Voltage Response of a Li-ion Battery Cell using OpenFOAM

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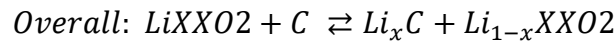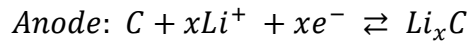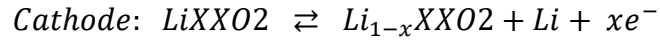Indian Institute of Technology, Bombay

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Abstract

The work involves the study of voltage response of Li ion cell and implementation using OpenFOAM for the evaluation of cell potential. The electrochemical response is implemented using the single particle model by modifications to the laplacianFoam and the ode-solver whereas the thermally coupled response has been modelled using the ode-solver utility.

Preface

Originally we set out to develop a Differential-Algebraic-Equation (DAE) solver where simultaneous solution of partial differential, ordinary differential and algebraic equations could be achieved using OpenFOAM for building an electrochemical battery model. However, with the current knowledge and the experience with OpenFOAM code we had, we were not able to use this package to our advantage and instead resorted to use different independent approaches to implement the single particle model.

Chapter 1 : Introduction

A Li-ion cell consists of an anode (positive electrode) made up of LiXXO$_2$ and the cathode (Negative Electrode) made up of Li$_x$C. The general reactions at the respective electrodes are:

$$Cathode: \ LiXXO2 \ \rightleftarrows \ Li_{1-x}XXO2 + Li + \ xe^-$$

$$Anode: \ C + xLi^+ \ + xe^- \ \rightleftarrows \ Li_xC$$

$$Overall: \ LiXXO2 + C \ \rightleftarrows Li_xC + Li_{1-x}XXO2$$

where XX represents combination of non-ferrous metals like Cobalt, Manganese and Nickel.

The Single Particle Model - The active material in each electrode is taken to be made of spherical intercalated particles.The charge/discharge cycle of Li cell is characterised by transport of Li ions and electrons.

Under the following assumptions single particle model holds good:

- Electrolyte conc. remain constant throughout the cell.

- Current variation with space in the electrolyte is neglected.

- Electrolyte conductivity is significantly large

For the formulation of the single particle model, side reactions are neglected, constant values for volume, transference number and solution phase diffusivity at all times and at all points in the cell are assumed. The Butler-Volmer type kinetic expression for the current density and kinetic potential has been opted.

The SPM model has been solved by (Rajinder Singh (IIT Bombay), n.d.) in his M.Tech Thesis which has further adopted parameters from (Suthar et al., 2015) for the implementation of isothermal SPM model. The non-isothermal model has been adopted from (Guo et al., 2011).

The directions to install and use the solvers and model the behavior are given in the appendix.

Problem Statement and Governing Equations

The Fick's second law of diffusion stated below has to be used to solve for Concentration of Lithium for the intercalated particle representative of cathode and anode. It is a partial differential equation giving us the concentration of Li ion at the surface of particle.

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \right)$$

(1.1)

C = Concentration of Li [mol/m³], D = Diffusivity Constant [m²/sec]

The ratio of this surface concentration to the maximum concentration is the state of charge at the electrode.

$$x_{p,soc} = \frac{C_{p,surf}}{C_{p,max}} \qquad and \qquad x_{n,soc} = \frac{C_{n,surf}}{C_{n,max}}$$

(1.2)

Algebraic empirical relations for the electrode potential as a function of state of charge of the system are evaluated by different research groups which are used here. Further, the kinetic potentials have been obtained from the Butler-Volmer kinetic expression as arc-sin function, which are again a function of the state of charge of the system. The potentials thus obtained are used to evaluate cell voltage at the current timestamp.

This scheme of solving has been used for isothermal conditions, however for non-isothermal systems, a separate model has been solved where the diffusivities and kinetic rate constants are a function of temperature and has been evaluated using Arrhenius type equations at each timestamp given by eqn 1.4 and 1.5.

$$D_{j,new} = D_j \times exp\left(\frac{E_{diff}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right)$$

(1.3)

$$k_{j,new} = k_j \times exp\left(\frac{E_{reac}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right)$$

(1.4)

D_j & k_j are reference diffusivity and kinetic constants, E_{diff} and E_{reac} are Activation Energies.

Further the coupled effect and response of temperature and cell voltage has been further accommodated using a transient heat balance. This equation represented as 1.3, is a partial differential equation but since the way we will be evaluating it at each timestamp it essentially becomes an ordinary differential equation.

$$\rho V C_p \frac{\partial T}{\partial t} = IT \left(\frac{\partial U_p}{\partial t} - \frac{\partial U_n}{\partial t} \right) + I \left(\eta_p - \eta_n + I R_{cell} \right) - hA(T - T_\infty) \qquad (1.5)$$

Note: Different research papers have been used to report different type of equations and therefore some equations have not been mentioned here but are presented in the solution strategies.

Chapter 2 : Solution Strategy –I
(spmBatFoam solver or Modified laplacianFoam)

Two Separate particles have been used with two concentration laplacian equations being solved on each of them representing cathode and anode. The boundary conditions have been manipulated such that variable corresponding to the electrode remains constant and fixed on the other electrode.
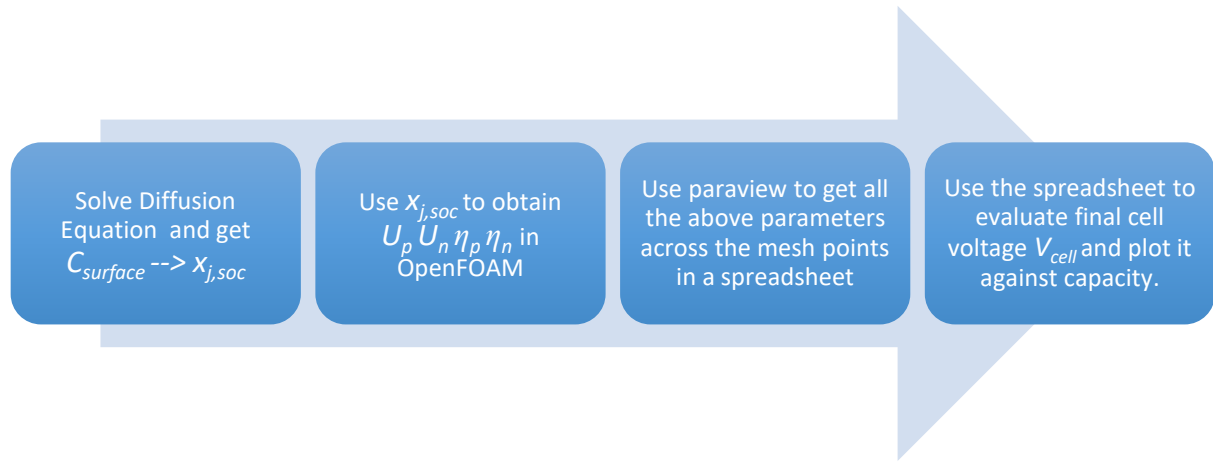
| Solve Diffusion Equation and get $C_{surface}$ --> $x_{j,soc}$ | Use $x_{j,soc}$ to obtain $U_p\,U_n\,\eta_p\,\eta_n$ in OpenFOAM | Use paraview to get all the above parameters across the mesh points in a spreadsheet | Use the spreadsheet to evaluate final cell voltage V_{cell} and plot it against capacity. |

Figure 2-1 : Schematic Flow of solving using modified LaplacianFoam

The boundary conditions are :

$$\frac{\partial C}{\partial r} = 0 \; at \; r = 0 \tag{2.1}$$

$$-D\frac{\partial C}{\partial r} = \pm\frac{I}{naF} \; at \; r = R \tag{2.2}$$

Here, 'I' represents the current density (A/m^2), 'a' represents specific surface area of the electrode which is $3/R \times (\varepsilon)$ for a spherical particle, where ε is the solid fraction. The value of n is 1 here, which is n-factor or the number of electrons involved in the electrochemical reaction.

