1. Introduction
Lithium-Ion Batteries (LIBs) are used in various contexts, from phone batteries to electric vehicles. However, due to their rechargeable nature, these batteries tend to degrade in performance over time due to extrinsic stress factors such as temperature or load and intrinsic battery characteristics leading to battery aging (Galatro *et al.*, 2020). Battery aging is characterized by Solid Electrolyte Interface (SEI) growth and decomposition mechanisms driven by a change in temperature, leading to an increased risk of aging due to thermal runaway. It is for this reason that VoltaEV has tasked the group with calculating the self-heating rate that leads to mesocarbon microbeads (MCMB) thermal runaway in electrolytes of (LIBs) using the model described by Richard et al in the Journal of The Electrochemical Society (Richard and Dahn, 1999a, 1999b). This report will outline a brief background on how LIBs function and overheat, the experimental procedure for discovering the LIB's self-heating phenomena, and the steps in which a model was developed to describe this phenomenon and conclude with preliminary results of modelling self-heating profile for different reaction orders.

2. Background (Galatro *et al.*, 2020)
In a LIB, lithium ions (Li+) are stored within the cell and travel internally between the positively and negatively charged ends of a cell, respectively known as the cathode and anode. The anode is usually made of graphite, while the cathode of a metal oxide like lithium cobalt oxide. In between the cathode and anode, the lithium-ion cell contains an electrolyte and a separator within it. The electrolyte is a liquid or gel that conducts electricity, and it is typically a lithium salt dissolved in a solvent.

During discharge, lithium ions travel from the anode, through the electrolyte, to the cathode, which creates a current. When the battery is recharged, the direction of the flow of the ions is reversed, with lithium ions moving from the cathode back to the anode. When lithium ions reach the electrode, the ions are quickly integrated into the electrode material.

During charge or discharge, self-heating occurs as heat is generated inside the battery from two sources: joule heating and electrochemical reactions. Electrochemical reactions generate heat due to enthalpy changes and electrochemical polarization. The cell's internal resistance is from electrodes and electrolytes, which are essentially conductors with low resistivity. Joule heating or resistive heating is the main source of heat generation. It describes the process where heat is generated as ions flow through internal resistance. The generated heat is usually transferred through conduction from the electrode to the electrolyte. The heat is then dissipated into the surrounding environment through convection. Heat transfer is necessary, or else the battery overheats, which can lead to a thermal runaway reaction, triggered when the cell temperature exceeds the critical temperature of materials within the battery. Large amounts of heat are generated rapidly that break down the material exothermically, while the heat cannot escape and dissipate to its surroundings as fast as heat generation. Overheating batteries are most likely a result of overcharging, over-discharging, or physical damage to the battery.

3. Methodology
Before a mathematical model could be developed for the self-heating process of the LIBs, Richard et al performed a calorimetry experiment in which the self-heating process was tested. This section outlines the experimental methodology and the parameters considered in order to come to this conclusion.

3.1 Accelerating Rate Calorimetry (Richard and Dahn, 1999a)
Richard et al used an Accelerating Rate Calorimeter (ARC) due to its adiabatic nature in order to observe the work done solely by the analyte sample (Richard and Dahn, 1999a). The experimental setup for the ARC is shown in Figure 1. The ARC is programmed to increase the temperature to some initial temperature T, which then increases the temperature of the sample through methods of convection and conduction. The temperature of the sample is measured by an attached thermocouple. When the sample is at the desired temperature T, the walls of the ARC are maintained at T-ε, such that ε is very small in order for the heat transfer

from the sample to the walls to be negligible, simulating near adiabatic conditions. Samples of Li-containing MCMB with electrolyte compositions of EC:DEC (33:67) in 1 M $LiPF_6$, EC:DEC (50:50) in 1 M $LiPF_6$, and EC:DEC (50:50) and 1 M $LiBF_4$ were then analyzed in coin batteries made by Richard et al. The coin batteries had their voltage profiles assessed in order to confirm they were consistent graphitic material. The discharge rates and voltages were determined to ensure the specific amounts of intercalated Li and keep it consistent among the samples (00 V - 376 mAh/g, 0.089 V - 231 mAh/g, 0.127 V - 121 mAh/g).

