CHE210/CHE222 Final Report:
Investigation of Thermal Runaway Models in MCMB Lithium Ion Batteries

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Executive Summary

This report focuses on the sensitivity analysis of self-heating models in lithium-ion batteries through various scenarios, examining factors such as reaction parameters, battery composition, and temperature mitigation strategies. Model used to perform this analysis was derived in a series of experiments performed by Richard et al in the Journal of The Electrochemical Society. The findings offer valuable insights into the behaviour of lithium-ion batteries under different conditions, providing guidance for improving battery design, enhancing safety features, and optimizing cooling systems to ensure efficient and reliable performance.

The modelling results determined that, in general, the increase of reaction parameters, such as reaction order and frequency, increased the overall self-heating rates. These parameter values were estimated by Richard et al and are thus likely to hold. The Reaction parameters were not something that can be controlled through design but, however, must be accounted for when modelling for other changes.

Controlling the initial intercalated Li content has been shown to help prevent excessive thermal runaway, which is a crucial aspect of battery safety. Further research is needed to determine how to effectively control Li content without negatively impacting battery performance factors, such as capacity and discharge rates. This will enable the development of more efficient and safer lithium-ion batteries for various applications.

Battery composition, specifically the surface area of MCMB (mesocarbon microbead) material in the electrode, significantly impacts the thermal performance and safety of lithium-ion batteries. High surface area MCMB leads to greater temperature increases and slower SEI (solid electrolyte interface) layer growth, offering higher battery capacity and longer cycle life. However, this also poses a higher risk of thermal runaway, which is a major safety concern. In contrast, low surface area MCMB is recommended for decreasing the risk of thermal runaway, although it may compromise capacity and cycle life to some extent.

A forced convective cooling system was modelled to observe the cooling dynamics and determine if it was possible to maintain the battery temperature at 30ºC. The model was successful in mitigating thermal runaway in addition to the cooling process taking only 2 minutes for the higher estimated heat capacities. This cooling model was significantly strong that changes in the self-heating parameters made virtually no change in the cooling process.

The convective model requires refinements to be suitable for industrial application. These refinements include determining the average heat capacity over the battery surface, obtaining precise battery dimensions, accurately weighing the battery, and experimentally ascertaining the heat capacity. Incorporating these refinements will lead to a more accurate and reliable model for the development of effective cooling systems in lithium-ion battery applications.

In conclusion, cooling systems should be designed to activate before reaching the self-heating temperature range for optimal safety and performance. The knowledge gained from this study will play a vital role in enhancing the performance and safety of lithium-ion batteries in the future, allowing for wider adoption in diverse industries.

1. Introduction

Lithium-Ion batteries are commonly used to power vehicles and smartphones. However, they tend to decrease in efficiency with time due to thermal runaways. Therefore, VoltaEV has tasked a group of engineers to investigate the self-heating rates of lithium-ion batteries in contrast to different factors that could cause a change in those rates. This report aims to showcase those factors and provide engineering recommendations and insight into the results obtained from a sensitivity analysis using the model described by Richard et al in the Journal of The Electrochemical Society (Richard and Dahn, 1999a, 1999b).

2. Results

The following are the graphical results for sensitivity analysis of the self-heating model proposed in Richard et al II. There are two complete self-heating rate models referred to as Set A (Equations 4a, 5a, 6 & 7a) and Set B (Equations 4b, 5b, 6, 7b). The Set A Equations are based on the tunnelling mechanism that considers a linear increase of the SEI layer thickness. The Set B Equations are based on the diffusion mechanism that considers the exponential increase of the SEI layer thickness. The results are presented in a series of scenarios investigating the effect of different reaction orders for the conversion of metastable SEI components (Scenario 1), the initial intercalated Li (Scenario 2), using low or high surface area of lithiated mesocarbon microbead (MCMB) material in electrolytes (Scenario 3), reaction input variables (h, C, A, E, n, m) (Scenario 5) and different initial starting temperatures (Bonus). The change in these variables analyzed the effect on the temperature profile, change in intercalated Li and metastable SEI in addition to the growth of the SEI layer. Lastly, a feasible way to mitigate the self-heating and maintain a battery temperature of 30ºC was also developed and modelled (Scenario 4). A detailed outline of the scenarios covered can be found in the project description (Professor Daniela Galatro *et al.*, 2023). All calculations and code used to perform the sensitivity and steady-state analysis can be found in the MATLAB files attached to this document as well as in Appendix B.