The model parameters are obtained from this thesis (Rajinder Singh (IIT Bombay), n.d.) and are given in Table 2-1 as follows:

Table 2-1 : Parameters values

Parameter	Symbol	Cathode (j=p)	Anode (j=n)
Particle Radius	R_j [m]	10e-6	10e-6
Maximum Solid Phase Concentration	$C_{j,max}$ [mol/m³]	51540	30550
Solid Phase Li Diffusion Coefficient	D [m²/sec]	3.7e-14	2e-14
Thickness of Electrode	L_j [m]	80e-6	88e-6
Solid fraction/ Porosity	ε	0.62	0.52
Mole fraction of 0% charged battery	$x_{j,0}$	0.95	0.05
Mole fraction of 100% charged battery	$x_{j,100}$	0.5	0.95
Reaction Rate Constant	$k_j \left[\dfrac{m^3}{mol^{0.5}sec}\right]$	2.33e-11	5e-11

Total Cell Area	A [m²]	0.072
Electrolyte Concentration	C_e [mol/m²]	1200
Faraday's Constant	F [C/mol]	96500
Universal Gas Constant	R [J/mol]	8.314
Temperature	T [K]	298

The set of empirical relations used for this model are:

$$U_p = \frac{-4.656 \;+\; 88.669x_{p,soc}^2 \;-\; 401.119x_{p,soc}^4 \;+\; 342.909x_{p,soc}^6 \;-\; 462.471x_{p,soc}^8 \;+\; 433.434x_{p,soc}^{10}}{-1 \;+\; 18.933x_{p,soc}^2 \;-\; 79.532x_{p,soc}^4 \;+\; 37.311x_{p,soc}^6 \;-\; 73.083x_{p,soc}^8 \;+\; 95.96x_{p,soc}^{10}} \tag{2.3}$$

$$\begin{aligned} U_n = \;&-0.057 + 0.53 \times exp(-57x_{n,soc}) - 0.184 \times tanh(20x_{n,soc} - 21) - 0.012 \times tanh(7.57x_{n,soc} - 4.431) \\ &- 0.0304 \times tanh(18.518x_{n,soc} - 3.24) - 0.01 \times tanh(0.255x_{n,soc} - 0.02653) \end{aligned} \tag{2.4}$$

The expressions used for over-kinetic potentials derived from Butler-Volmer kinetics are:

$$\eta_p = 2 \times R \times \left(\frac{T}{F}\right) \times asinh\left(-\frac{I}{2 \times F \times a_p \times L_p \times k_p \times C_{p,max}\sqrt{C_e \times x_{p.soc} \times (1 - x_{p.soc})}}\right) \qquad (2.5)$$

$$\eta_n = 2 \times R \times \left(\frac{T}{F}\right) \times asinh\left(-\frac{I}{2 \times F \times a_n \times L_n \times k_n \times C_{n,max}\sqrt{C_e \times x_{n.soc} \times (1 - x_{n.soc})}}\right) \qquad (2.6)$$

Note : asinh means inverse sine hyperbolic function

These η_p and η_n are formulated as kinetic over-potentials for our model and U_p and U_n are standard electrode potentials which are evaluated using curving fitting from experiments.

Cell Voltage:

$$V_{cell} = U_p - U_n - \eta_p - \eta_n \qquad (2.7)$$

This strategy however, lays more emphasis on post-processing the results. The code will evaluate U_p , U_n , η_n and η_p. However, for cell voltage and plotting we have to resort to the use of spreadsheet software like Libre-Office or Excel.
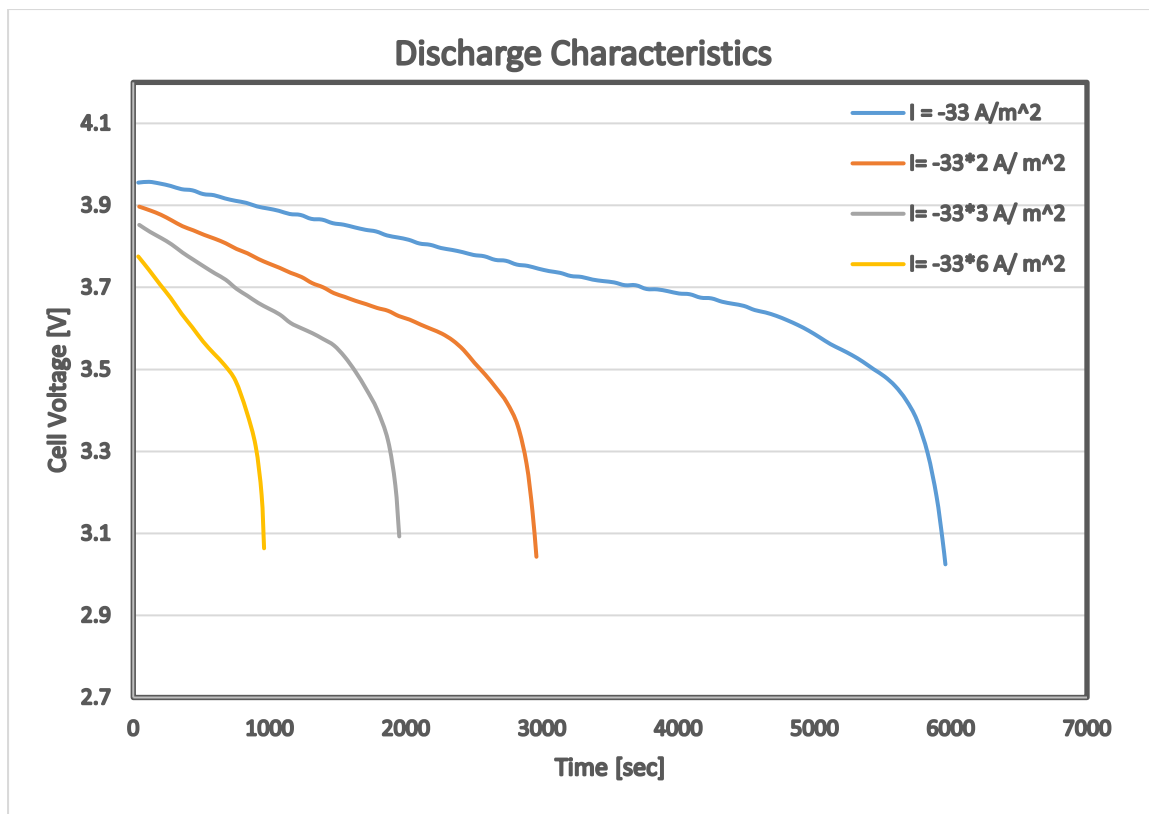
Figure 2-2: Comparison of discharge characteristics obtained at different discharge currents.
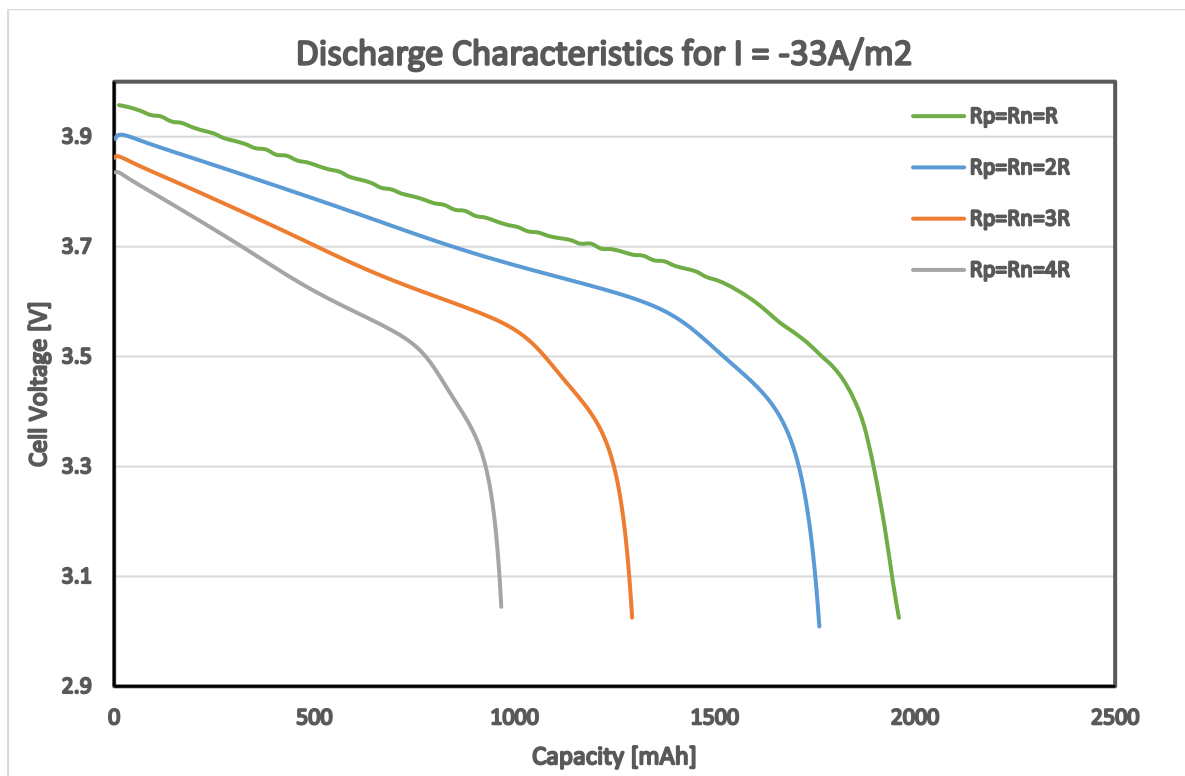

Figure 2-3 : Variation of Cell voltage with different radius of particles at constant discharge current of -33A/m^2.

Chapter 3 Solution Strategy –II (The use of ode-solver utility)

The model described in the previous section has been solved more effectively using the ode-solver utility in OpenFOAM. It reduces the emphasis on post-processing of the result and bypasses the use of paraview to obtain the data.
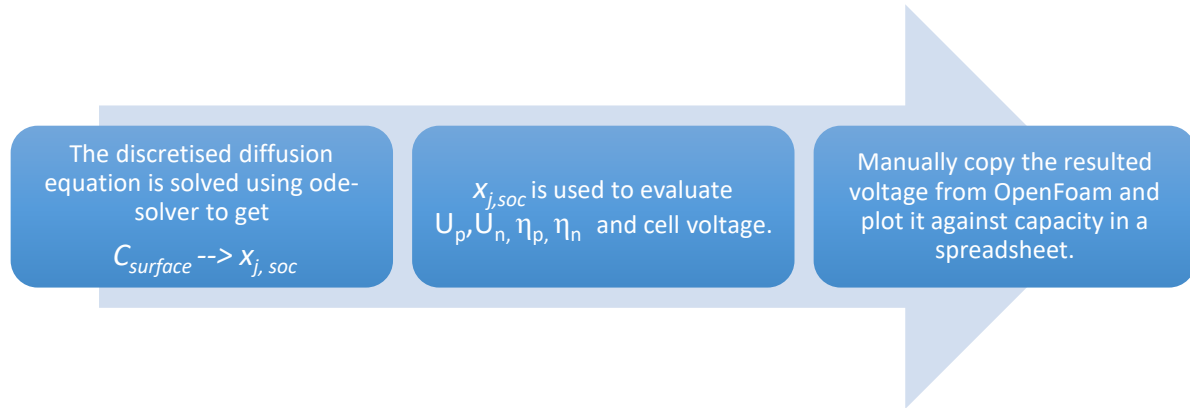
The discretised diffusion equation is solved using ode-solver to get

$C_{surface} \rightarrow x_{j, soc}$

$x_{j,soc}$ is used to evaluate U_p, U_n, η_p, η_n and cell voltage.

Manually copy the resulted voltage from OpenFoam and plot it against capacity in a spreadsheet.

Figure 3-1 : Scheme of solving using ode-utility

In this method, partial differential equation has been discretised over a mesh of 10 points (from *i=1* to *i=n*, where *n* is taken as 10), thereby getting converted into 10 ordinary differential equations at each electrode. This constitutes a set of 20 ode equations.

$$\frac{\partial C}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = \frac{D}{r^2}\left(\frac{2r\partial C}{\partial r} + \frac{r^2\partial^2 C}{\partial r^2}\right) \tag{3.1}$$

$$\frac{\partial C}{\partial t} = D\left(\frac{2\partial C}{r\partial r} + \frac{\partial^2 C}{\partial r^2}\right) \tag{3.2}$$

$$\frac{dC_i}{dt} = D\left(\frac{(C_{i+1} - C_{i-1})}{r_i\Delta r} + \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta r^2}\right) \tag{3.3}$$

$$\frac{dC_i}{dt} = \frac{D}{\left(\frac{R}{n}\right)^2}\left(\frac{(C_{i+1} - C_{i-1})}{i} + C_{i+1} - 2C_i + C_{i-1}\right) \tag{3.4}$$

The convective term and diffusive terms of the equation have been centrally discretised with the order of accuracy being 2. Further incorporating higher order of accuracy can be easily accomplished.

