Simulation Modelling of Thermal Runaway Propagation in Li Ion Batteries

BY

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ABSTRACT

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Li Ion batteries are highly engineered systems which have become part and parcel of our daily lives. Safety of these systems has been in jeopardy ever since they were created. Mechanical abuse, shot circuit, overcharging or unfavorable working conditions can lead to catastrophic repercussions which might destroy complete battery pack. Previous works have investigated this problem, but many important aspects of design characteristics were left folded.

This work not only investigates behavior of a single cell under adverse conditions but also lays emphasis on important factors such as thermal conductivity of the medium and cell gaps in a pack of multiple cells.

This work found its motivation from the severe accidents in the history which have not only caused damage to the system but have also endangered lives.

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Chapter 1

INTRODUCTION

As compared to predecessor technologies Li ion cells offer outstanding mechanism for energy storage and conversion with higher power density and better energy storage [1-4]. Even Small temperature rise while operating can be alarming when it comes to safety and reliability as the performance of these batteries is highly temperature sensitive. Exothermic reactions inside a cell include degradation of separator, reaction between active materials present in anode and electrolyte, reaction between positive active material and electrolyte, electrolyte decomposition. As, the cell temperature rises as a result of these processes heat generation rate is increased to a great extent and other exothermic reactions inside the cell also add to it. This set of chain reactions continues till temperature becomes increasingly large and uncontrollable which pushes cell into catastrophic thermal run-away conditions.

In order to investigate this phenomenon various techniques have been used which are based on Arrhenius kinetics. Various processes in this case require reaction rate parameters which are determined experimentally. For these experiments heat generation rates have been measured in both nominal and thermal runaway conditions. At cell level there are many ways to introduce thermal runaway for

example, by wrapping a krypton heater, nail penetration and internal short circuit etc.

Parameter	Description	Value
A_{sei}	Frequency factor (s^{-1})	1.667×10^{15}
A_{ne}		2.5×10^{13}
A_{pe}		6.667×10^{13}
A_e		5.14×10^{25}
$E_{a,sei}$	Activation energy ($J\ mol^{-1}$)	1.3508×10^5
$E_{a,ne}$		1.3508×10^5
$E_{a,pe}$		1.396×10^5
$E_{a,e}$		2.74×10^5
H_{sei}	Reaction heat ($J\ kg^{-1}$)	2.57×10^5
H_{ne}		1.714×10^6
H_{pe}		3.14×10^5
H_e		1.55×10^5
c_{sei0}	Initial dimensionless content	0.15
c_{ne0}		0.75
α_0		0.04
c_{e0}		1
m_{sei}	Reaction order	1
m_{ne}		1
m_{pe1}		1
m_{pe2}		1
m_e		1
t_{sei0}	Initial SEI thickness	0.033
W_c	Material content ($kg\ m^{-3}$)	1.39×10^3
W_p		1.3×10^3
W_e		5.0×10^2

Fig1. Reaction Parameters in Thermal Runaway

C.F. Lopez, J.A. Jeevarajan, P.P. Mukherjee, J. Electrochem. Soc. 162 (2015) A2163.

Reaction	Heat Generation	Rate of Reaction	Starting Temperature
SEI Decomposition	$Q_{sei} = H_{sei} W_c R_{sei}$	$R_{sei} = A_{sei} \exp\left(-\frac{E_{a,sei}}{R_u T}\right) c_{sei}^{m,sei}; \quad \frac{dc_{sei}}{dt} = -R_{sei}$	90-120 °C
Negative-Solvent Reaction	$Q_{ne} = H_{ne} W_c R_{ne}$	$R_{ne} = A_{ne}\left(-\frac{t_{sei}}{t_{sei,ref}}\right) \exp\left(-\frac{E_{a,ne}}{R_u T}\right) c_{ne}^{m,ne}; \quad \frac{dc_{ne}}{dt} = -R_{ne}$	120 °C
Positive-Solvent Reaction	$Q_{pe} = H_{pe} W_p R_{pe}$	$R_{pe} = A_{pe} \alpha^{m,pe} (1-\alpha)^{m,pe} \exp\left(-\frac{E_{a,pe}}{R_u T}\right); \quad \frac{d\alpha}{dt} = R_{pe}$	170 °C
Electrolyte Decomposition	$Q_e = H_e W_e R_e$	$R_e = A_e \exp\left(-\frac{E_{a,e}}{R_u T}\right) c_e^{m,e}; \quad \frac{dc_e}{dt} = -R_e$	200 °C

Fig2. Arrhenius equations for thermal runaway modelling

Parhizi, M., Ahmed, M.B., Jain, A., 'Determination of the core temperature of a Li-ion cell during thermal runaway,' *J. Power Sources*, 370, pp. 27-35, 2017.