2.1 Change in Reaction Order Modeling Results (Scenario 1)

This scenario shows the self-heating rate and how it changes depending on different reaction orders by modelling only the first term of Equation 7. The rate at which the self-heating rate changes is affected by how much Lithium is reacted from the metastable layer and grown into the stable layer. The property that governs this growth is the reaction order "n". As seen in Figure 1, the rate at which temperature changes will increase as the temperature increases until a peak rate is reached, and after reaching the peak temperature rate, the battery's temperature will decrease until around 0°C/min. Physically speaking, this makes sense since the battery's temperature will increase until the metastable layer has been consumed, at which point the self-heating profile peaks and decreases. As the reaction order (n) is decreased, the starting temperature rate and peak temperature rate will be higher. This makes sense mathematically because our x_{fo} is a rational number that is less than 1, a lower reaction order number will make the value x_f^n larger.
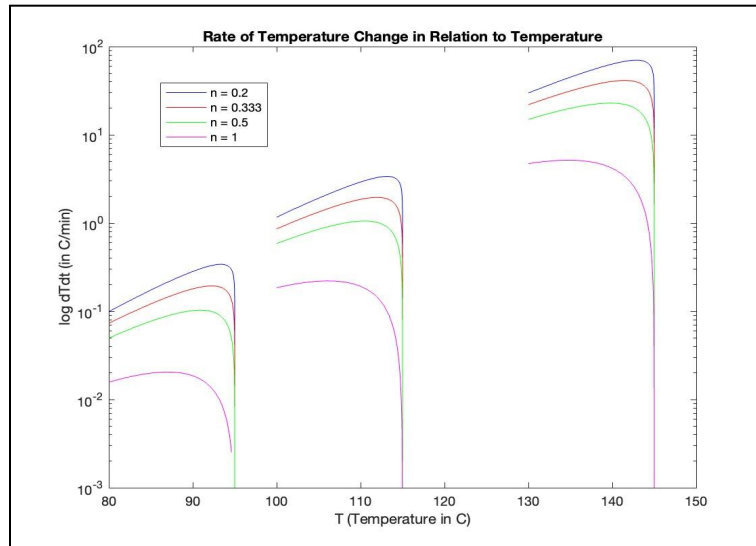
Figure 1: Scenario 1 Results - Rate of Temperature Change with varying reaction orders

2.2 Change in Initial Intercalated Li Content Results (Scenario 2)

This scenario aims to look at how the temperature profile, the change in intercalated Li, the change in metastable SEI and the growth of the SEI layer change with the different voltage samples. Each sample contains a different amount of initial intercalated Li (0.00 V - 0.75, 0.089 V - 0.45, 0.127 V - 0.25) (Richard and Dahn, 1999b). As shown below in Figure 2. The temperature profile seems to run out of x_i much quicker, causing the change in temperature to not only be lower overall but also drop off significantly quicker. Additionally, the change in intercalated Li, despite starting at different levels, decreases at the exact same rate. The decrease in the metastable SEI layer, however, is much faster for lower initial concentrations of intercalated Li. Lastly, the growth in the SEI Layer, while initially reflecting different rates, is consistent among all samples after roughly 120ºC.
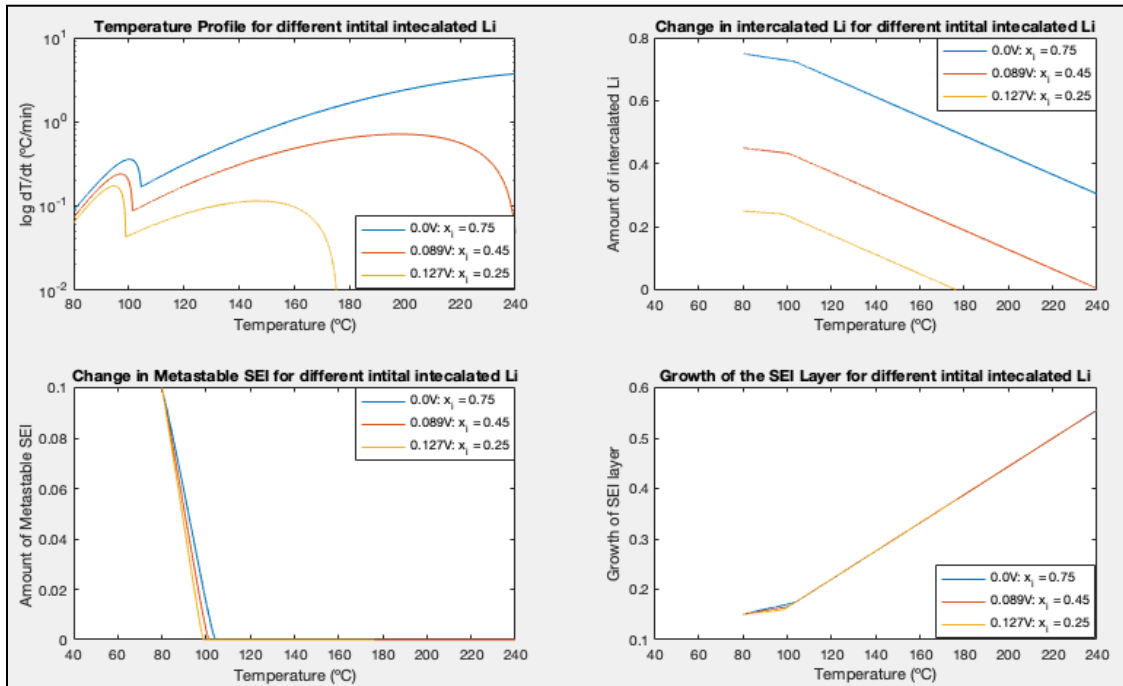

Figure 2: The graphs for the Temperature Profile (top left), Change in Intercalated Li (top left), Change in Metastable SEI (bottom left) and Growth of the SEI layer (bottom right)