The boundary conditions have been discretised as below:

1. The spatial variation of concentration at the centre of particle is zero

$$\frac{\partial C}{\partial r} = 0 \; at \; r = 0 \tag{3.5}$$

Using forward difference at the centre of particle we get:

$$\frac{-1.5C_0 + 2C_1 - 0.5C_2}{\Delta r} = 0 \; which \; is \; C_0 = \frac{4}{3}C_1 - \frac{1}{3}C_2 \tag{3.6}$$

On substituting this C_0 expression in the first differential equation we get

$$\frac{dC_1}{dt} = \frac{D}{\left(\frac{R}{10}\right)^2}(2(C_2 - C_1)) \tag{3.7}$$

2. The flux of concentration of Li ion at the interface of particle is :

$$-D\frac{\partial C}{\partial r} = -\frac{I}{naF} \; at \; r = R \tag{3.8}$$

Using forward difference at the surface of particle we get:

$$\frac{1.5C_n - 2C_{n-1} + 0.5C_{n-2}}{\Delta r} = \frac{I}{DnaF} \tag{3.9}$$

$$(1.5C_{10} - 2C_9 + 0.5C_8) = \frac{I\Delta r}{DnaF} \tag{3.10}$$

$$C_{10} = \frac{I\Delta r}{1.5 \; DnaF} + \frac{4}{3}C_9 - \frac{1}{3}C_8 \tag{3.11}$$

The difference equation for the centre of particle is given below and the above equation is substituted into it.

$$\frac{dC_9}{dt} = \frac{D}{\left(\frac{R}{10}\right)^2}(\frac{1}{9}(C_{10} - C_8) + (C_{10} - 2C_9 + C_8)) \tag{3.12}$$

$$\frac{dC_9}{dt} = \frac{D}{\left(\frac{R}{10}\right)^2}(\frac{1}{9}\left(\frac{I\Delta r}{1.5\ DnaF} + \frac{4}{3}C_9 - \frac{4}{3}C_8\right) + (\frac{I\Delta r}{1.5\ DnaF} - \frac{2}{3}C_9 + \frac{2}{3}C_8)) \tag{3.13}$$

Hence we have an equation template for mesh points that lie within centre and surface as well as two modified equations for the these two points in our computational domain. Solving these set of equations we get the discharge characteristics of our cell. The capacities have been scaled by 2.13 and the data obtained has been compared with OpenModelica from the thesis:
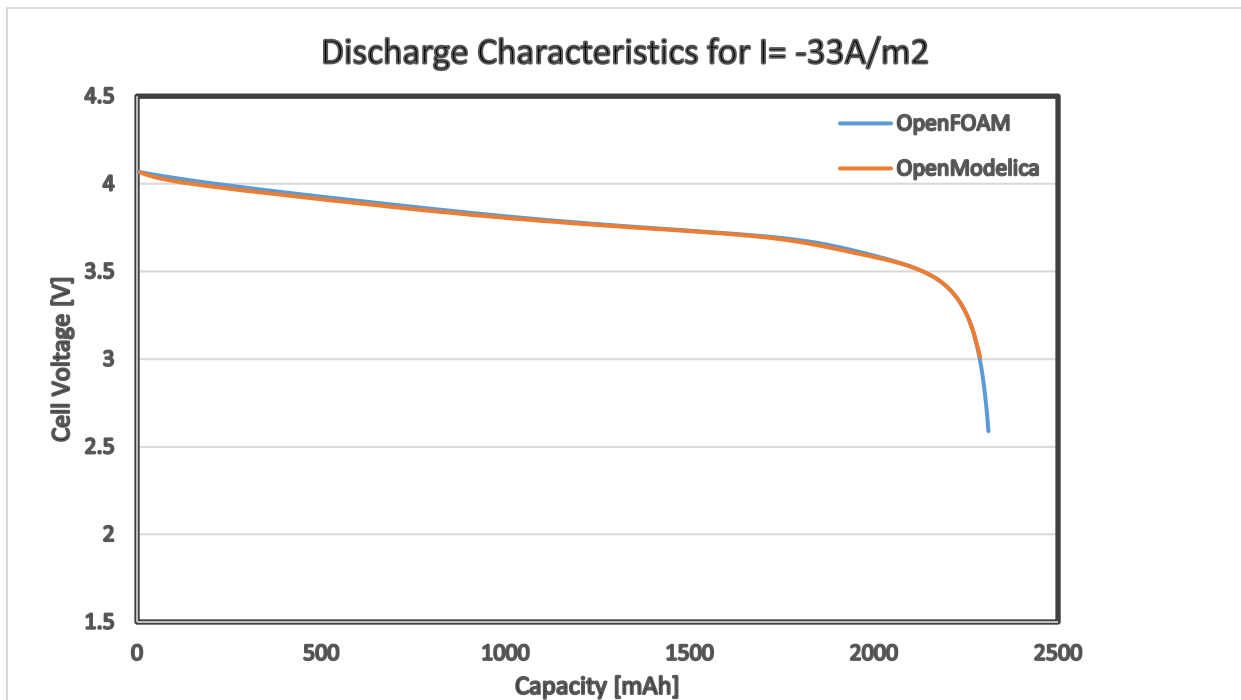

Figure 3-2 : Comparison of Discharge Characteristics obtained from OpenFoam and OpenModelica

The variation in discharge characteristics for different radius of particle size as before been evaluated by modified laplacianFoam is given in Figure 3-3 which has been found using ode-utility:
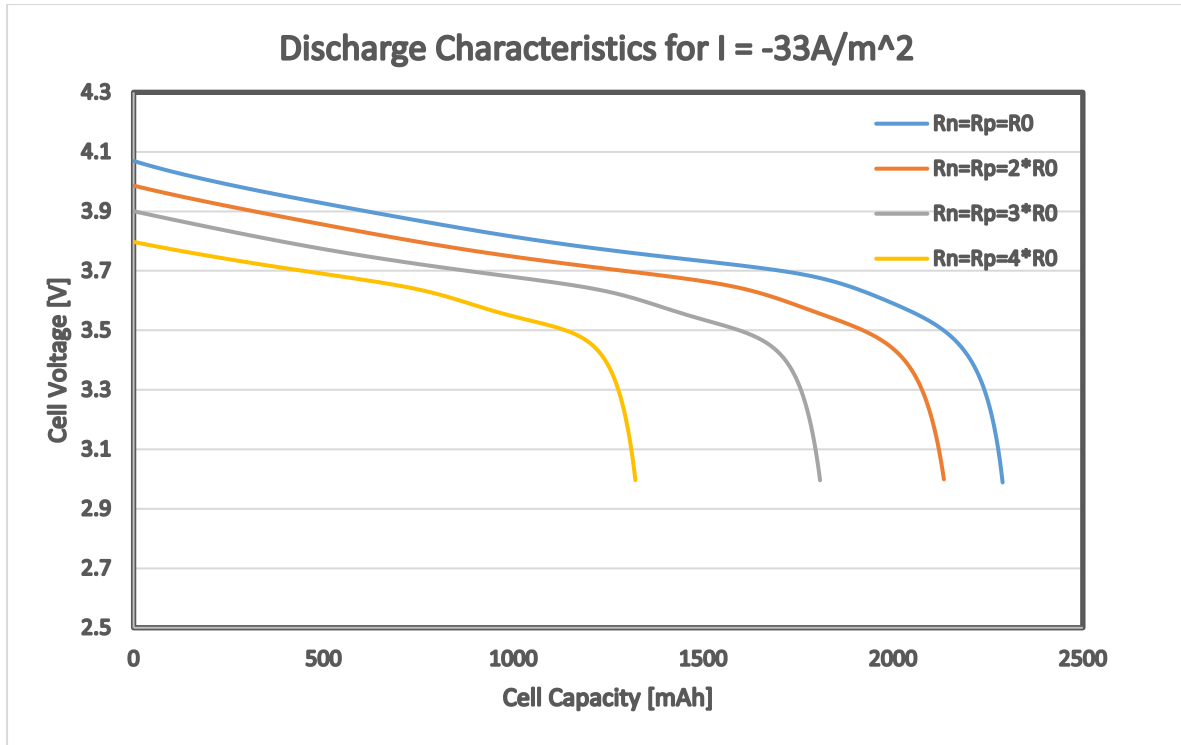