This work concentrates on not only single cell but also on a battery pack as a whole. In other words there are many surrounding factors that can also force a cell into thermal runaway. For example, in a battery pack thermal conductivity of the medium between cells is as important as any other cooling technique. Greater thermal conductivity reduces the risk of onset in trigger cell but can easily cause propagation in neighboring cells. Thus determining an optimum range is very important in designing analysis as lower thermal conductivity can make environment so insulating for a cell that there is no place for heat to escape and can cause propagation even in normal working conditions. Small cell gaps can also have similar repercussions on the battery pack therefore a vital combination of cell gap and thermal conductivity is needed for adequate performance of a battery pack.

However, this combination can vary based on heating and working conditions of a battery pack.

Chapter 2

Simulation Set Up

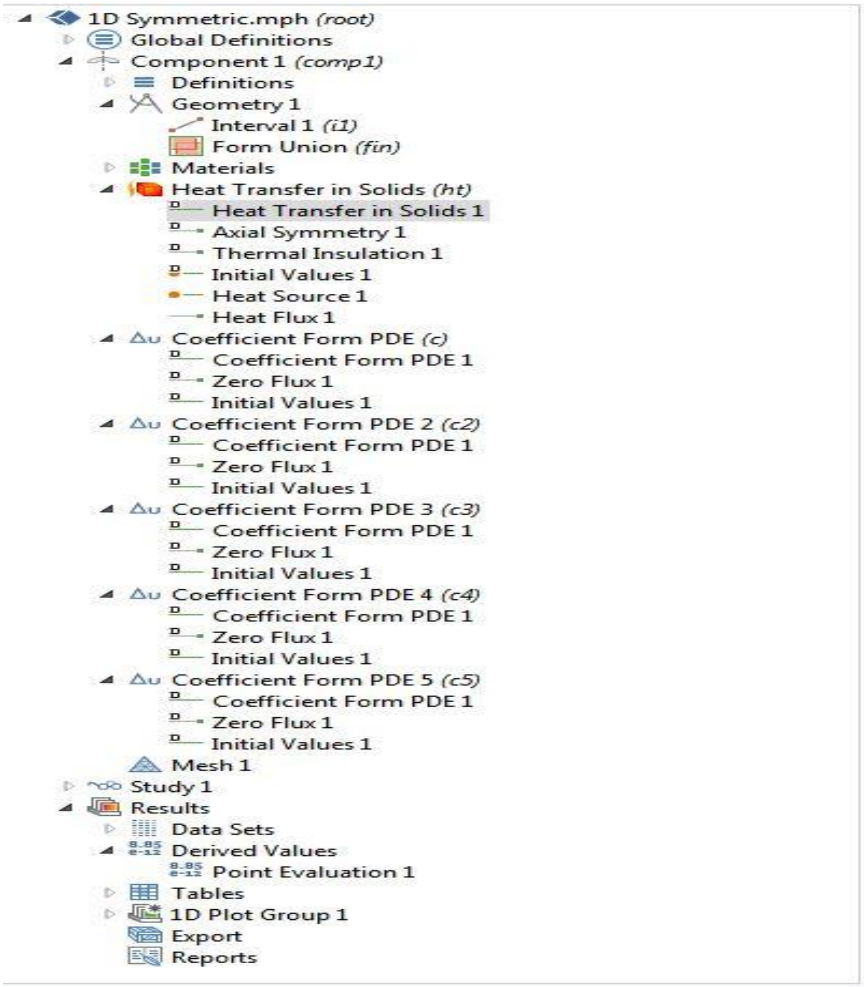

Fig3. Simulation set up

Comsol provides graphical user interface to solve multiple FEM problems. The software is equipped with many tools which are very helpful in capturing those

phenomena which are not easily captured in other FEA packages. First step in solving any problem in this software is to select the module. Some of the modules offered by comsol include 1D, 1D Symmetric, 2D, 2D Symmetric, 3D and 3D Symmetric. After the module has been selected we define different parameters which are used in solving Arrhenius electrochemical exothermic reactions.