2.3 Change in the MCMB Surface Area Results (Scenario 3)

This scenario aims to display the difference between low and high surface area MCMB based on Set A and Set B equations. The low and high surface area is abbreviated as a_L and a_H, respectively, in all Figures 3, 4, 5 and 6. Overall, the self-heating trends are similar. The temperature rate profile modelled by Set B shows a much faster increase compared to the temperate rate profiles modelled by Set A (Figure 3). The changes in intercalated Li, metatable SEI, and the SEI layer are identical for the model of Set A or Set B equations, as shown in Figures 4, 5 and 6. As shown in Figure 3, the high-surface area MCMB has a higher overall temperature rate profile than with low-surface area. For both Set A and Set B models, the temperature peak of the high-surface area MCMB seems to end at 140ºC and 120ºC. This is due to the higher initial metastable SEI content present in the high-surface-area MCMB model, as shown in Figure 4. The rate at which the metastable SEI is depleted is the same regardless of the surface area of MCMB, however, since the low-surface area MCMB has less initial metastable SEI content, it becomes fully depleted at much lower temperatures. The intercalated Li depletion rate is initially different for both MCMB samples but then approximately equalizes at roughly 140ºC. Lastly, in contrast to the intercalated Li trend, the growth in the SEI layer starts off at the same rate for both samples however, the low-surface area MCMB has a more rapid growth at 120ºC compared to the high-surface area MCMB, where the size is relatively constant.
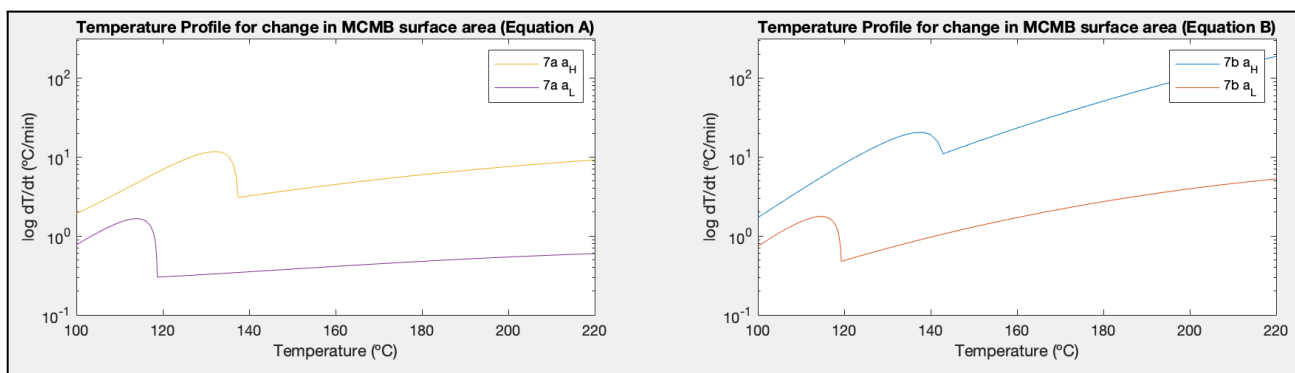

Figure 3: Temperature Profiles for high & low surface area using Set A (left) and Set B (right)
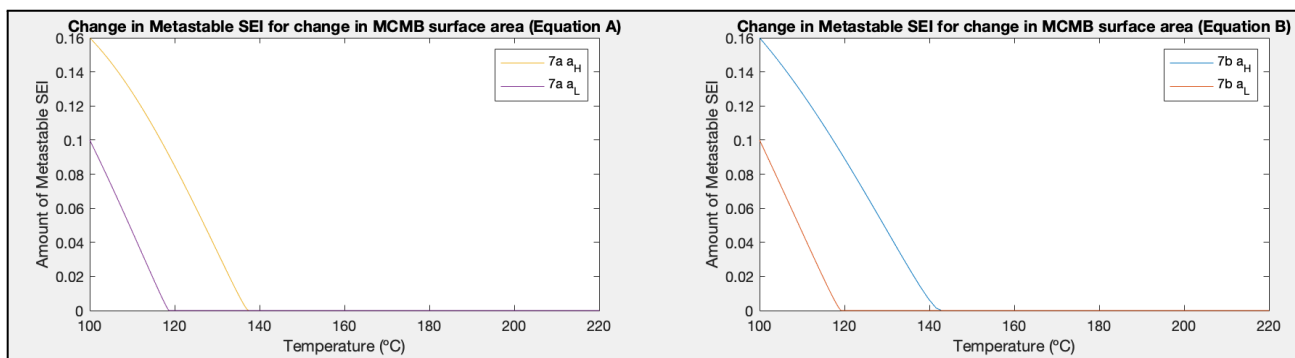