Figure 3-3 : Variation of Cell voltage with radius of particle at constant discharge current of -33A/m^2 obtained using ode-utility

Chapter 4 : Non- Isothermal System using ode-solver

Due to generation of cell voltage, energy has been dissipated which affects the cell voltage via temperature-dependent variables in resonance. The temperature dependent terms in our model were: Diffusivity, Kinetic Rate Constant and the Kinetic potentials. The governing equation for temperature evaluation is ordinary differential equation already and so, it is solved directly using ode-solver utility along with concentration and voltage equations at each time step.

For the demonstration of Non-Isothermal Model we have used (Guo et al., 2011) for model parameters.

Table 4-1: Model parameters given by Guo et al. 2011

Parameter	Symbol	Cathode (j=p)	Anode (j=n)
Particle Radius	R_j [m]	8.5 10e-6	12.5 10e-6
Maximum Solid Phase Concentration	$C_{j,max}$ [mol/m^3]	51410	31833
Solid Phase Li Diffusion Coefficient	D [m^2/sec]	1e-14	3.9e-14
Thickness of Electrode	L_j [m]	70e-6	73.5e-6
Surface Area	S_j [m^2]	1.1167	0.7824
Reaction Rate Constant	$k_j \left[\dfrac{m^3}{mol^{0.5}sec} \right]$	6.777e-11	1.764e-11
Arrhenius Energy for reaction	$Ea_{re,j}$ [J/mol]	58000	20000
Arrhenius Energy for diffusion	$Ea_{di,j}$ [J/mol]	29000	35000
Mole fraction of 100% charged battery	$x_{j,100}$	0.4952	0.7522

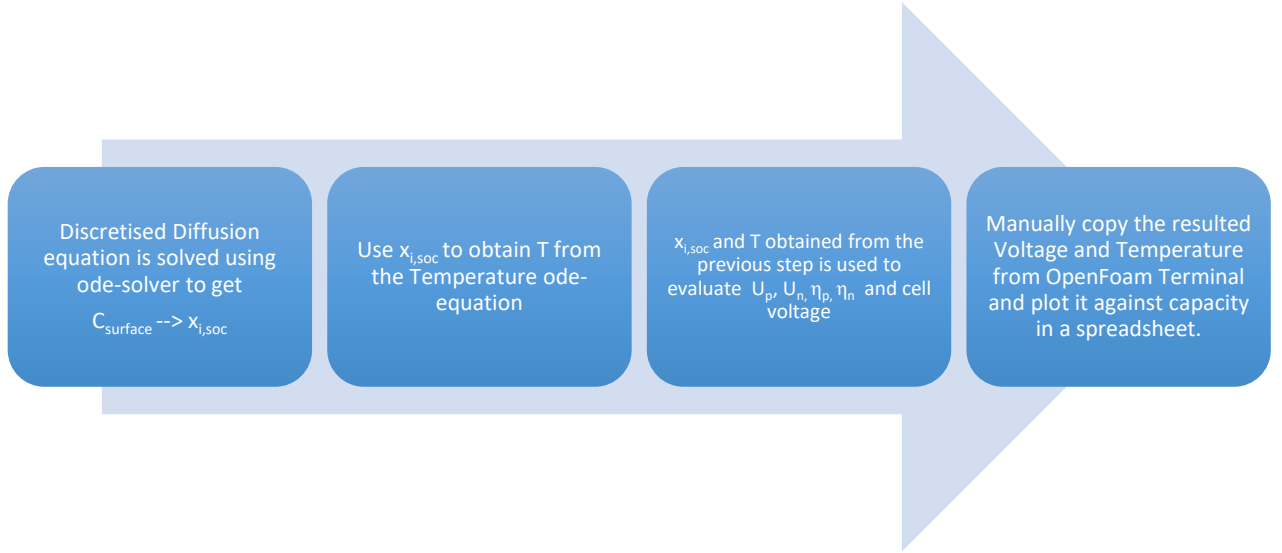|		
Electrolyte Concentration	C_e [mol/m^3]	1000
Density	ρ [kg/m^3]	1626
Temperature	$Tref$ [K]	298
Volume	v [m^3]	0.199×0.08499×0.002
Heat transfer coefficient × Area of cell	hA [J/Ksec]	0.085
Specific Heat Capacity at constant pressure	C_p [J/K. kg]	750
Faraday's Constant	F [C/mol]	96500

Figure 4-1 : Scheme of solving the Non-Isothermal model using ode-utility.

The model presented by (Guo et al., 2011) has been used here which constitutes the following set of emperical relations describing potentials and their variation with temperature:

$$Un = 0.13966 + 0.68920 \times \exp(-49.20361 x_{n,soc}) + 0.41903 \times \exp(-254.40067 x_{n,soc})$$
$$- exp(49.97886 x_{n,soc} - 43.37888) - 0.028221 \times atan(22.52300 x_{n,soc} - 3.65328)$$
$$- 0.01308 \times atan(28.34801 x_{n,soc} - 13.43960)$$

(4.1)

$$Up = 4.04596 + exp(-42.30027 x_{p,soc} + 16.56714) - 0.04880 \times atan(50.01833 x_{p,soc} - 26.48897)$$
$$- 0.05447 \times atan(18.99678 x_{p,soc} - 12.32362) - exp(78.24095 x_{p,soc} - 78.68074)$$

(4.2)

$$\frac{\partial Up}{\partial T} = \frac{-0.19952 + 0.92837 x_{p,soc} - 1.36455 x_{p,soc}^2 + 0.61154 x_{p,soc}^3}{(1 - 5.66148 x_{p,soc} + 11.47636 x_{p,soc} - 9.82431 x_{p,soc}^3 + 3.04876 x_{p,soc}^4)}$$

(4.3)

$$\frac{\partial Un}{\partial T} = \frac{0.00527 + 3.29927 x_{n,soc} - 91.79326 x_{n,soc}{}^2 + 1004.91101 x_{n,soc}{}^3 - 5812.27813 x_{n,soc}{}^4 + 19329.75490 x_{n,soc}{}^5 - 37,147.89470 x_{n,soc}{}^6 + 38,379.18127 x_{n,soc}^7 - 16,515.05308 x_{n,soc}^8}{1 - 48.09287 x_{n,soc} + 1017.23480 x_{n,soc}^2 - 10481.80419 x_{n,soc}^3 + 59431.30001 x_{n,soc}^4 - 195881.64880 x_{n,soc}^5 + 374577.31520 x_{n,soc}^6 - 385,821.16070 x_{n,soc}^7 + 165,705.85970 x_{n,soc}^8}$$

(4.4)

Note : atan means inverse tan function.

