A

DISSERTATION REPORT

ON

"SIMULATION OF LI-ION BATTERY AND ITS OPTIMIZATION USING SIMULATED ANNEALING ALGORITHM"

Submitted for partial fulfillment of the requirement for award of the degree of

INTEGRATED MASTER OF TECHNOLOGY

IN

POLYMER SCIENCE & TECHNOLOGY

Submitted By:
KUNAL KUMAR
Enrolment No. : 09412008

Under the Guidance of :

Dr. Sujay Chattopadhyay (Advisor)
Department of Polymer & Process Engineering
IIT Roorkee

Dr. Manoj Kumar Ramteke (Co-Advisor)
Department of Chemical Engineering
IIT Delhi

DEPARTMENT OF POLYMER & PROCESS ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
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6th June 2014

Kunal Kumar

CANDIDATE'S DECLARATION

I hereby declared that the work which is being presented in this Dissertation Report entitled **"SIMULATION OF LI-ION BATTERY AND ITS OPTIMIZATION USING SIMULATED ANNEALING ALGORITHM"** in partial fulfillment of the requirement for the award of the degree of Integrated Master of Technology in Polymer and Process Engineering at IIT Roorkee and solely exists as a record of my own work carried out, under the supervision of Dr.Sujay Chattopadhyay and Dr. Manoj Kumar Ramteke Department of Polymer and Process Engineering, IIT Roorkee.

The matter embodied in this project report has not been submitted by me for the award of any other degree.

Date: 6th June 2014

Place: Saharanpur

Kunal kumar

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Chattopadhyay

Dr.Sujay Chattopadhyay
(Assistant Professor)
IIT Roorkee

ABSTRACT

This report is a comprehensive collection of the design, simulation and optimization of lithium ion battery systems. The battery is simulated using code Dualfoil which is taken from Doyle's thesis.

It includes theoretical data and aims to provide a computational model of lithium rechargeable battery system, which can be used for industrial level simulation. All the modelling equations have been provided where needed.

The outputs files generated after simulations are used to study concentration profile of Li-ions in the electrolytes. It is optimized using MOSA algorithms at different iterations of 100, 10000, 20000 and 30000. Then it is compared with genetic algorithms at different generation.

INTRODUCTION

The worldwide market for electrochemical devices and processes was estimated to be thirty billion dollars in 1987. This comprises fieldof metal winning, chemical and semiconductor production, electroplating, corrosion, and batteries and fuel cells. Energy conversion and storage continues to be an important application for electrochemical systems. The global battery market is around $50000 million dollar, of which around $5500 million is related to secondary battery. The projected growth of battery market is 6% per annum.Thestrongest market for battery will be countries like China, India, Brazil and South Korea.

There are two main kinds of battery systems - Primary and Rechargeable. Most of the rechargeable batteries are lead-acid based for SLI (Starting, Lighting and Ignition) automotive applications. However in recent times there is a huge market demand for small-scale rechargeable batteries.

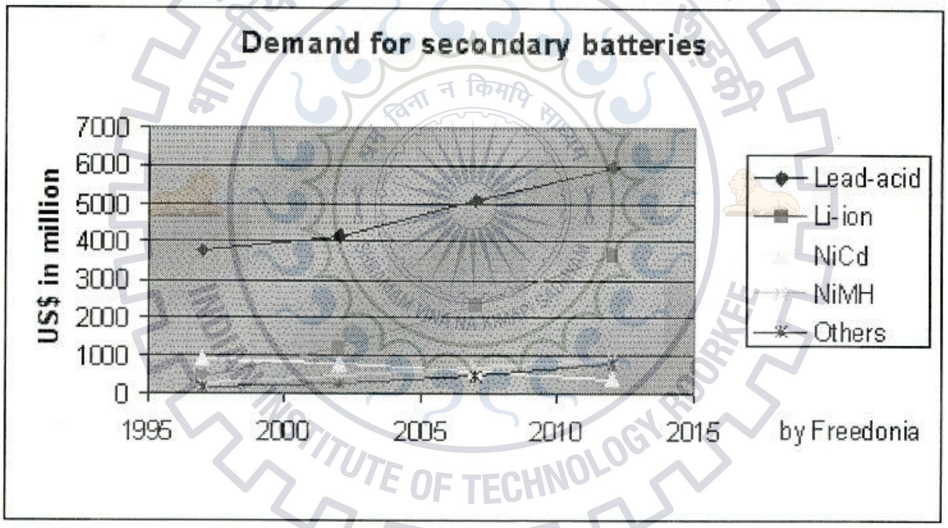


Figure: It clearly depicts demand of secondary batteries

There is a huge public demand for even smaller devices. Development on this from has led to the battery comprising a major part of the device's volume and weight. Since newer phones are tending to be very thin and light, it is required that they use a thin-film battery system. The effectiveness of the device is finally based on the capacity of the battery, and hence it is of utmost importance that the capacity of the battery is also increased. While considering all this, once must also keep in mind the stricter environmental laws and regulations. Novel ideas for battery technology are also required on the environmental side.

Generally lithium batteries have a high specific energy, which is because of the low equivalent weight, and reactivity of the Lithium metal. This also facilitates a wide range of operation temperatures, high unit cell voltage and long life.