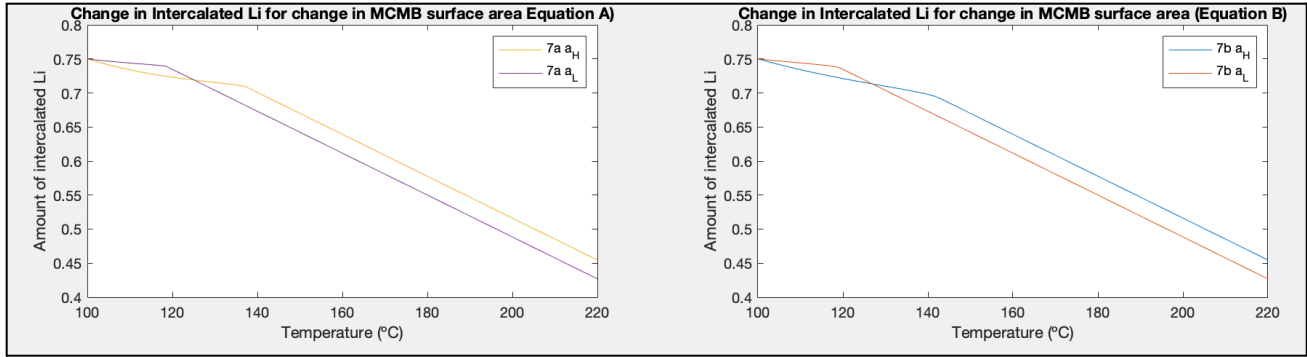*Figure 4: Change in Metastable SEI for high & low surface area using Set A (left) and Set B (right)*

Figure 5: Change in Intercalated Li for high & low surface area using Set A (left) and Set B (right)
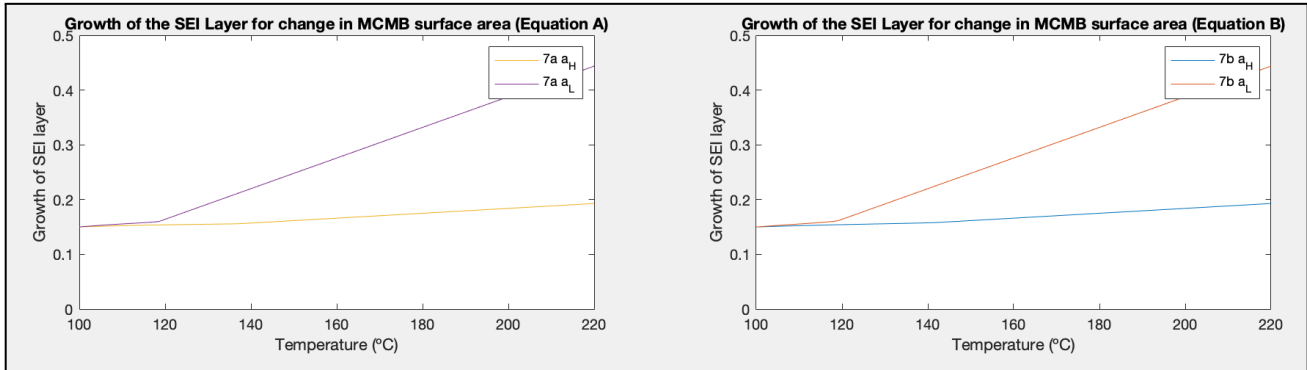

Figure 6: Growth of the SEI Layer for high & low surface area using Set A (left) and Set B (right)

2.4 Steady State Analysis for Self-Heating Mitigation (Scenario 4)

The objective of Scenario 4 was to determine the time it takes to cool a lithium-ion battery from an initial temperature of 80 ^{o}C to 30 ^{o}C through forced convection using room temperature air (25 ^{o}C). In order to model this relationship, we first had to create an approximate model of a battery that would be cooled. We decided to use a lithium-ion coin battery with a diameter of 24mm and a thickness of 6mm. The mass was set as 3 g, which is typical for a coin battery of that size and material. The relationship between the temperature of the surface of the battery and time was then modelled using the lumped heat capacity model (Appendix B). Typically under forced convection, the heat transfer coefficient (h) varies with position, but to simplify the model, we have chosen 3 reasonable values from the range of 10 to 500 J/sec.m² (600 to 30,000 J/min.m²) (*Convection Heat Transfer Coefficient*, no date). Figure 7 employs h values toward the lower end of the scale to demonstrate cooling under suboptimal conditions. This was modelled using Set B equations with low-surface area MCMB.