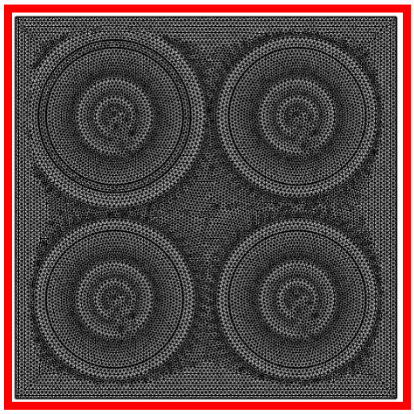

Fig4. Cell Geometry

After all important parameters have been defined next step in comsol is to create geometry. In order to do so comsol provides various features which are capable of producing highly complex shapes and structures.

Once geometry has been created different materials are assigned to the geometry according to simulation set up. For example, in all simulations set ups the cells in the geometry were assigned a material named “battery mat” which exactly resembles the thermo electrical properties of a cell. The material for medium differs in different simulation cases depending upon the working conditions.

Heat transfer equations are then induced in the form of partial differential equations with coefficients. These time dependent coefficients include concentration of solid electrolyte interface, concentration of active material in negative electrode, concentration of active material in positive electrode and concentration of electrolyte. Major heat source for all simulations is the sum of all four Arrhenius equations and secondary source is the heater wrapped around trigger cell. Major heat source is applied to all four cells whereas the secondary heating source is applied to only trigger cell. Convective heat transfer to the boundaries is also applied in the form of heat flux to account for natural convection.

Once all heating conditions have been applied the next step is meshing. Comsol offers wide variety of meshing techniques as per requirements such as inflation, manual size reduction of elements, changing number of elements, mapped meshing techniques and different element types. .i.e. 2 D elements and 3D elements.

The most important step in solving any problem in comsol is choosing proper solver techniques. This software offers coupled and segregated approaches for converging a solution. Other important factors include number of iterations and refinements. During all these settings one can also change the smallest time step that a solver can take, this is particularly important when there is extremely high gradient and the calculations at a particular timestep fail to fit in tolerance limit window.

Based on requirements one can also set both relative and absolute tolerances in order to get desired results with maximum possible accuracy.

Getting a correct combination of all solver settings not only helps in convergence but can also lower the simulation time to a great extent. Thus it is always desirable to get most accurate solution in least possible time.

Chapter 3

Simulation Geometries

Simulations were carried out for carious cell geometries and under various ambient conditions, but before publishing these results it was equally important to validate simulation code.

3.1. Validation

The code was implemented on 1 D symmetric cell model which considered cell as semi-infinite cylinder symmetric about central y axis. The results were then compared to a well-established Matlab code which depicted similar working conditions.

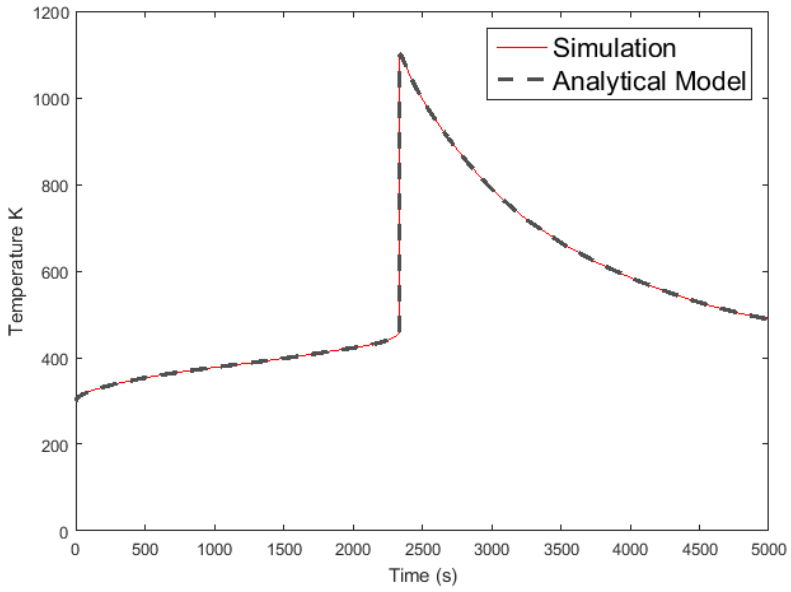

Fig.5 Temperature Validation

After a good agreement between two models it was important to carry out grid independence test in order to make these simulations more time efficient.