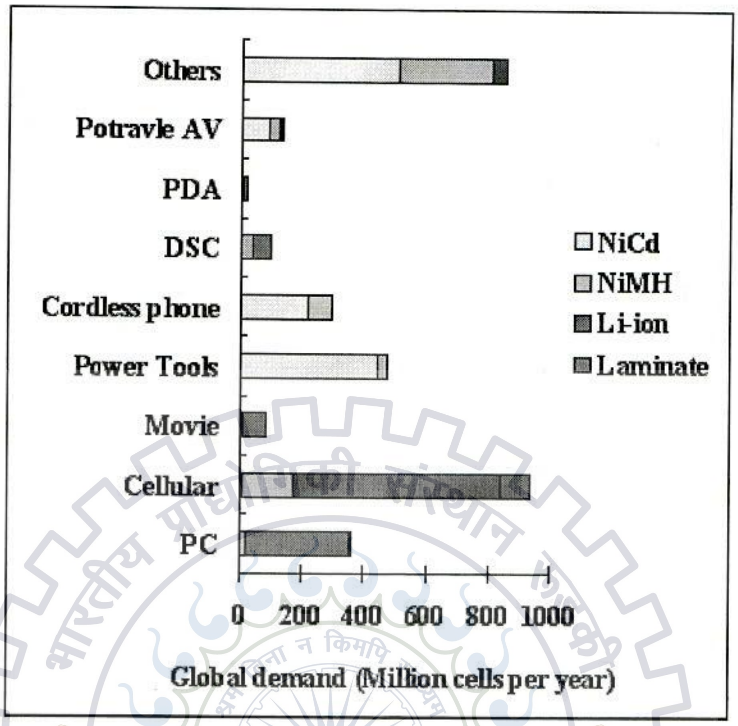


Fig2:Demand of different battery

Generally lithium batteries have a high specific energy, which is because of the low equivalent weight, and reactivity of the Lithium metal. This also facilitates a wide range of operation temperatures, high unit cell voltage and long life.

Lithium-Ion battery

A lithium-ion battery is a rechargeable battery used mostly for consumer electronics. Their uses include portable energy storage. Compared to various alternative battery technologies, Li-ion batteries provide various benefits such as:

- Wider Operation Range
- Flexible Design
- Economy Relatively low self-discharge
- Low Maintenance (no periodic discharge is needed)
- Specialty cells can provide very high current to applications such as power tools

Applications for batteries range from implantable cardiovascular defibrillators operating at 10 μA, to hybrid vehicles requiring pulses of up to 100 A. Some of the common applications are:

- Auto-mobiles
- Military Applications
- High Performance Engineering (Space Shuttles/ Satellites etc.)
- Mobile-Station
- Consumer Electronics
- Medicine
- Computing

Currently a large variety of cell designs and cell chemistries are considered to be under the classification of Lithium-ion Battery. Due to this, there is major confusion and misinterpretation of the various failure mechanisms of the different battery systems. This is a problem because different degradation paths are followed by cells of different chemistries. Quite often cells with the same chemistry but made by different manufacturers also provide different performance. This performance that is observed at the cell level or component level does not translate to the system level.

The cell electrolyte should almost always be a non-aqueous solvent because of the very high reducing power of Lithium (Li, U9 = - 3.045 V vs. NHE). Some of the various electrolytes that have been developed and are being used are:

- Ethylene Carbonate
- Dimethyl Carbonate
- Propylene Carbonate

However, since most of these solutions have an ionic conductivity that is lower than aqueous-solutions, very thin cells are used to reduce the solution phase ohm drop. Nonetheless even in highly stable solvents, Lithium metal (Li) will react to some extent. Therefore the solvent reaction with lithium should only proceed until the passivation of the surface of the Li metal, in a successful system. Industries and researchers try to achieve a highly reversible cell reaction, while simultaneously trying to retain the large specific energy of these Li-based systems. However because of the poor cycling efficiency of Li, this becomes a problem. This reversibility is hampered due to a continual reaction of the solution with the freshly deposited Li metal, during charging. Using solid polymer electrolytes has the possible advantage to develop more stable polymers that have better efficiency in Li plating/stripping. Poly (ethylene oxide) shows this property to some extent, but even most of the recent polymer electrolytes have similar reactions with Li-metal just as the non-aqueous liquids.

Some of the major problems that exist in current generation lithium-ion technology are:

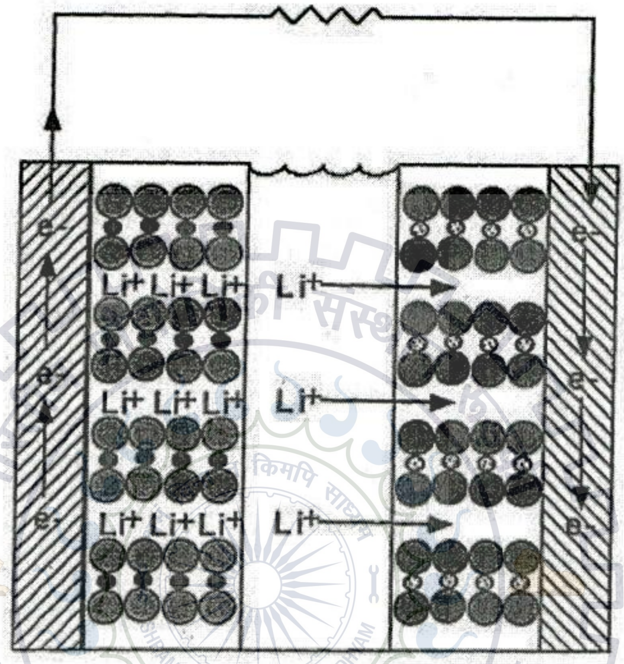
- Maintaining voltage and current under safe limits.
- Subject to aging.
- Transportation restrictions
- Expensive to manufacture - about 40 percent higher in cost than nickel-cadmium.
- Stress-induced damage to material
- Loss of capacity
- Thermal runaway

These limitations are associated with the following:

- (SEI) Solid-Electrolyte Interface layer growth
- Mechanical Degradation
- Side Reactions
- Active material loss
- Internal Resistances (ohmic and mass transfer)

CELL STRUCTURE

A basic Li-ion battery cell structure is shown below:



The Li-ion battery consists of the following components

- Positive Electrode
- Negative Electrode
- Electrolyte

Standard, conventional Li-ion cells have carbon as a negative electrode, a metal oxide acts as positive electrode, and electrolytes is a lithium salt in an organic solvent. Based on the current flow direction the electrodes can freely change between the anode and the cathode. Commercially, the most popular electrodes are:

- Negative – Graphite
- Positive – Layered Oxide / Poly-anion / Spinel(Li-Mn Oxide - spinel)

Examples of positive electrodes include (Li-Co Oxide, Lithium iron phosphate, Li-Mn Oxide - spinel) A mixture of organic carbonates with Li-ion complexes are used as electrolytes. Example: [Ethylene Carbonate / Diethyl Carbonate + Li-ion complexes]

Non-coordinating anion salts are used in these electrolytes (non-aqueous by nature), such as:

- Lithium hexafluorophosphate (LiPF6)
- Lithium perchlorate (LiClO4)
- Lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI)
- Lithium tetrafluoroborate (LiBF4)
- Lithium triflate (LiCF3SO3).

Choice of material and cell architecture greatly affects the various properties of a Li-ion battery like its capacity, voltage, life, and safety procedures. Improving technological standards also greatly drive performance forward. The primary reason of being limited to using non-aqueous electrolytes is that Li-metal is highly reactive. With water the vigorous reaction forms Lithium Hydroxide and H2 (hydrogen) gas. This also enforces the need to properly seal the battery pack in order to prevent damage to the device or user. Economically, Ni-Cd battery systems are inexpensive in comparison to Li-ion batteries, but Li-based batteries have a higher energy density and operate over a wider temperature range. They are also lighter in weight and can be made smaller. They however are highly fragile and require a protective circuit which limits peak voltage levels.

Electrochemistry

All the electrochemical reactions in lithium-ion battery occur between the pair of electrodes and the electrolyte. At each of the electrodes one of the following processes takes place.

1. Insertion / Intercalation: This is the process when the ions (Li, here) migrate into the electrode.
2. Extraction / De-Intercalation: This is the reverse process of insertion, and occurs when the ions migrate back out from the electrode. Therefore the charging and discharging of a cell can be understood as follows:

- Charging:positiveli-ion extracted from negative electrode,inserted into positive electrode.
- Discharging:reverse of charging.

Hence, chemically these processes can be shown as:

The positive electrode half-reaction is: $LiCoO_2 \leftrightarrows \mathrm{Li}_{1-x}\mathrm{CoO}_2 + x\mathrm{Li}^+ + x\mathrm{e}^-$
The negative electrode half reaction is: $x\mathrm{Li}^+ + x\mathrm{e}^- + x\mathrm{C}_6 \leftrightarrows x\mathrm{LiC}_6$

Over-Discharge eventually supersaturates the Li-Co Oxide, which leads to creation of Lithium Oxide, by this irreversible mechanism:

$$\mathrm{Li}^+ + \mathrm{e}^- + \mathrm{LiCoO}_2 \rightarrow \mathrm{Li}_2\mathrm{O} + \mathrm{CoO}$$

Overcharge to 5.2 volts creates Cobalt (IV) Oxide. This is clearly evident by inspection using x-ray diffraction.

$$\mathrm{LiCoO}_2 \rightarrow \mathrm{Li}^+ + \mathrm{CoO}_2 + \mathrm{e}^-$$

In the battery system these Li-ions transferred from one electrode (the cathode / anode) to the other, along with the transition metal (Co) which is oxidized (Co^{3+} to Co^{4+})during the charge cycle and reduced (Co^{4+} to Co^{3+})during the discharge cycle. The energy that is generated can be calculated by multiplying the charge with voltage.

Modelling

The following modelling approach uses the isothermal discharge of many lithium batteries. The model is intended to be general in the sense as to be applicable to many of the specific systems.

Hence there are 2 main divisions of Li-based cells

- **Dualfoil –** 2 insertion-type electrodes. (rocking-chair cell)
- **FOIL –** 1 insertion-type electrode and solid lithium foil.

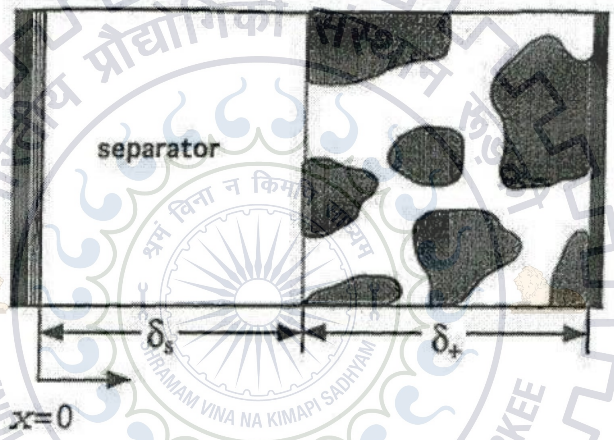


Fig: single foil

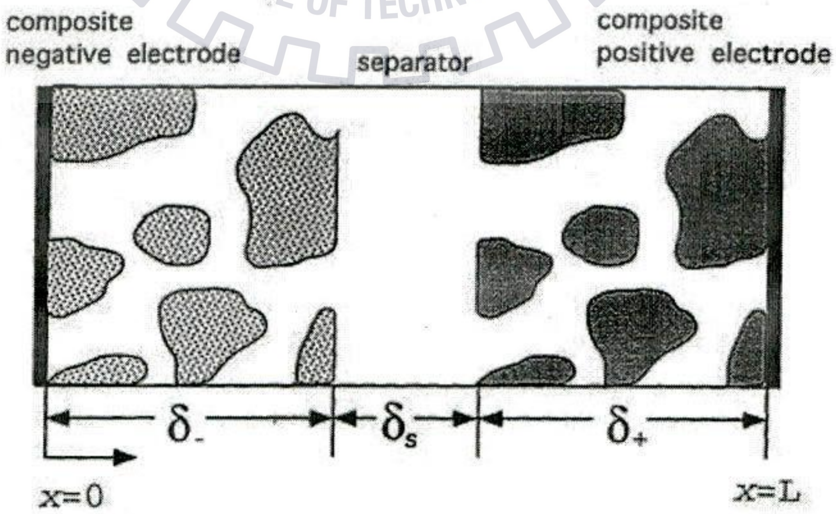


Fig:dualfoil

Modelling

Full Cell Sandwich Approach Assumptions

- It is a multi-region problem that involves coupled (differential) equations
- Three cell regions