Both before ARC and after ARC, powder recovered from the cells was used to measure the 002 graphite X-ray diffraction peak position with a similar process being used for the MCMB. The difference in these peaks is then used to measure the amount of Li consumed in the experiment.
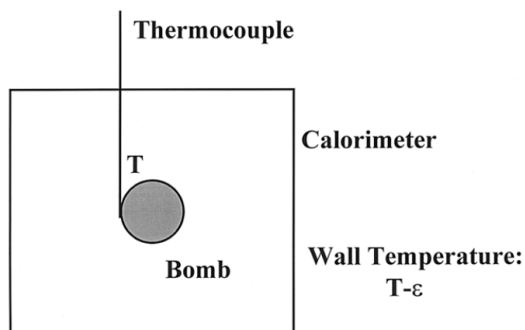

Figure 1: Accelerating Rate Calorimetry experimental Set up (Richard and Dahn, 1999a)

Experiment 1:
Samples were prepared in the ARC and then heated to an initial temperature of 40ºC. Once at equilibrium, the ARC would search for a temperature increase of 0.02ºC/min minimum to determine the presence of the exothermic reaction. If no temperature increase were detected, the ARC would increase by 10ºC at 5ºC/min, then again equilibrate and search for the minimum temperature increase. This would continue until the ARC reached an environment temperature of 220ºC or an exothermic temperature increase was detected.

Experiment 2:
Samples were heated to temperatures of 100ºC, 115ºC and 130ºC at which self-heating is known to occur.

4. Workflow
This section outlines the results of the calorimetric experiments performed by Richard et al and how these results led to the derivation of a mathematical model for the LIBs self-heating process regarding the SEI formation and temperature. The purpose of this generalized model is to analyze the effects of different parameters on the system without having to perform subsequent experiments.

4.1 Calorimetry Results (Richard and Dahn, 1999a)
First samples containing $LiPF_6$ EC:DEC(33:67) were measured in the ARC to determine if fresh MCMB is a significant factor in the heat production in the self-healing process. When comparing a sample containing 300mg of electrolyte vs a sample of 400mg of MCMB in 400mg of electrolyte. The results showed that MCMB does not react with the electrolyte when the temperature is below 190ºC, meaning that below this temperature, heat is produced due to the decomposition of the electrolyte.

The $LiPF_6$ EC:DEC(33:67), when run at the specified voltages, showed that the samples with more intercalated Li require less time to reach the endpoint than samples with the least intercalated Li. (Figure 2). In addition, the self-heating rate profile of these samples reaches a peak at roughly 95ºC, independent of the intercalated Li, which is indicative of a reaction depleting its reactants, causing the reaction rate and, conversely, the rate of

heat generation to decrease (Figure 3). Heat generation due to electrolyte decomposition was not detected until 190ºC, signifying that there is at least one other process that causes the temperature change between 105ºC and 190ºC. This region's heating was determined to be dependent on the amount of intercalated Li through the X-ray diffusion measurements taken before and after the ARC was run. Figure 4 shows a clear difference in the diffraction peak position indicating the removal of Li.
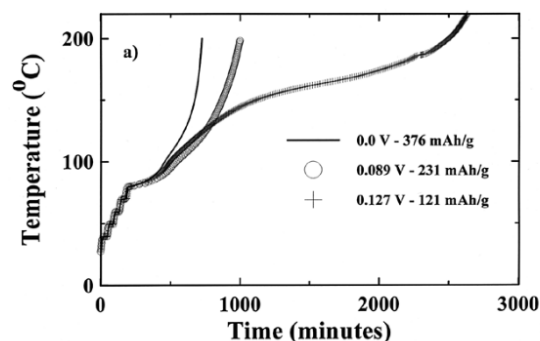