In Scenario 4, forced air convection is utilized to model the time required to cool a battery from an initial temperature of 80°C, as this is when self-heating is first detected. The relationships are plotted using three different heat transfer coefficient (h) values. Under forced convection, the h values of air can range from 10 to 500 J/sec.m² (600 to 30,000 J/min.m²), depending on the position (*Convection Heat Transfer Coefficient*, no date). The plot employs h values toward the lower end of the scale to demonstrate cooling under suboptimal conditions. Figure 7 illustrates that when h = 600 J/min.m², the battery takes approximately 8 minutes to reach a temperature of 30°C and when h = 2000 J/min.m², the battery cools to 30°C in approximately 2 minutes (Appendix A).It should be noted that the forced convection heat transfer is so dominant due to the high heat transfer coefficient in this model that changes in any parameters within the thermal runaway model did not substantially affect the cooling process and resulted in a graph that is optically identical to the one in Figure 7.
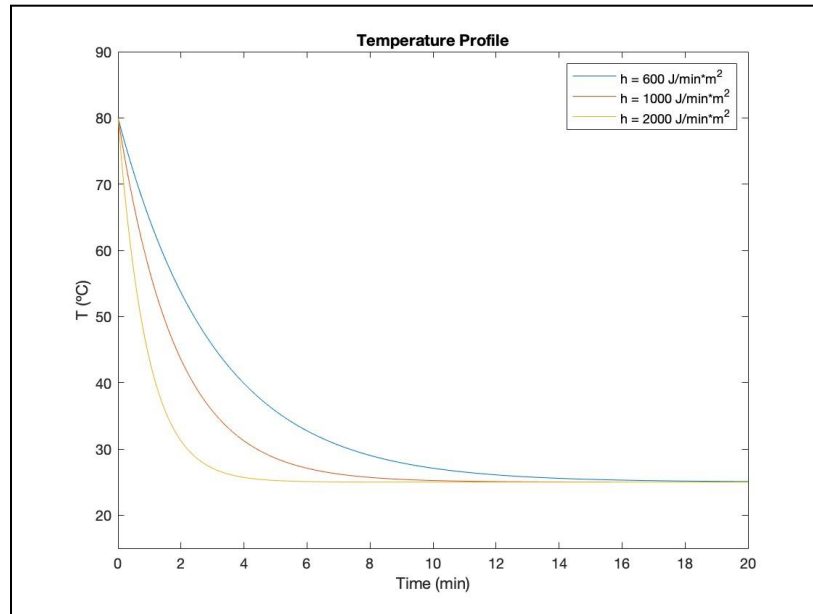
Figure 7: Temperature profile of self-heating model subjected to forced convection with a fluid temperature of 25ºC with varying heat transfer coefficients

2.5 Sensitivity Analysis of Reaction Input Variables (Scenario 5)

The sensitivity analysis highlights the factors that increase or decrease the self-heating rate. The sensitivity analysis was performed on scenario 3, with equation 7b being utilized. Six parameters were changed, namely h1/C, h2/C, A1, A2, E1, and E2. Values were chosen to reflect a linear increase of parameters (for example, a stepwise increase of 0.2 for E2 values). As seen in Appendix B, Figures 9-10, show the self-heating rate with respect to temperature at different parameter values. The main takeaway from these figures is that as a parameter is increased, so is the self-heating rate, although at different rates. For example, increasing h/1C does not have as much of an impact on the self-heating rate compared to A1 or E2 values. The reasoning behind this comes from the width of each line on the graphs, as seen in Figure 11 in Appendix A, the width between each line is much higher than the width in Figure 9, meaning that changing A1 has the potential to be more impactful on self-heating rate than h1/C.

2.6 Change in the Initial Temperature Results (Bonus)

This scenario shows the difference when the same lithium cells are heated to different initial temperatures, 80ºC, 100ºC, and 115ºC. The self-heating rate profile for each of the temperatures is shown in Figure 8. Each profile shares a similar trend, a peak after the initial temperature is seen as the metastable SEI is converted to stable SEI. As the initial temperature increases, this peak also increases. After the conversion of SEI, all three temperature changes experience the same rate of increase. This is due to the same rate of SEI growth at each initial temperature.
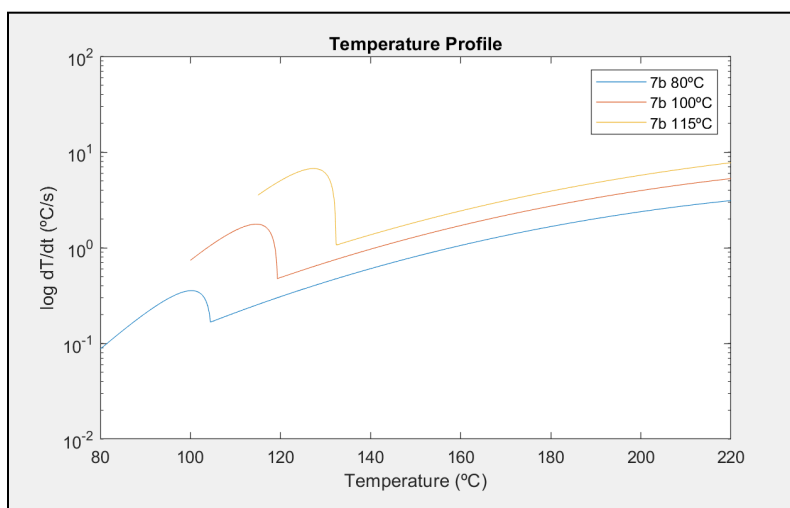
Figure 8: Temperature Profile of LIBs when heated at different initial temperatures

3. Discussion

This section outlines the parameters which mainly influence the self-heating profile in lithium-ion batteries. Reaction parameters, battery composition, and initial temperature are discussed. Furthermore, a cooling model was developed, and recommendations for mitigating temperature are outlined.