    1. Negative electrode :It is a solid lithium foil or an insertion type electrode
    2. Positive electrode :Insertion type electrode which is configured as porous electrode
    3. Separator: It consists of salt in the solvent. The solvent can be non-aqueous liquid or a solid polymer

- No internal or external reservoirs for the solution.
- Current collectors have infinite conductivity
- All models equations are considered to be one dimensional.

Theory used

- **Porous electrode theory** to treat the composite insertion electrodes. The insertion process itself is treated with a charge-transfer process at the surface obeying Butler-Volmer kinetics, followed by diffusion of the lithium ion into the host structure.
- **Concentrated solution theory** to describe the transport processes in the solution phase.

Concentrated solution theory

Salt concentrations used in lithium batteries are generally large (c>1M).Thus transport of the electrolyte should be treated rigorously by using concentrated solution theory.

- According to this the gradient of the electrochemical potential for an ionic species acts as the driving force for mass transfer at constant temp. and press is for the ith species.

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T \mathcal{D}_{ij}} \left(\mathbf{v}_j - \mathbf{v}_i \right)$$

Where Dij are diffusion coefficients describing the interactions between the ith and jth species

- Thus flux in term of driving forces.
- Thus for polymer electrolytes $v_o = 0$ can be assumed.
- The current density is given by

$$\mathbf{i} = F \sum_i z_i \mathbf{N}_i ,$$

Thus flux expression obtained is

$$\mathbf{N}_+ = -\frac{\nu_+ \mathcal{D}}{\nu RT} \frac{c_T}{c_0} c \nabla \mu_e + \frac{\mathbf{i} t_+^0}{z_+ F} + c_+ \mathbf{v}_0 ,$$

$$\mathbf{N}_- = -\frac{\nu_- \mathcal{D}}{\nu RT} \frac{c_T}{c_0} c \nabla \mu_e + \frac{\mathbf{i} t_-^0}{z_- F} + c_- \mathbf{v}_0 ,$$

Converting fluxes to a concentration driving force

$$\mathbf{N}_i = -\nu_i \left[1 - \frac{d \ln c_0}{d \ln c} \right] D \nabla c + \frac{\mathbf{i} t_i^0}{z_i F} + c_i \mathbf{v}_0 .$$

Where the salt diffusion coefficient D is given by

$$D = \mathcal{D} \frac{c_T}{c_0} \left[1 + \frac{d \ln \gamma_\pm}{d \ln m} \right]$$

Material balance for species i in below equation the form

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i .$$

Concentrated solution theory

Combining Flux and material balance
Material balance on the salt gives below equation:

$$\frac{\partial c}{\partial t} + \nabla \cdot \left(c\,\mathbf{v}_0\right) = \nabla \cdot \left[D\left(1 - \frac{d\ln c_0}{d\ln c}\right)\nabla c\right] - \frac{\mathbf{i}\,\nabla t_+^0}{z_+\nu_+F}$$

Continuity equation for the solvent velocity

$$\frac{\partial c_0}{\partial t} = -\nabla \cdot \left(c_0\,\mathbf{v}_0\right)$$

When $v_o = 0$ i.e the solvent velocity is sufficiently small to be neglected.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\left(1 - \frac{d\ln c_0}{d\ln c}\right)\frac{\partial c}{\partial x}\right] - \frac{i_x}{z_+\nu_+F}\frac{\partial t_+^0}{\partial x}$$

Where D and t^o_+ are the transport properties which is arbitrary function of salt concentration

Potential in solution is given by

$$\nabla\Phi = -\frac{\mathbf{i}}{\kappa} + \frac{RT}{F}\left(1 + \frac{d\ln f_A}{d\ln c}\right)\left(1 - t_+^0\right)\nabla\ln c$$

Porous electrode theory

Porous electrode theory to treat the composite insertion electrodes. The insertion process itself is treated with a charge-transfer process at the surface obeying Butler-Volmer kinetics, followed by diffusion of the lithium ion into the host structure.

- Provides large interfacial area.
- Porous electrode is treated as a superposition of continuous electrode and solution phases, each of known volume fraction.
- Denoting the porous electrode by its specific interfacial area, a, and volume fractions of each phase, ϵ.
- Material balance on the salt in the pores of the electrode (no homogenous chemical reaction occurring).

$$\varepsilon \frac{\partial c}{\partial t} + \mathbf{v}_0 \cdot \nabla c = \nabla \cdot \left[\varepsilon D \left[1 - \frac{d \ln c_0}{d \ln c} \right] \nabla c \right] + \left[1 - t_+^0 \right] \frac{a j_{+n}}{\nu_+}$$

$$+ \left[1 - t_+^0 \right] \frac{a j_{-n}}{\nu_-} - \frac{\mathbf{i} \cdot \nabla t_+^0}{z_+ \nu_+ F} - c \left[\frac{\partial \varepsilon}{\partial t} + \nabla \cdot \mathbf{v}_0 \right] .$$

- Potential in the solution phase of the porous electrode wrt lithium reference electrode in solution.

$$\nabla \Phi_2 = -\frac{\mathbf{i}_2}{\kappa_{\text{eff}}} + \frac{RT}{F} \left[1 + \frac{d \ln f_A}{d \ln c} \right] \left[1 - t_+^0 \right] \nabla \ln c$$

Boundary Condition

Iterating the cell current density and solving the galvano-static equations until the desired cell potential is achieved simulate a potentio-static charge or discharge. At the positive electrode/current collector boundary, the flux of ions is zero, and the electrons carry all the current. This gives us the boundary conditions on the salt concentrationsolution-phase current density.

$$\nabla c = -\frac{I\left[1 - t_+^0\right]}{FD} \quad \text{at} \quad x = 0.$$

$$\nabla \Phi_1 = -\frac{I}{\sigma} \quad \text{at} \quad x = \delta_s + \delta_+ .$$

The following condition must also be obeyed by the solid-phase potential at either boundary.

$$\nabla \Phi_1 = 0.$$

Solid State Diffusion

The slowest step in the lithium insertion process has long been thought to be the diffusion of lithium into the oxide lattice. Hence, this diffusion process cannot be ignored in the battery models.