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The kinetic potentials, derived from the Butler-Volmer expression as coded are as follows:

$$\eta_p = \frac{2RT}{F} ln\left(\frac{\sqrt{m_p^2 + 4} + m_p}{2}\right) \quad where, \quad m_p = \frac{I}{Fk_p S_p C_{p,max} \, C_e^{0.5}\left(1 - x_p\right)^{0.5} x_p^{0.5}} \tag{4.5}$$

$$\eta_n = \frac{2RT}{F} ln\left(\frac{\sqrt{m_n^2 + 4} + m_n}{2}\right) \quad where, \quad m_n = \frac{I}{Fk_n S_n \, C_{n,max} \, C_e^{0.5}(1 - x_n)^{0.5} x_n^{0.5}} \tag{4.6}$$

The cell voltage evaluated by our model was found to show close resemblence with the actual cell voltage. At a discharge current capacity of of 1.656A-h (C), the cell voltage obtained via OpenFOAM at different initial temperatures have been compared with actual voltage under non-isothermal conditions. The Figure 4-2 compares the variation of temperature obtained by solving our model in OpenFOAM to the experimental results of (Guo et al., 2011). The capacities have been scaled by a constant of 2.3 to model proximity to the actual voltages and make up for numerical errors. The temperature and cell voltage variations obtained from OpenFOAM have been found to obey actual variations in the range of 0.25Ah to 2Ah capacity.
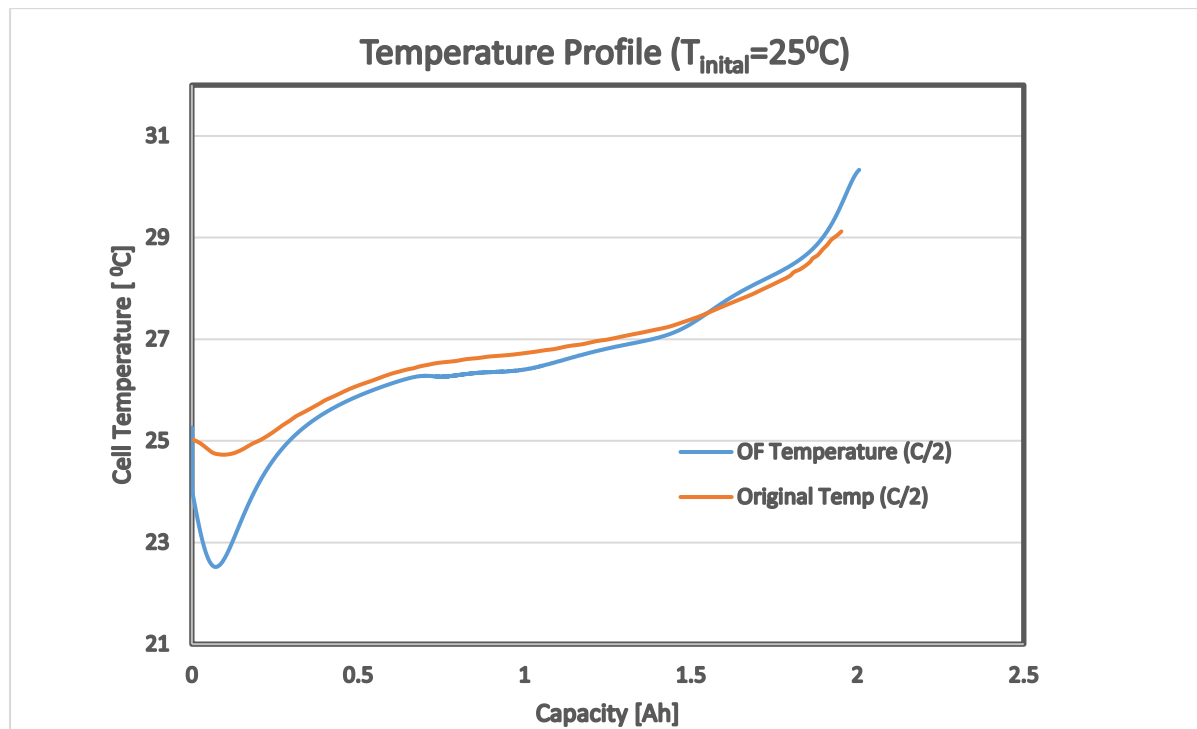