Figure 2: LiPF$_6$ EC:DEC(33:67) Results for Temperature vs Time at voltage compositions Li0.8C6 (0.0 V), Li0.5C6 (0.089 V), and Li0.25C6 (0.127 V) (Richard and Dahn, 1999a)
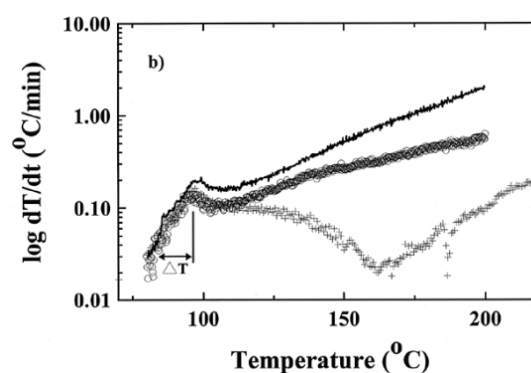
Figure 3: Self-Heating Rate profile for LiPF$_6$ *EC:DEC(33:67) Samples at different voltagcompositions Li0.8C6 (0.0 V), Li0.5C6 (0.089 V), and Li0.25C6 (0.127 V) (Richard and Dahn, 1999a)*
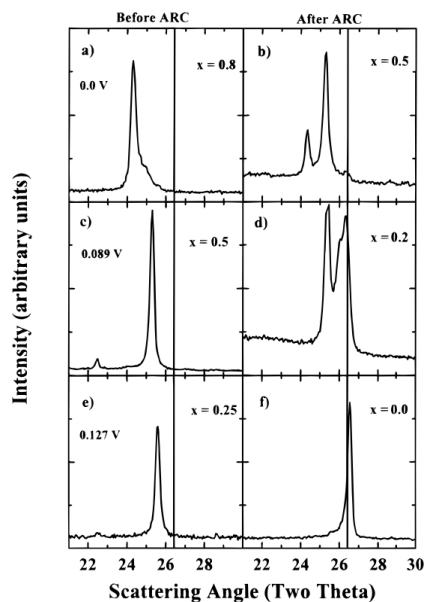

Figure 4: X-Ray diffraction profiles before and after ARC of the different voltage compositions Li0.8C6 (0.0 V), Li0.5C6 (0.089 V), and Li0.25C6 (0.127 V) (Richard and Dahn, 1999a)

Since the peaks of the self-heating rate profiles were determined to be independent of the intercalated Li content leading up to this region, and since this region is relatively consistent with all of the samples, the self-heating portion must be caused by a reactant with the same concentrations within all samples. The reagent was determined to be the SEI layer due to the carbon being inert and electrolyte decomposition not occurring until 190ºC. The metastable components of the SEI layer composed of Lithium-alkyl carbonates (LiAC) are not thermally stable at high temperatures and in the presence of Li atoms. Therefore the experiment concluded that the decomposition reactions of metastable SEI layer components into stable SEI components are the cause of the LIB self-heating up to the peak. The peak in the self-heating profile is then the result of the depletion of

the metastable SEI components. Since the self-heating region after the peak is dependent on Li content, it is determined that the Li content is consumed through a reaction with the solvent resulting in the production of new SEI (Figure 5). This process continues until all the Li is consumed or the SEI layer is too thick, as shown in Figure 4 for the 0.127 V sample where the temperate rate drops at 165ºC, signifying the Li has been depleted. This means the consistent increase after 105ºC causes the thermal runaway to be caused by the consistent formation of the SEI layer.
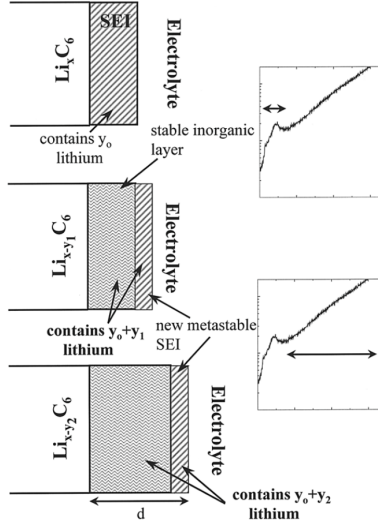