Summary of Model Equations

The model can be divided into the separator and porous positive electrode regions. In the solution phase of the positive electrode the equations are

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D_{\text{eff}}\left[1-\frac{d\ln c_0}{d\ln c}\right]\frac{\partial c}{\partial x}\right] + \left[1-t_+^0\right] a j_{+n} - \frac{i_{2,x}}{F}\frac{\partial t_+^0}{\partial x},$$

The solid-phase diffusion problem is solved and relegated to a surface integral equation leading to:

$$j_{+n} = \frac{i_{0,2}}{F}\left[\exp\left[\frac{\alpha_{a,2}F\eta_{s,2}}{RT}\right] - \exp\left[-\frac{\alpha_{c,2}F\eta_{s,2}}{RT}\right]\right].$$

The two phases are also related through the Butler-Volmer kinetic expression,

$$j_{+n} = -D_s\left[\sum_{k=0}^{n-2}\frac{\left[c_{s,k+1}-c_{s,k}\right]}{\Delta t}A_{n-k} + \frac{\left[c_{s,n}-c_{s,n-1}\right]}{\Delta t}A_1\right].$$

The instantaneous cell temperature can also be calculated at each time step from an energy balance of the form:

$$M\hat{C}_p \frac{dT}{dt} = I\left[U(T^0) - V - T^0\frac{dU}{dT}\right] + h_0\left[T_{\text{amb}} - T\right],$$

Doyle's Program

Open Source programs for the simulation of these electrochemical systems are available as a combination of the Dualfoilfortran programs, written originally by Doyle.Dualfoil.f is a FORTRAN program which is used for the simulation of batteries like lithium-metal, lithium-ion, sodium-ion, and nickel metal-hydride chemistries. The equations that are used in the program are taken from the following publications:

- Marc Doyle, Thomas F. Fuller, and John Newman, J. Electrochem. Soc., 140 (1993), 1526-1533.
  Thomas F. Fuller, Marc Doyle, and John Newman, J. Electrochem. Soc., 141 (1994), 1- 10.
- Thomas F. Fuller, Marc Doyle, and John Newman, J. Electrochem. Soc., 141 (1994), 982-990.

Following is a list of what an average user is able to change. Most of these parameters are changed inside the input file (dualfoil.in)

- Alter parameters including operating mode, current, etc.
- Cell geometry can be changed. This includes parameters like porosity, thickness, etc.
- Adjust ambient and initial temperatures.
- Select run mechanism – isothermal / non-isothermally
- Modify activation energies. This change is done in the ebar.in file
- Alter rate constants
- Change solid-state diffusion coefficients and solid-phase conductivity.
- Modify system materials (anode / cathode / electrolyte)
- Simulate the system in impedance mode.
- Simulate the system with a variable diffusion coefficient. One can define functions for this requirement.
- Add extra custom user defined materials like electrodes/electrolyte.
- Alter the size, fraction and number of particles in the electrodes.
- The new materials can be added according to material. The property of new material can be added in different subroutines
  - ✓ Nneg:for negative electrode
  - ✓ Nprop:forelectrolyes
  - ✓ npos:for positive electrode

Software and Compliers

The simulation and testing is carried on Microsoft Developers Studio.

Challenges faced

- Input variable access for optimization
- Output variable access for optimization
- Math Error in during execution after build in MS Developer Studio

The major problem in this part being that after the program was successfully compiled and run it would always give a Math Error. Multiple compilations later and not finding any reason for this anomaly, the solution came into light. The problem was that MS Developer Studio 95 is a very old compiler. It was unable to properly compile some of the newer functions used in DualFoil 5.1f. Hence we had to use a more recent fortran compiler. One of the freely available compilers is Gfortran (g77), which is included in the GNU Compiler Collection (gcc).

MinGWMinGW (Minimalist GNU for Windows) is typically used for compiling Windows applications. It is a software port of the GCC and GNU Binutils. It runs as a tool on Windows or as a cross compiler with the target as Windows. Deployment of this tool is done along with free import libraries and header files. Hence we install and use MinGW on our Windows Environment to compile DualFoil without any errors. The command used is quite simple:

1. Install MinGW from www.mingw.org
2. Press Windows Key + R – Launches Run Command
3. Type cmd – Launches a Command Prompt
4. In the command prompt, use cd to change directory to the source file folder
5. Enter the following to compile FORTRAN CODE with MinGW:

```
G77 –o dualfoil.exe dualfoil.f
```

Input of Dualfoil5.1

DualFoil takes all its inputs from a single input file called “dualfoil.in”. The various inputs included in this are(http://www.cchem.berkeley.edu/jsngrp/fortran_files/li-ion.in)

