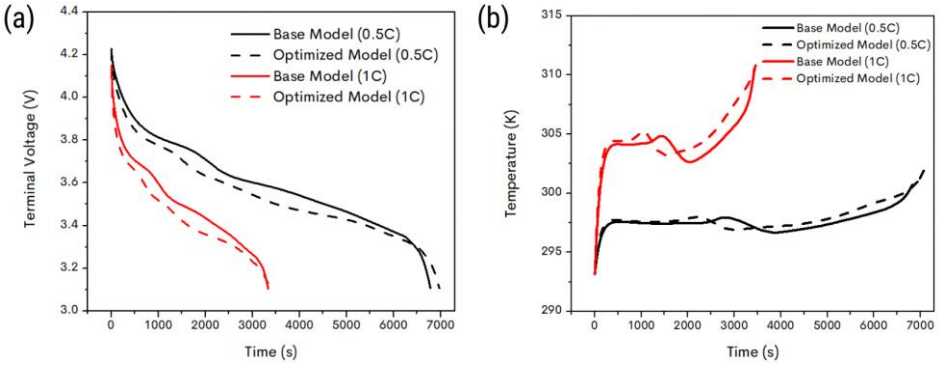

Figure 3: Comparison between the base (solid lines) and optimized (dash lines) battery models for the (a) discharge curve and (b) temperature profile for 1 C (red lines) and 0.5 C (black lines) discharge rate

The optimized model's discharge voltage is slightly lower than the base model, as illustrated in Figure 3a. This decrease is inferred to be the result of decreasing the electrode thicknesses since a fixed amount of current must be extracted from less active material. In addition, increasing the active material fraction reduces the anode's porosity, constricting the lithium-ion transport in the electrolyte. This increases the concentration of lithium ions in the electrolyte, as these ions cannot quickly migrate to the cathode. This limits the rate of the intercalation reaction at the cathode, necessitating an increase in overpotential to compensate. These phenomena are theorized to be the major contributors to the slight reduction in discharge voltage.

The thermal behavior at both discharge rates is illustrated in Figure 3b. Thermal performance is critical to a lithium-ion battery's safety since thermal runaway can occur at excessively high temperatures. The optimized model temperature profile is observed to be slightly higher than that of the base model of around 1 K. It can be said that the optimized model does not operate at significantly higher temperatures than the base model. In addition, the base model temperature increases at around 40 % into the discharge process, then falls, until finally rising again continuously until the end of the discharge process. This phenomenon occurs presumably due to the endothermicity of the intercalation reaction at the cathode (Domalanta et al., 2023). The optimized model's thermal behavior experiences the same trends, though the changes in the temperature profile onset are earlier than in the base model. Such difference arises from the lower amount of cathode active material in the optimized model; the endothermic stage of the cathode intercalation process, which occurs when the cathode reaches a certain degree of lithium saturation, occurs sooner since the cathode saturates faster in the optimized model. Finally, the temperature increase in the 1 C model is greater than that of the 0.5 C model because of the greater ohmic heat generation brought about by the increased current density.

4. Conclusions

A coupled electrochemical-thermal lithium-ion battery model was developed and fit to actual battery discharge data via parameter estimation. The produced model was then used for sensitivity analysis of ten battery design parameters for the most effective optimization. Based on sensitivity analysis data, the selected design parameters for optimization are the anode active material fraction, the anode active particle size, and the lengths of the anode, cathode, and separator. These parameters were optimized towards maximizing energy density with given constraints on power density reduction, maximum allowable discharge time, and heat generation limitation. In conclusion, optimization models yielded an approximate of about 25 % increase in energy density at both 1 C and 0.5 C discharge rates.

Nomenclature

c_p – isobaric specific heat, J/(kg·K)
$D_{Li,s}$ – solid-phase diffusion coefficient, m^2/s
g_i – power/energy density parameter for x
k – rate constant, $m^{2.5}/(mol^{0.5}·s)$
M_i – calculated sensitivity of parameter i
T – local temperature, K
t – time, s
x_n – generated values for parameter analysis of n
q – battery heat generation, W/m^3
α – specific surface area, 1/m
λ – thermal conductivity, W/(m·K)
ρ – density, kg/m^3

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