Figure 4-2: Comparison of Temperature profile found by using OpenFOAM vs experimentally evaluated by Guo et al. starting with a temperature of 25⁰C.
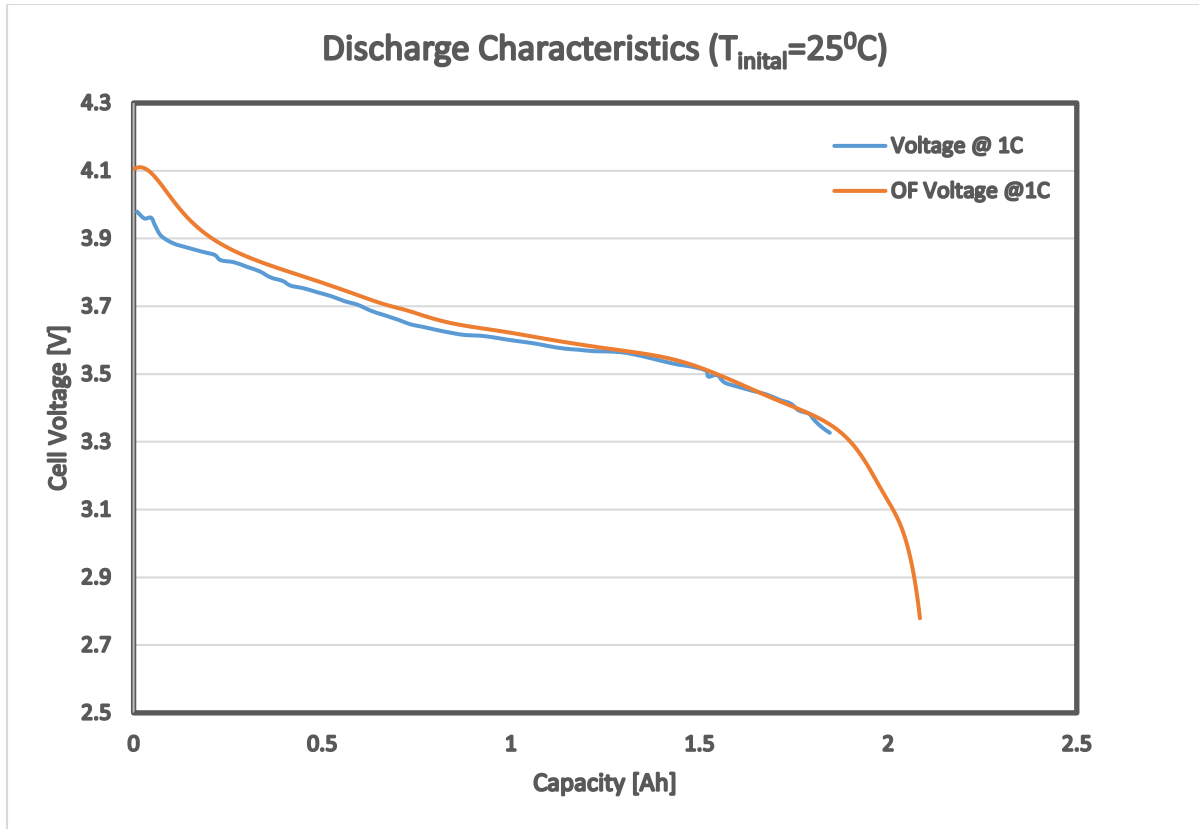
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Figure 4-3: Comparison of Cell Voltage obtained using OpenFOAM and experimentally found by Guo et al. at C discharge current starting with an initial temperature of 25^0C.
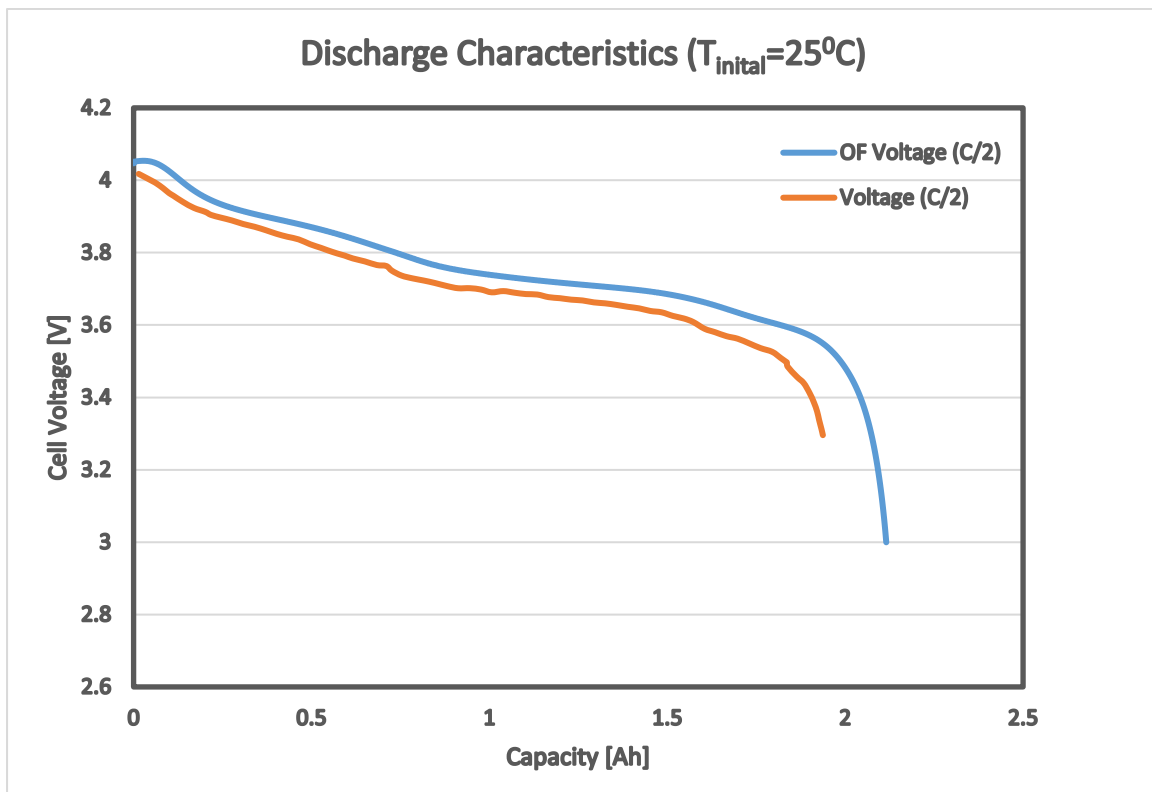