- *lim, limit on number of iterations*
- *h1, thickness of negative electrode (m)*
- *h2, thickness of separator (m)*
- *h3, thickness of positive electrode (m)*
- *hcn, thickness of negative current collector (m)*
- *hcp, thickness of positive current collector (m)*
- *n1, number of nodes in negative electrode(set=0 if in foil mode)*
- *n2, number of nodes in separator*
- *n3, number of nodes in positive electrode*
- *n4, number of nodes in solid particle*
- *mvdc1, flag for variable solid diff coeff in anode*
- *mvdc3, flag for variable solid diff coeff in cathode*
- *lims, number of iterations for solid phase convergence*
- *T, temperature (K)*
- *xi(1,1), initial salt concentration (mol/m3), 1200 needed for constant load short circuit*
- *x, initial stoichiometric parameter for neg. (ignored if n1=0) 0.67*
- *y, initial stoichiometric parameter for positive based on formula unit where 0<y<1*
- *tmmax, maximum time step size (s)*
- *dfs1, (ignored in Foil mode) diffusion coef. in negative solid (m2/s) 0.58d-14,*
- *dfs3, diffusion coef. in positive solid (m2/s) 0.8d-14, 3.d-14*
- *Rad1, radius of negative particles (m) (ignored in Foil mode) 0.0000042, 0.0000078*
- *Rad3, radius of positive particles (m) 0.000002, 17*
- *ep1, volume fraction of electrolyte in negative electrode*
- *epp1, volume fraction of polymer in negative electrode*
- *epf1, volume fraction of inert filler in negative electrode*
- *epg1, volume fraction of gas in negative*
- *ep2, ep2+epp2=1.0 volume fraction of electrolyte in separator*
- *epp2, volume fraction of polymer in separator*

- *epg2, volume fraction gas in separator*
- *ep3, volume fraction of electrolyte in positive electrode*
- *epp3, volume fraction of polymer in positive electrode*
- *epf3, volume fraction of inert filler in positive electrode*
- *epg3, volume fraction of gas in positive*
- *sig1, conductivity of negative matrix (S/m) (ignored in Foil mode) 124.28*
- *sig3, conductivity of positive matrix (S/m) 23.43*
- *rka1, rate constant for negative reaction 2d-9*
- *rka3, rate constant for positive reaction, changed from 3 to 4 4d-9*
- *ranode, anode film resistance (ohm-m2) 0.88d-2*
- *rcathde, cathode film resistance (ohm-m2) 2.0d-2 1.0d-2, 1.2d-2*
- *cot1, coulombic capacity of negative material (mAh/g)*
- *cot3, coulombic capacity of positive material (mAh/g)*
- *re, density of electrolyte (kg/m3)*
- *rs1, density of negative insertion material (kg/m3)*
- *rs3, density of positive insertion material (kg/m3)*
- *rf, density of inert filler (kg/m3)*
- *rpl, (not used here) density of polymer material (kg/m3)*
- *rc, density of inert separator material (kg/m3)*
- *rcn, density of negative current collector (kg/m3) [copper foil]*
- *rcp, density of positive current collector (kg/m3) [aluminum foil]*
- *htc, heat-transfer coefficient at ends of cell stack (W/m2K) 0.36*
- *Cp, heat capacity of system (J/kg-K) 1200*
- *Tam, ambient air temperature (K)*
- *ncell, number of cells in a cell stack*
- *lht, 0 uses htc, 1 calcshtc, 2 isothermal*
- *il1, 1 for long print-out 0 for short print-out*
- *il2, prints every il2 th node in long print-out*
- *il3, prints every il3 th time step in long print-out*
- *lflag, 0 for electrolyte in separator only, 1 for uniform*
- *imp, 0 for no impedance, 1 for impedance*
- *capp1, capacitance of negative material (F/m2)*
- *capp3, capacitance of positive material (F/m2)*
- *lpow 0 for no power peaks, 1 for power peaks*
- *jsol calculate solid profiles if 1 <jsol<nj*
- *nside flag to turn on (1) or off (0) side reactions*
- *rksa1 rate constant side reaction 1 negative (ignored if nside=0)*
- *rksc1 rate constant side reaction 1 positive (ignored if nside=0)*
- *rksa2 rate constant side reaction 2 negative (ignored if nside=0)*
- *rksc2 rate constant side reaction 2 positive (ignored if nside=0)*
- *rksa3 rate constant side reaction 3 negative (ignored if nside=0)*
- *rksc3 rate constant side reaction 3 positive (ignored if nside=0)*
- *nneg negative electrode*
- *nprop electrolyte*
- *npos positive electrode*
- *lcurs, number of current changes*
- *Discharge at 10A/m2 for 60min, low/high cutoff 2.0/4.7 V*

Output files of Dualfoil

DualFoil gives multiple output files. Each of these outputs contains battery details while simulation. These are:

1. Dualfoil.out:It can be simuate for a short output or for a short output with long output. This can be made by changing value in input file by changing lht.Iflht=0 it produces a short output, when lht=1 it produces long output. The dualfoil.out file consists following information.

- A table containing time(minutes), cell temperature(Celsius), cell potential(volt), current(A/m2), and heat generated (W/m2)
- Mass (kg/m2)
- Specific energy segment (W-h/kg)
- Specific power segment (W/kg)
- Total heat(W-h/m2)

2. Resistances.out: Resistances in each portion of the cell, from a simple (delta V) / I
3. Halfcells.out, profiles.out and solidprofiles.out
4. Concentarion profiles: It gives simulation of variation of concentration profiles wrt electrode thickness

Simulation of Some battery system

The simulation is carried using dualfoil code .It takes almost 20-30 seconds to give output files.

- **Negative electrode:MCMB 2528 graphite (Bellcore)**
- **Electrolyes:LiPF6 in EC:DMC**
- **Positive electrode:CoO2 (Cobalt dioxide)**

The property of electrodes and electrolyte are adjusted in input file of code which takes value from code. Simulation is carried for discharge at current of 20(A/m2) for 60 minutes.