Figure 5: Schematic showing the corresponding Li consumption for forming the SEI layer. (Richard and Dahn, 1999a)

4.2 Derivation of Self-Heating Rate Profile Model (Richard and Dahn, 1999b)

As discussed in the results calorimetry results section, the self-heating rate is dependent on first, the decomposition of metastable SEI into stable SEI (Reaction 1), and the reaction between intercalated Li and the solvent resulting in a new layer of SEI forming (Reaction 2). As such, the rate of temperature increase is determined by

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{h_1}{C}\left|\frac{\mathrm{d}x_\mathrm{f}}{\mathrm{d}t}\right| + \frac{h_2}{C}\left|\frac{\mathrm{d}x_\mathrm{i}}{\mathrm{d}t}\right|$$

(1)

Where h_1 and h_2 is the heat generated from reactions 1 & 2 in J/g, x_f is the unitless amount of metastable SEI and x_i is the unitless amount of intercalated Li. The h/C values represent the temperature increase from the consumption of all reactants. The rate of change of the reagents for both of the reactions can be represented by an nth-order reaction rate expression.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -kx^n$$

(2)

Where k is the rate constant of the reaction given by the Arrhenius equation.

$$k = Ae^{\frac{-E}{k_\mathrm{B}T}}$$

(3)

Where A is the frequency factor, E is the activation energy for the reaction, k_B is the Boltzmann's constant, and T is the temperature. Since the SEI layer is relatively stable at lower temperatures, the decomposition requires higher activation energies for its reaction. This being $E = 1.4$ eV. For reaction 2, the new SEI layer forms over the surface of the electrode, causing it to thicken. This means that the rate at which the SEI layer thickens can be described inversely by the rate at which the intercalated Li is consumed in the reaction and the specific surface area.

$$\frac{dz}{dx_i} = \frac{a_0}{a}$$

<div align="right">(4)</div>

Where a_0 is a constant of proportionality, a is the specific surface area, and dz is the change in the SEI thickness. The increase in the SEI layer affects the effectiveness of the Li to transport through the layer, which in turn inhibits Reaction 2 and the consumption of the intercalated Li. Richard et al have determined the functional forms for this relationship to be linear (z_0/z) or exponential (e^{-z/z_0}). With the effect of the transport and SEI thickness on the change in Li expressed below.

$$\frac{dx_i}{dt} = -k_2 x_i^m \frac{a}{a_0} \left\{ \frac{z_0}{z} \text{ or } e^{\frac{-z}{z_0}} \right\}$$

<div align="right">(5)</div>

Combining equations (5) and equations (2) and (3) for reaction 1 in equation (1) yields the models or the temperature rate of change.

$$\frac{dT}{dt} = \frac{h_1}{C} A_1 x_f^n e^{\frac{-E_1}{k_B T}} + \frac{h_2}{C} A_2 x_i^n e^{\frac{-E_2}{k_B T}} \frac{a}{a_0} \frac{z_0}{z}$$

or

$$\frac{dT}{dt} = \frac{h_1}{C} A_1 x_f^n e^{\frac{-E_1}{k_B T}} + \frac{h_2}{C} A_2 x_i^n e^{\frac{-E_2}{k_B T}} \frac{a}{a_0} e^{\frac{-z}{z_0}}$$

Where the reaction rate of Reaction 2, m, is assumed to be 1 for simplicity.