3.1 Reaction Parameters

The different reaction orders explored in Scenario 1 are not particularly useful as the order of the reaction is not a parameter that can be controlled. Richard et al determined the reaction order that best fits experimental data to be n = 0.5, and thus, was used in all subsequent modelling (Richard and Dahn, 1999b). Scenario 5 also displays a sensitivity analysis of parameters associated with the self-heating reactions. These reaction parameters cannot be controlled through the design of the battery and are simply the nature of the chemical reactions present in the phenomenon. Richard et al have outlined values that best reflect the experimental values in addition to literature values for A1, A2, E1, E2, h1/C, and h2/C, and thus these parameters were used in all subsequent modelling (Richard and Dahn, 1999b). Should any of the assumptions not hold true based on further experimental data, the relationships described in sections 2.1 and 2.5 can provide insight into how the models and thermal runaway mitigation systems can be adjusted. It is unlikely that the assumptions do not hold, as these values were calculated by Richard et al in a series of trials to determine the best fit for the experimental data (Richard and Dahn, 1999b).

3.2 Battery Composition & Initial Temperature Self-Heating Temperature

Scenario 2 suggests that the self-heating rate is not only significantly lower for lower initial intercalated Li content but that intercalated Li is depleted at much lower temperatures preventing excessive thermal runaway. This suggests that by accurately controlling the presence of initial intercalated Li, battery design can prevent the extent to which the thermal runaway progresses and thereby prevent a major accident. Despite this, controlling the amount of intercalated Li is increasingly difficult as the amount of intercalated Li increases through the discharge of the battery, as shown in the experimental samples used in Richard et al (Richard and Dahn, 1999a). Further investigation is required to determine if it is plausible to control or reduce the amount of Li without hindering battery performance.

Scenario 3 indicates that high surface area MCMB will lead to greater temperature increases and slower growth of the SEI layer. The increased surface area allows more sites for the intercalation and deintercalation of lithium ions (Tarascon and Armand, 2001). Higher intercalation and deintercalation rates indicate higher battery

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capacity and longer cycle life (Tarascon and Armand, 2001). The disadvantages of high surface area MCMB include a greater risk of thermal runaway. The increased surface area of the MCMB allows more reactions between the electrode surface and the MCMB material in the electrolyte. The reaction leads to more formation of the metastable SEI layer. A higher metastable SEI content results in elevated self-heating rates. Furthermore, high surface area MCMB has more irreversible capacity, which is the capacity loss of the battery that cannot be recovered. This loss is from the formation of a stable SEI layer that consumes lithium ions, an irreversible reaction (Richard and Dahn, 1999b). Subsequently, low surface area MCMB has the advantages of lower risk of thermal runaway and lower irreversible capacity. It has the disadvantages of having a shorter cycle life and lower battery capacity due to fewer sites for the intercalation and deintercalation of lithium ions (Tarascon and Armand, 2001). Therefore, there are certain trade-offs when choosing between low or high surface area MCMB. For the objective of decreasing the possibility of self-heating that eventually leads to thermal runaway, a low surface area MCMB is recommended.

Scenario 6 highlights the need for cooling early on in the runaway process due to a much faster self-heating rate when self-heating begins at higher temperatures. This means that simply allowing the battery to reach higher temperatures furthers not only the possibility of self-heating and thermal runaway but also the intensity should the thermal runway start at higher temperatures. Therefore, when designing for thermal runaway mitigation, cooling systems should be prompted well before the self-heating temperature range has been reached.

3.3 Temperature Mitigation & Recommendation
The Scenario 4 model utilizes a fluid temperature of 25°C, representative of ambient room temperature air typically used for cooling electronics. This temperature is slightly below the 30ºC steady-state target and thus was effective at reducing the time taken to reach steady state. Additionally, the cooling rate was so effective that changes in the initial intercalated Li and metastable SEI did not impact the cooling rate relationship significantly. Based on this fact alone, it is highly recommended that a forced convective cooling system be used on MCMB Lithium Ion batteries to mitigate the self-healing process.

The model employed in Scenario 4 is not directly applicable to industrial implementation due to significant approximations and assumptions. One of the most critical assumptions involves the selection of heat transfer coefficients (h). Conventionally, the average h value over the surface is utilized for modelling temperature changes over time. However, reasonable values were chosen in this case to simplify the model, as calculating the average heat transfer coefficient is a complex task. Additionally, battery dimensions, heat capacity, and mass were approximated to develop the model. To create a more accurate and industrially viable model, several refinements must be made. These include determining the average heat capacity over the surface, obtaining precise battery dimensions, accurately weighing the battery, and experimentally ascertaining the heat capacity. Incorporating these updated values will facilitate the development of a reliable model suitable for industrial applications.

4. Conclusion
In conclusion, this study has investigated various parameters and scenarios to gain insights into thermal runaway mitigation in MCMB Lithium-ion batteries. It has been demonstrated that controlling the initial intercalated Li content, choosing low surface area MCMB, and employing forced convective cooling systems can help reduce the risk of thermal runaway. However, further investigation is required to determine the feasibility of controlling intercalated Li without affecting battery performance. The models and findings presented herein provide a foundation for understanding the complex relationships between battery composition, self-heating, and cooling strategies. Nevertheless, refinements to the models, such as more accurate battery dimensions and experimentally determined heat capacity, are necessary to make them suitable for industrial applications. By enhancing our knowledge of these factors and their interplay, we can develop safer and more efficient MCMB Lithium-ion batteries, thus mitigating the risks associated with thermal runaway.