Simulation results:

Specific power segment =91.20 W/kg

Total heat = 0.8568 W-h/m2

Profiles out files give following data

Distance (microns)	C Elec C (mol/m3)	Distance (microns)	C Elec C (mol/m3)
t =	4.145296E-	t =	1.55E-02
0.0,	1000.3,	0.0,	1001.2,
12.5	1000.3,	12.5,	1001.3,
25.0,	1000.4,	25.0,	1001.6,
37.5,	1000.5,	37.5,	1002.1,
50.0,	1000.7,	50.0,	1002.9,
62.5,	1001.0,	62.5,	1004.0,
75.0,	1001.5,	75.0,	1005.4,
87.5,	1002.1,	87.5,	1005.8,
100.0,	1000.5,	100.0,	1001.5,
106.2,	1000.2,	106.2,	1000.9,
112.5,	1000.0,	112.5,	1000.4,
118.7,	999.9,	118.7,	999.9,
125.0,	999.8,	125.0,	999.5,
137.5,	998.9,	137.5,	996.6,
150.0,	998.9,	150.0,	996.0,
162.5,	999.0,	162.5,	996.1,
175.0,	999.0,	175.0,	996.2,
187.5,	999.0,	187.5,	996.4,
200.0,	999.1,	200.0,	996.5,
212.5,	999.1,	212.5,	996.5,
225.0,	999.1,	225.0,	996.5,

In the code the properties of electrodes and electrolytes are called by these subroutines in main code

For negative electrode (subroutine nneg)

MCMB 2510 carbon (Bellcore)

```
c    c1  -0.160d0
c    c2  1.32d0
c    c3  -3.0d0
c    g0  c1  c2*expg(c3*xx(2  mpa,j) ct1)
c    g0  g0  10.d0*expg(-2000.d0*xx(2  mpa,j) ct1)
c    g1  c2*c3*expg(c3*xx(2  mpa,j) ct1) ct1
c    g1  g1-10.d0*2000.d0 ct1*expg(-2000.d0*xx(2  mpa,j) ct1)
c   MCMB 2528 graphite measured by Chris Bogatu 2000, Telcordia and PolyStor materials
c   for 0.01    x    0.9
     sto    xx(2  mpa,j) ct1
     g0    0.194d0  1.5d0*expg(-120.0d0*sto)
    &    0.0351d0*dtanh((sto-0.286d0) 0.083d0)
    & - 0.0045d0*dtanh((sto-0.849d0) 0.119d0)
    & - 0.035d0*dtanh((sto-0.9233d0) 0.05d0)
    & - 0.0147d0*dtanh((sto-0.5d0) 0.034d0)
    & - 0.102d0*dtanh((sto-0.194d0) 0.142d0)
    & - 0.022d0*dtanh((sto-0.9d0) 0.0164d0)
    & - 0.011d0*dtanh((sto-0.124d0) 0.0226d0)
    &    0.0155d0*dtanh((sto-0.105d0) 0.029d0)
     g1    -1.5d0*(120.0d0 ct1)*expg(-120.0d0*sto)
    &   (0.0351d0 (0.083d0*ct1))*((dcosh((sto-0.286d0) 0.083d0))**(-2))
    &-(0.0045d0 (ct1*0.119d0))*((dcosh((sto-0.849d0) 0.119d0))**(-2))
    &-(0.035d0 (ct1*0.05d0))*((dcosh((sto-0.9233d0) 0.05d0))**(-2))
    &-(0.0147d0 (ct1*0.034d0))*((dcosh((sto-0.5d0) 0.034d0))**(-2))
    &-(0.102d0 (ct1*0.142d0))*((dcosh((sto-0.194d0) 0.142d0))**(-2))
    &-(0.022d0 (ct1*0.0164d0))*((dcosh((sto-0.9d0) 0.0164d0))**(-2))
    &-(0.011d0 (ct1*0.0226d0))*((dcosh((sto-0.124d0) 0.0226d0))**(-2))
    &   (0.0155d0 (ct1*0.029d0))*((dcosh((sto-0.105d0) 0.029d0))**(-2))
c assumed temperature dependence for exchange current
     ti0n   dexp((Ebarka)*(t-298.0d0) (t*298.0d0))
     rka1   rka1save*ti0n
     dudt    0.0d0

     if(nneg.ne.0) go to 97 ! bypass new form
c    MCMB 2528 graphite measured by Chris Bogatu 2000,
c    Telcordia and PolyStor materials.
c    Modified May 2003 to match data from Joongpyo Shim
c    for 0.01    x    0.99
     sto    xx(2  mpa,j) ct1
     g0    0.124d0  1.5d0*expg(-150.0d0*sto)
    &    0.0351d0*dtanh((sto-0.286d0) 0.083d0)
    & - 0.0045d0*dtanh((sto-0.9d0) 0.119d0)
    & - 0.035d0*dtanh((sto-0.99d0) 0.05d0)
    & - 0.0147d0*dtanh((sto-0.5d0) 0.034d0)
    & - 0.102d0*dtanh((sto-0.194d0) 0.142d0)
    & - 0.022d0*dtanh((sto-0.98d0) 0.0164d0)
    & - 0.011d0*dtanh((sto-0.124d0) 0.0226d0)
    &    0.0155d0*dtanh((sto-0.105d0) 0.029d0)
     g1    -1.5d0*(150.0d0 ct1)*expg(-150.0d0*sto)
    &   (0.0351d0 (0.083d0*ct1))*((dcosh((sto-0.286d0) 0.083d0))**(-2))
    &-(0.0045d0 (ct1*0.119d0))*((dcosh((sto-0.9d0) 0.119d0))**(-2))
    &-(0.035d0 (ct1*0.05d0))*((dcosh((sto-0.99d0) 0.05d0))**(-2))
    &-(0.0147d0 (ct1*0.034d0))*((dcosh((sto-0.5d0) 0.034d0))**(-2))
    &-(0.102d0 (ct1*0.142d0))*((dcosh((sto-0.194d0) 0.142d0))**(-2))
    &-(0.022d0 (ct1*0.0164d0))*((dcosh((sto-0.98d0) 0.0164d0))**(-2))
    &-(0.011d0 (ct1*0.0226d0))*((dcosh((sto-0.124d0) 0.0226d0))**(-2))
    &   (0.0155d0 (ct1*0.029d0))*((dcosh((sto-0.105d0) 0.029d0))**(-2))
```