5. Rate Constant Modelling Results (Scenario 1)

In this section, the self-heating rate of lithium-ion batteries was estimated using set values and parameters. The parameters used for this scenario are as follows: h_1/C = 150°C, E_1 = 1.4 eV, A_1 = 1x10^{17} min^{-1}, and x_{fo}= 0.10. A model was created to find the change in self-heating in relation to temperature. To model this, equations 1 and 7b were used from the Richard et al second paper on ARC (Richard and Dahn, 1999b).
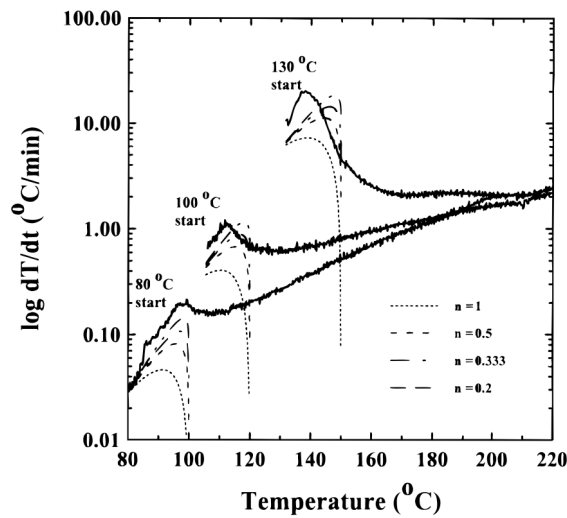

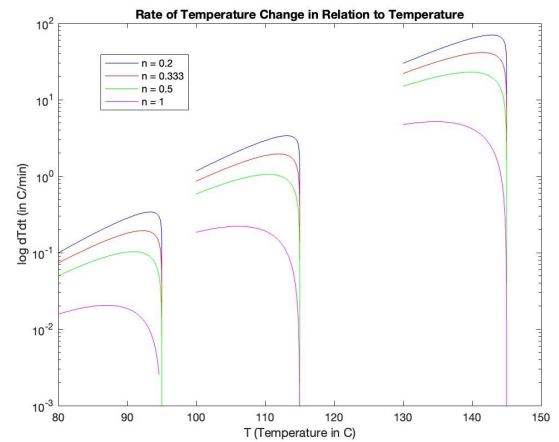Figure 6: Rate of Temperature Change Measured Experimentally (Richard and Dahn 1999b)

Figure 7: Scenario 1 - Rate of Temperature Change with varying reaction orders

As seen in Figure 6, 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.

With different electrolyte formulations, different variables are changed. If the initial metastable SEI content is higher, then x_{fo} increases, thus the self-heating rate will also increase. Other variables changed are the surface area (which affects reaction order, n), the electrolyte used, and the initial heating temperature of the sample. If the surface area is increased, then the reaction order (n) will increase, causing the self-heating rate to decrease, assuming x_{fo} is 0.10. As shown in Figure 6 and Figure 7, if the initial heating temperature is increased, then the self-heating rate also increases. Based on the findings of Richard and Dahn, in electrolytes ratios of EC:DEC(50:50), there is not as much metastable SEI content initially ($x_{fo} \approx 0$), leading to a reaction that does not give a noticeable peak compared to an EC:DEC ratio of 33:67. This means it can be assumed that the self-heating rate in the 50:50 ratio of EC:DEC is effectively zero because the reaction occurs quickly due to the lack of initial reagent (x_{fo}). While both Figure 6 and Figure 7 look almost identical, Figure 6 contains a line that continues to increase despite reaching a peak self-heating rate. This occurs due to the experimental data accounting for the stable layer denoted in the second half of equation 7b (Richard and Dahn, 1999b).

6. Conclusion - Daniel
In conclusion, Richard et al's research shed light on critical factors that contribute to the self-heating process in lithium-ion batteries. The presence of intercalated Li is critical in determining self-heating rate profiles, and the peak in the self-heating profile results from the decomposition of the metastable SEI layer into stable SEI components. After 105°C, the continuous formation of the SEI layer causes a temperature increase, consuming Li content via solvent reaction. These findings have important implications for improving the safety and performance of lithium-ion batteries. Furthermore, the reaction order modelling results revealed that initial lithium content, surface area, the electrolyte used, and initial heating temperature all have an effect on the self-heating rate. Reducing the reaction order increases the starting and peak temperature rates. Furthermore, raising the initial heating temperature raises the self-heating rate. Finally, the type of electrolyte used affects the initial content of metastable SEI, causing the 50:50 EC:DEC ratios to not exhibit a self-heating profile with a peak, unlike the 33:67 EC:DEC ratio.

References

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