Figure 4-4 : Comparison of Cell Voltage obtained using OpenFOAM and experimentally found by Guo et al. at C/2 discharge current starting with an initial temperature of 25^0C.
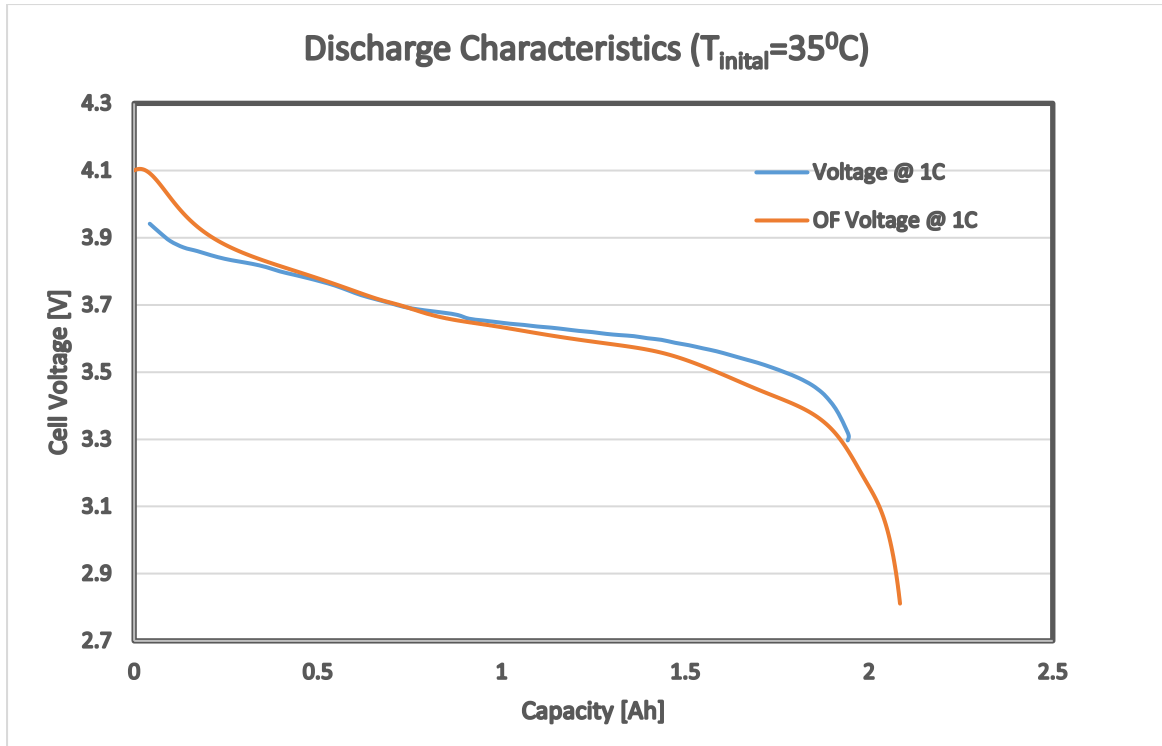
Figure 4-5: Comparison of Cell Voltage obtained using OpenFOAM and experimentally found by Guo et al. at C discharge current starting with an initial temperature of 35°C.
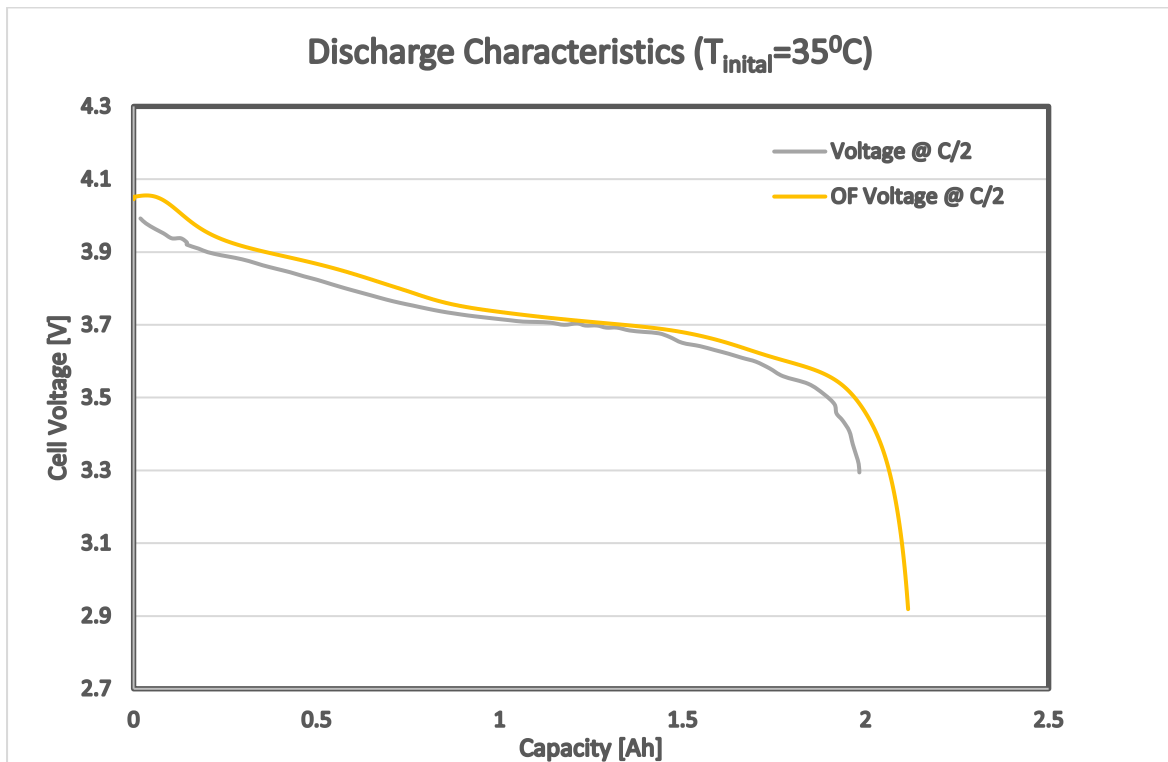

Figure 4-6 :Comparison of Cell Voltage obtained using OpenFOAM and experimentally found by Guo et al. at C/2 discharge current starting with an initial temperature of 35°C.

Directions for Future Work:

Due to lack of appropriate coding experience with OpenFOAM we were unable to code an independent standalone DAE solver which could be used to model a proper electrochemical cell taking OpenFOAM and Paraview to their utmost advantage as is taken by different flow governing phenomena's such as icoFoam, eulerFoam etc. A proper guide to build such a model would be to use solve the temperature equation to get T as scalar value and assign its values to fvm cells. Further laplacianFoam teaches you how to solve laplacian equation over fvm cells which would solve the diffusion problem.

Since the electrochemical model has 3 different zones namely cathode, electrolyte and anode, it would be wise to study chtMultiRegionFoam in order to be able to solve different equations across the three zones with different constants and boundary conditions.

BIBLIOGRAPHY

Guo, M., Sikha, G., & White, R. E. (2011). Single-Particle Model for a Lithium-Ion Cell: Thermal Behavior. *Journal of The Electrochemical Society*, *158*(2), A122. https://doi.org/10.1149/1.3521314

Rajinder Singh (IIT Bombay). (n.d.). *Dynamic Simulation in OpenModelica*.

Suthar, B., Northrop, P. W. C., Rife, D., & Subramanian, V. R. (2015). Effect of Porosity, Thickness and Tortuosity on Capacity Fade of Anode. *Journal of The Electrochemical Society*, *162*(9), A1708–A1717. https://doi.org/10.1149/2.0061509jes

APPENDIX

Changes in model parameters and function changes can be accommodated by modifying solver files easily, all of them can me located by trial-and-error method and modified suitably to observe their effects on compilation and running.

Directions to use spmBatFoam method

Install the spmBatFoam

1. Copy the spmBatFoam solver into "~/OpenFOAM/username-7/applications/solvers/".

2. If you need to change potential functions or do some manipulations, it can be done inside this write.H file inside spmBatFoam

3. Using command terminal locate this open this folder and type "wmake".

Running the case files:

1. Copy the Case file spmodel into run folder.

2. Locate this folder using terminal "~/OpenFOAM/arham-7/run/spmodel".

3. Type "spmBatFoam" and hit enter to run the solver

4. Type and run paraFoam.

5. Mark Cp and Cn in paraview volumeFields.

6. Use the following filters with configuration ExtractBlock (surfacen)>ExtractSurface>Plot data over time

7. Display the data in a spreadsheet and export the data for Vn and etan of surfacen in a spreadsheet.

8. Likewise do for surfacep by creating a branch inside our main paraFoam object and following step 6 and 7 for surfacep.

9. Extract Columns of etap etan Up and Un.

10. Use them to evaluate Cell voltage V= Up-Un-etap-etan.

11. Also copy the time column to evaluate cell capacity.

12. Plot Cell Voltage vs Cell Capacity in the spreadsheet.

Directions to use ode-solver utility as well as Non-isothermal model

1. Copy the folder to the run directory

2. Locate the this folder inside run and type the following commands in your terminal

wclean

wmake

Test-ODE.C RKF45

3. Plot the given results against cell capacity in a spreadsheet.