Appendix

Appendix A: Scenario 4 hand written calculation

$h = 2000 \frac{J}{min.K}$

$D = 24mm \longrightarrow r = 12mm$

$L = 6mm$

$A_s = 2\pi rL + 2\pi r^2 = 2\pi(12)(6) + 2\pi(12)^2 = 1357.168mm^2 = 0.001357m^2$

$m = 3g = 0.003kg$

$c_p = 830 \frac{J}{kg.K} \longrightarrow$ heat capacity of a Lithium Nickel Cobalt Aluminium Oxide battery (Nigel, 2022)

$b = \frac{hA_s}{\rho V c_p} = \frac{hA_s}{mc_p} = \frac{(2000)(0.001357)}{(0.003)(830)} = 1.0899min^{-1}$

$t = ln(\frac{T(t)-T_\infty}{T_s - T_\infty}) \div (-b) = ln(\frac{30-25}{80-25}) \div (-1.0899) = 2.2min$

Appendix B: Sensitivity Analysis Graphs
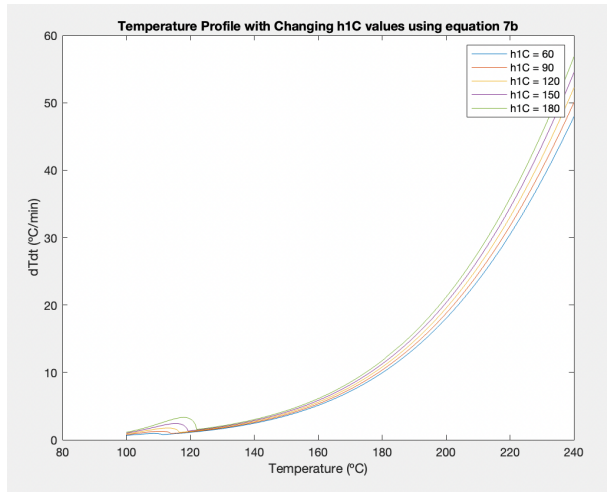
Figure 9: Change in Self Heating Rate With a Changing h1/C
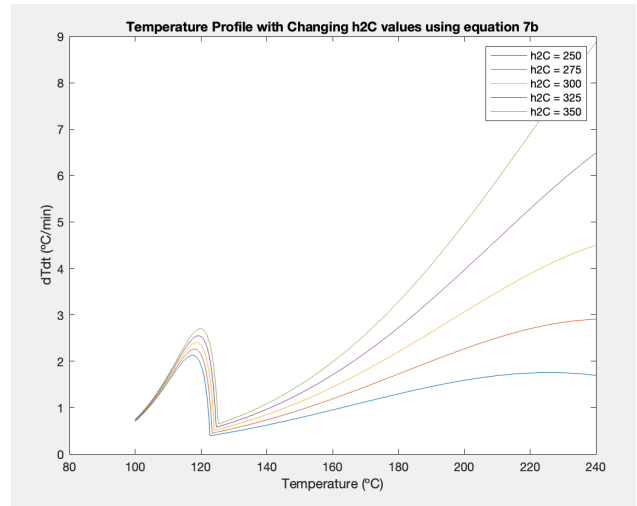
Figure 10: Change in Self Heating Rate With a Changing h2/C
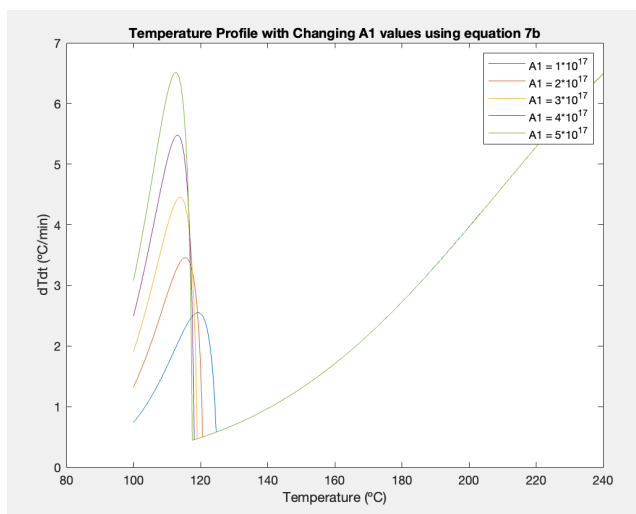
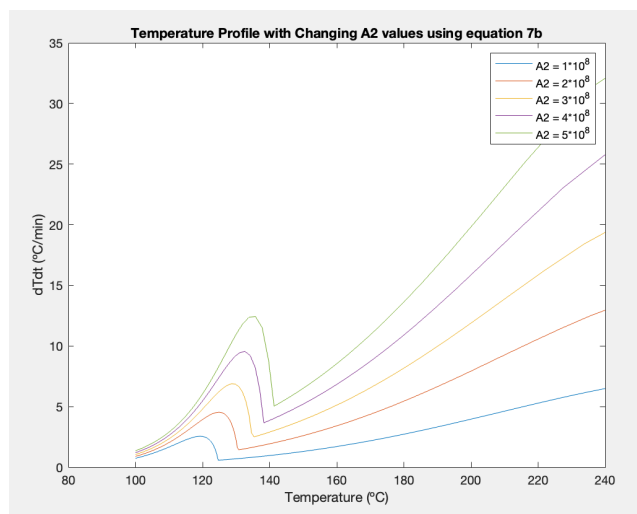*Figure 11: Change in Self Heating Rate With a Changing A1*