For the same, three mesh qualities were chosen i.e. extremely fine mesh, normal mesh and coarse mesh.

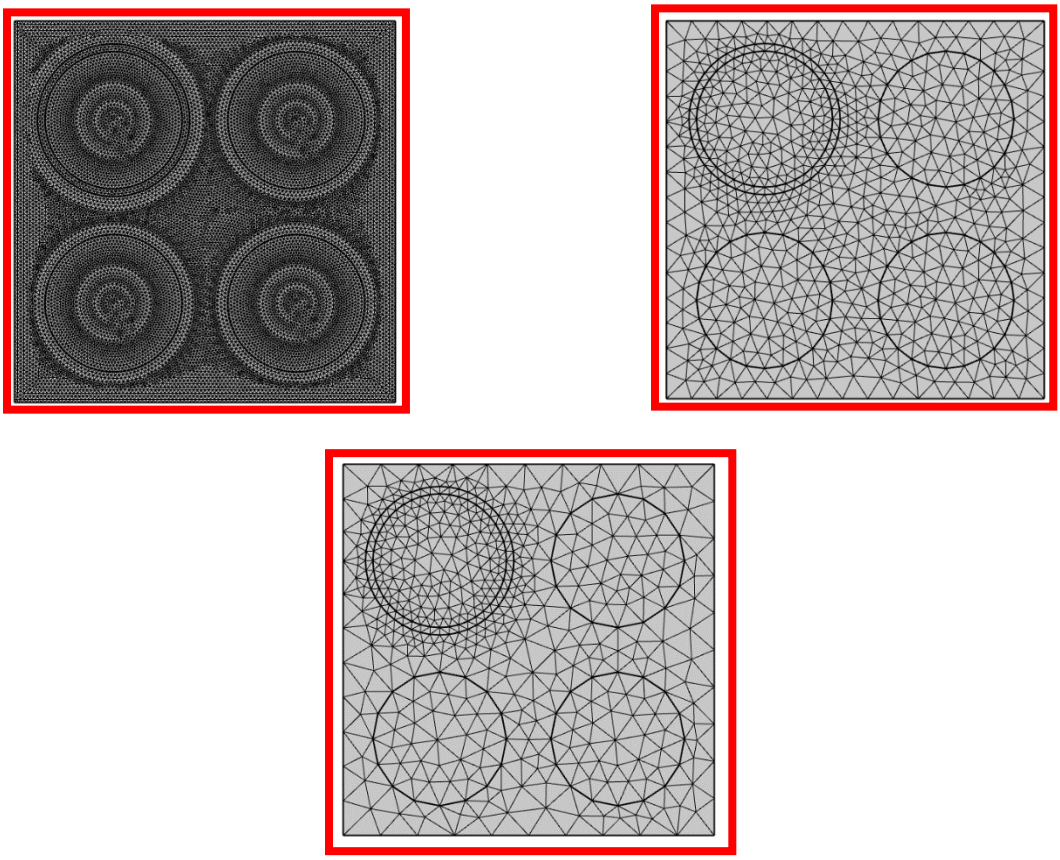

Fig 6a. Extremely fine; 6b. Normal; 6c. Coarse

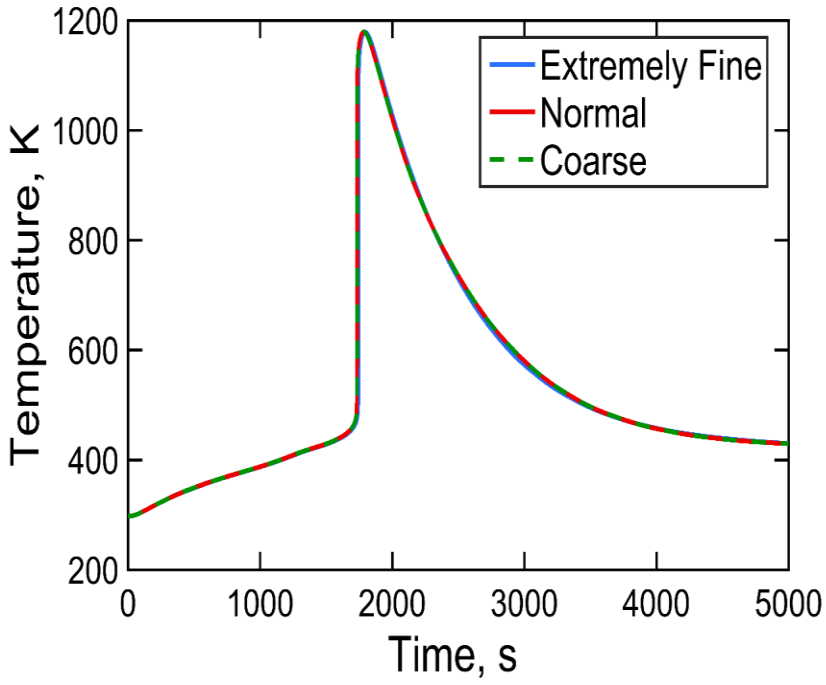

Fig7. Grid independence

Temperature results of grid independence test showed that there was not much difference between temperature profiles obtained from three mesh qualities, but simulation time reduced significantly.

3.2. Quarter Cell Simulations

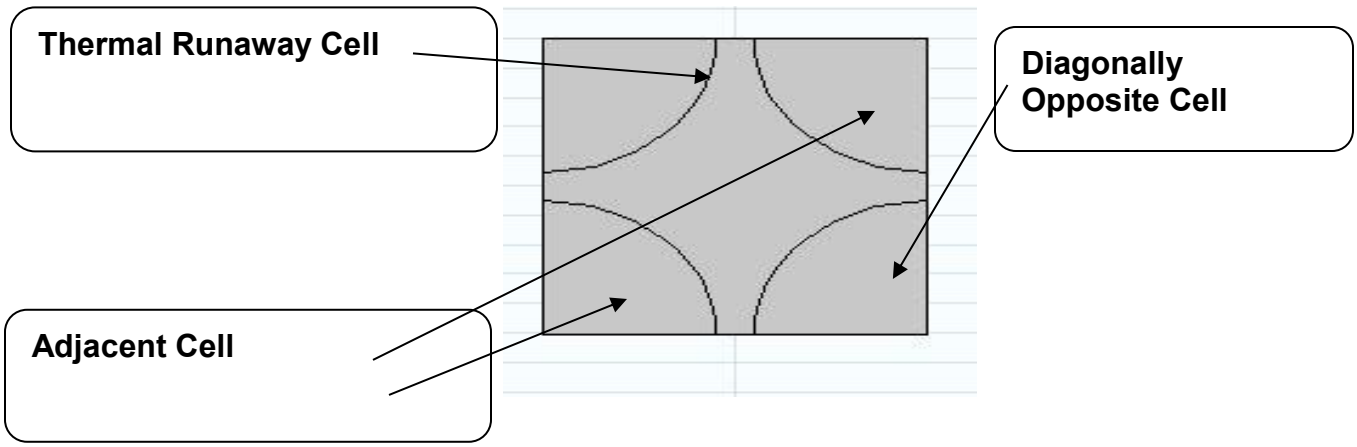

Fig8. Schematic of quarter cell geometry

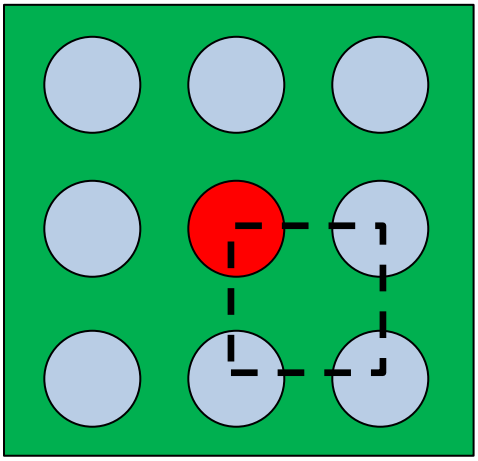

Fig9. Cell matrix

Quarter cell geometry is a symmetric cut out from a cell matrix which resembles its exact characteristics. This is done primarily to reduce computational time and avoid convergence issues. The only difference that segregates these two

geometrical setups is the boundary conditions i.e. all external boundaries are adiabatic in nature whereas in a cell matrix these boundaries posses convective heat transfer characteristics due to natural cooling from surroundings.

3.3. 2x1 Cell Geometry

Since quarter cell geometry was not able to replicate actual cell matrix in order to determine optimum cell gap and thermal conductivity of the medium a 2x1 model was created in order to get a better glimpse of working conditions of the battery pack. Although this model was not able to account for various phenomena like, radiation and venting but it was quite successful in defining the trends of cell behaviours in various working conditions.

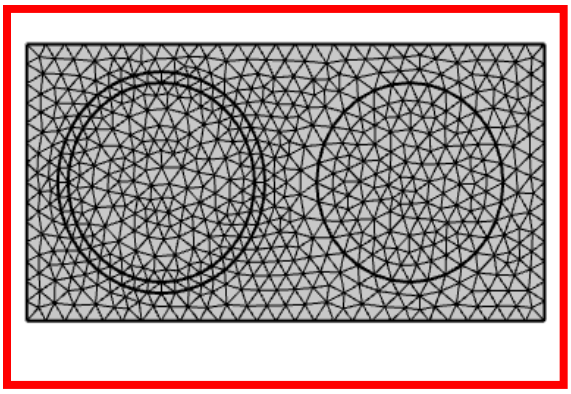

Fig10. 2x1 Cell Geometry

The passive heat source in this geometry is a heater wrapped around cell 1 which can be easily seen in Fig10. Both cylindrical cells are a replica of 18650 cell which

can be abbreviated as 18 mm being the diameter of the cylinder and 65 mm as the height. The cells are enclosed in a rectangular box which is being cooled by natural convection from surroundings.

3.4. Simulation Challenges

During thermal runaway propagation temperature gradient is so large even for a microsecond that it is very difficult for a nonlinear solver to capture this phenomenon. In order to solve this problem three factors play very important role i.e. tolerance, mesh quality and iterations. An optimum combination of these factors is essential as excessive iterations and very dense mesh will add to the simulation time and extremely less number of iterations might result in convergence issues.

Apart from these three factors selection of solver and its operational settings is equally important. Comsol offers two kinds of approaches for solving non linear problems viz. segregated approach and coupled approach. In this work segregated approach has been used as it is highly recommended for heat transfer problems, from the list of non linear solvers which includes MUMPS, and Pardiso, the latter is used as it works best with segregated approach and is more time efficient.

Selection of damping factor is important as it helps to determine how small steps a solver can take. This not only helps in proper approximation but also accounts for vital timesteps during simulations.

Having tighter tolerances during a solution results in very high accuracy but it also adds to convergence difficulties faced by solvers. On the other hand large tolerances limits might help in better convergence but will surely increase degree of errors in the final results.

Thus while solving any nonlinear problem in comsol both linear and non linear solver work together to provide results with best possible accuracy.

Chapter 4

Results

Main aim of this work was to determine optimum limits of cell gap and thermal conductivity of the medium in order to prevent propagation and onset of thermal run away in a battery pack. In order to do so, many simulations have been carried out with different cell gaps and mediums.