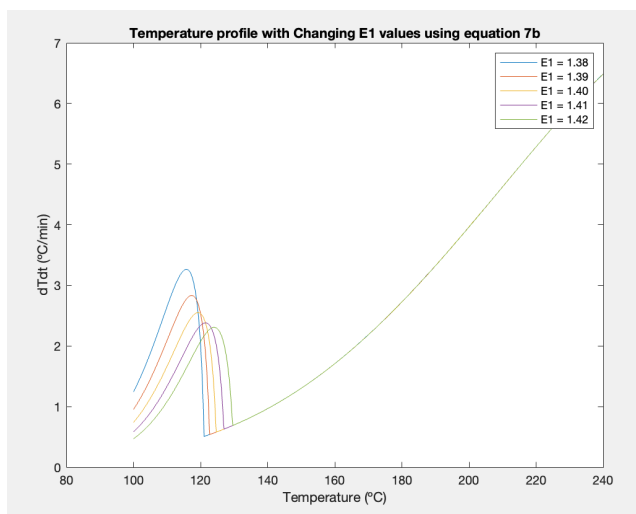*Figure 12: Change in Self Heating Rate With a Changing A2*

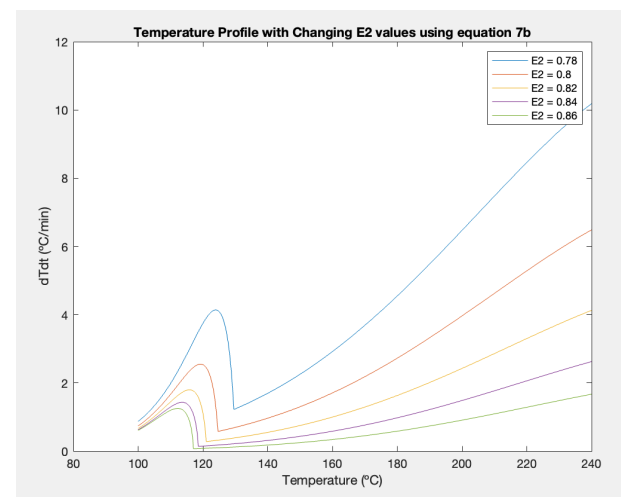*Figure 13: Change in Self Heating Rate With a Changing E1*

Figure 14: Change in Self Heating Rate With a Changing E2

Contribution Statement and Time Sheet

	Cairo Cristante	Anastasia Dimov	John Larsen	Daniel Moore	Miranda Su
Before 10/04/23	Worked on the base code for Scenario 2, 3 and the bonus (3 hours)		Worked on Scenario 1 code and writing for mid-report (3 hours)	Researched potential cooling options. (1 hour)	
10/04/23			Sensitivity Analysis and wrote scenario 1 discussion (1 hour)	Researched industry standards and how I would model the cooling system (1 hour)	
11/04/23	Wrote the results section for scenario 2 (1 hour)	Adapted Scenario 2, 3 and bonus code to be more reflective of research paper graphs (3 hours) Wrote introduction (1 hour).	Sensitivity Analysis(1 hour)	Began coding in matlab scenario 4 (1 hour)	Adapted Scenario 2, 3 and bonus code to be more reflective of research paper graphs (1 hour) Wrote results section for scenario 3 (1 hour)
12/04/23		Adjusted Scenario 2,3 and bonus codes, and wrote bonus section (3 hours).	Sensitivity Analysis(1 hour)	Continued coding in matlab scenario 4 (2 hour)	Adjusted Scenario 3 MATLAB code (3 hours)
13/04/23	Assisted with Scenario 4 MATLAB code (2 hours) Wrote discussion section 3.1 and helped write 3.2 (1 hour)	Wrote discussion (1 hour) Adjusted Scenario 5 code and graphs (2 hours) Wrote Conclusion (1 hour)	Wrote scenario 5 discussion (1 hour)	Completed Scenario 4 MATLAB code and graph (2 hour) Wrote results and discussion section for scenario 4 (2 hour)	Wrote scenario 3 discussion (2 hours)

				Wrote hand calculation in appendix A (30 min)	
14/04/23	Edited all sections And assisted with exclusive summary (5 hours total)	Edited and formatted references (2 hours)		Helped write executive summary and conclusion. (2 hour)	

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Cairo Cristante	
Anastasia Dimov	
Miranda Su	*Miranda Su*
John Larsen	

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Professor Daniela Galatro *et al.* 2023. *CHE210/222 Integrated Project (Winter 2023)*. Available at: https://q.utoronto.ca/courses/289542/files/24477548?module_item_id=4454374 (Accessed: 20 March 2023).

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