4.1. Predictive Capabilities

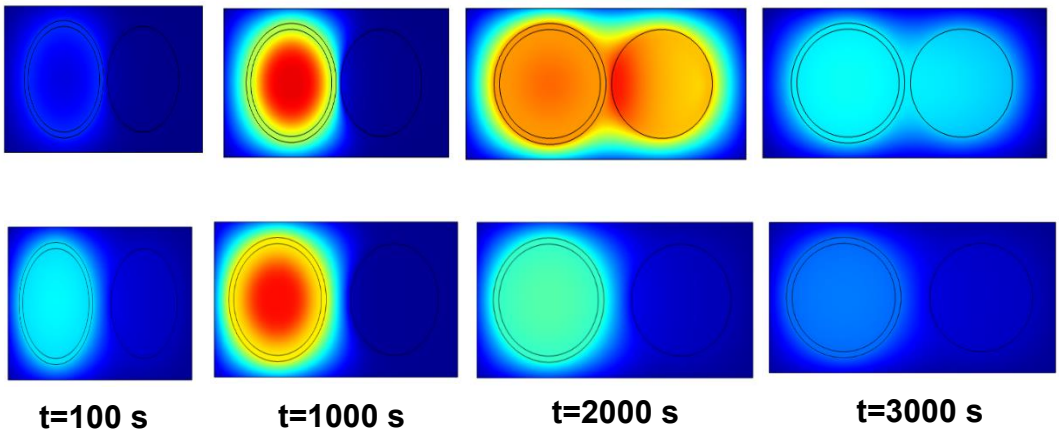

Fig 11. Colour Plots for 2x1

As can be seen in Fig 11, the model beautifully captures thermal runaway propagation and onset for two different cases. In the first case i.e. colour plots in

the first line the gaps between cells is 1 mm. In this case we can see propagation in both the cells whereas in the second case when cell gap in 4mm there is no propagation in the adjacent cell. A point worth noting is k=0.03 W/mK in both cases and heating conditions are also same.

4.2. Lower Limit For Filler Thermal Conductivity

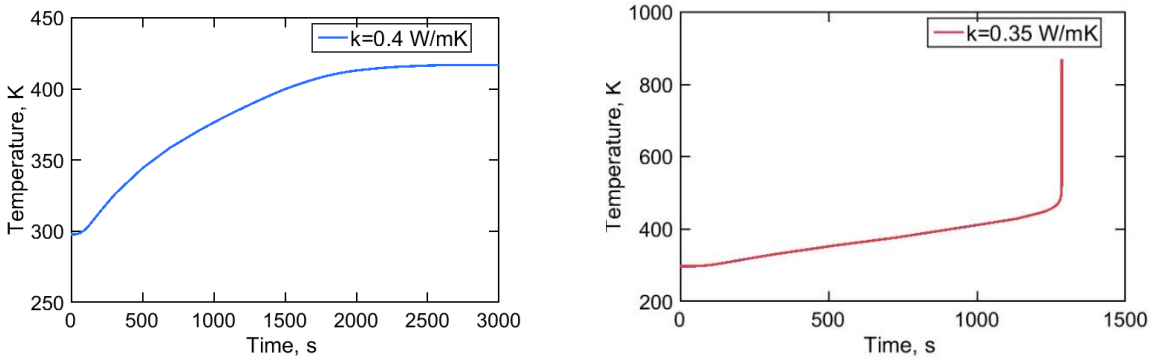

Fig12. Lower Limit For Thermal Conductivity

Above figures show results from a set of simulations where heating power was 3.85 MW/m^3. These simulations were carried out on a single 18650 model in order to determine lower limit for thermal conductivity. It can be seen from the graphs that k=0.4 W/mK does not cause onset whereas when thermal conductivity is reduced to 0.35 W/mK a thermal runaway onset can be seen in the graph. Thus if thermal conductivity of the medium is reduced from 0.4 w/mK even nominal heating conditions will cause onset which might propagate to other cells in a battery pack.

4.3. Upper Limit For Filler Thermal Conductivity

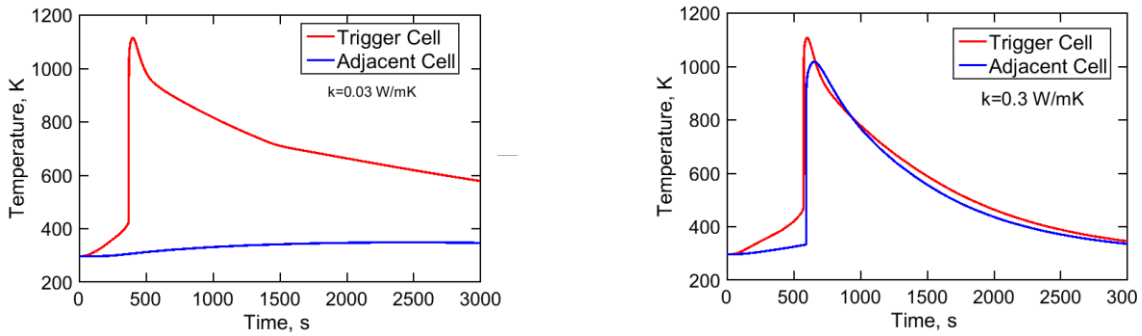

Fig13. Upper Limit For Thermal Conductivity

In this case we can see that in a battery pack of two cells when heating power is 3.85 MW/mK and cell gap is 4mm there is no propagation with k=0.03 W/mK but when thermal conductivity is increased to 0.3 W/mK the adjacent cell also enters thermal runaway. This is because when thermal conductivity is larger heat is transported faster and thus leads to propagation in the adjacent cell.

4.4. Limit for Cell Gap

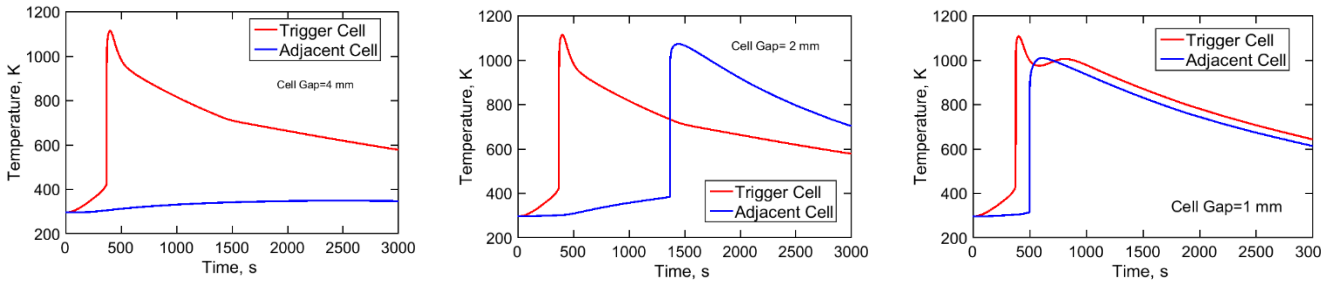

Fig14.Temperature Profiles for different Cell Gaps

In this case battery pack with 3.85 MW/m^3 heating power and with air as the medium between cells was tested with different cell gaps. Results show that when cell gap is 4 mm there is no propagation in the adjacent cell but when gap is reduced to 2 mm we see thermal runaway propagation in the adjacent cell and similar behaviour is depicted when gap is further reduced to 1 mm. Thus for given heating conditions with natural cooling from surroundings 2 mm is the tripping point.

Chapter 5

Conclusion

Many critical insights have been presented by the results shown in the pervious chapter. These results might differ based on different heating and ambient conditions, but trends shown will remain unchanged. Battery pack is highly vulnerable to temperature change, mechanical abuse or shot circuiting, hence it is always desirable to design it such that even if one cell fails or has an onset its effects must not propagate to its adjacent cells.

In order to do so an optimum combination of material with optimum thermal conductivity and cell gap is required, as seen from the results failure to meet any of these characteristics might result in catastrophic ramifications which might destroy whole battery pack.

These simulations do not take into account many thermo chemical processes which might aggravate or prevent thermal runaway in a cell viz. radiation and venting etc. If radiation is taken into account, it will enhance propagation to the adjacent cells whereas venting on the other hand prevents propagation as it removes most of the heat from the cell which has gone into thermal run away. Yet it is still uncertain to decide which factor of the two will dominate.

Chapter 6

Future Work

Future work can be expanded in two domains specifically. First in a battery pack it would be worth finding if position of the trigger cell will have an effect on the response of a battery pack to propagation i.e. it is a hypothesis that if the center cell has an onset it is much likely to propagate to the adjacent cells than if corner cell or cell on the edge has an onset because centre cell is somewhat insulated in a better fashion than corner cells or cells on the edge as there convection on the walls of the battery pack which is capable of removing heat to some extent.

Cooling mechanisms for a battery pack is also an important are to explore. There have been many effective proposals ranging from using a phase change material around a cell to cooling mechanisms for battery pack, but these techniques have not been successful to counter this aberrant behaviour of the cell once it has been abused hence it is worth finding a solution to this enormous problem.

BIOGRAPHY

Dhananjay Received completed his bachelor's in technology from University of Petroleum and Energy Studies Dehradun in Aerospace with specialization in Avionics. He worked for Aerosphere Solutions Inc. for one year as associate research engineer. He started his MS. in Fall 2017 in mechanical engineering and started working with Dr, Ankur Jain from January 2018. His research areas include heat transfer in lithium ion batteries.

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