For positive electrode:npos

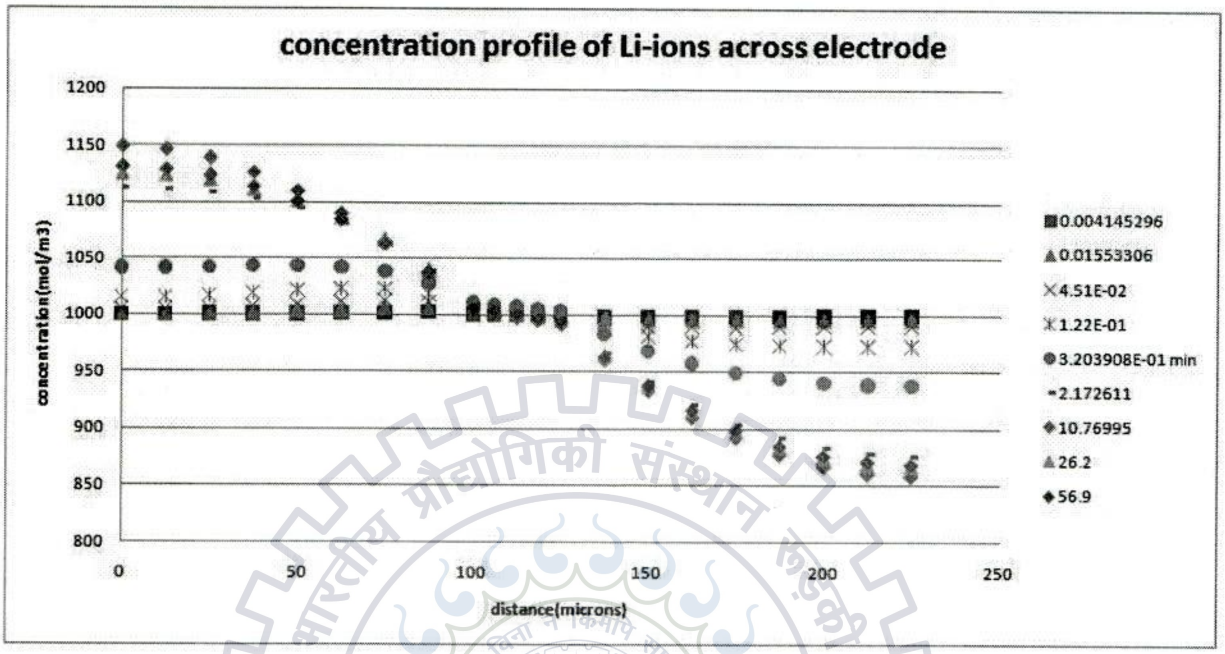
```
c    Marc Doyle's fit
c    r1   4.825510d0
c    r2   0.950237d0
c    r3   0.913511d0
c    r4   0.600492d0
c    g0   r1-r2*expg(-((xx(2  mpa,j) ct3-r3) r4)**2)
c    g1   2.0d0*r2*(xx(2  mpa,j) ct3-r3)*expg(-((xx(2  mpa,j) ct3
c   1-r3) r4)**2) r4 r4 ct3
c
c    Measured by Oscar Garcia 2001 using Quallion electrodes for
c    0.5    x    0.99   Fit revised by Karen Thomas in May 2003 to
```

```
c    match Doyle's fit for y    0.4 and Garcia's data at larger y.
c    Valid for 0    y    0.99. Note that capacity fade is found to
c    occur experimentally if y goes below 0.5; this is not included
c    in the model.
     sto    xx(2 mpa,j) ct3
     g0    2.16216d0 0.07645d0*dtanh(30.834d0-54.4806d0*sto)
     &    2.1581d0*dtanh(52.294d0-50.294d0*sto)
     & - 0.14169d0*dtanh(11.0923d0-19.8543d0*sto)
     &    0.2051d0*dtanh(1.4684d0-5.4888d0*sto)
     &    0.2531d0*dtanh((-sto 0.56478d0) 0.1316d0)
     & - 0.02167d0*dtanh((sto-0.525d0) 0.006d0)
     g1    0.07645d0*(-54.4806d0 ct3)*
     &((1.0d0 dcosh(30.834d0-54.4806d0*sto))**2)
     &  2.1581d0*(-50.294d0 ct3)*((dcosh(52.294d0-50.294d0*sto))**(-2))
     &  0.14169d0*(19.854d0 ct3)*((dcosh(11.0923d0-19.8543d0*sto))**(-2))
     &-0.2051d0*(5.4888d0 ct3)*((dcosh(1.4684d0-5.4888d0*sto))**(-2))
     &-0.2531d0 0.1316d0 ct3*((dcosh((-sto 0.56478d0) 0.1316d0))**(-2))
     & - 0.02167d0 0.006d0 ct3*((dcosh((sto-0.525d0) 0.006d0))**(-2))
c assumed temperature dependence for exchange current
     ti0p  dexp((Ebarkc)*(t-298.0d0) (t*298.0d0))
     rka3  rka3save*ti0p
```

For electrolytes:

```
c LiPF6 in EC:DMC.
c D and t+ are fit to data from J. Power Sources, vol. 82, 1999, p. 859
c for LiPF6 in EC:EMC.
c cd is from measurements made at
c Bellcore, as reported in Marc Doyle's dissertation.
c
 111 continue
    df(j) = (ee**1.5d0)*5.34d-10*expg(-0.65d0*xx(1,j)/1000.0d0)
    ddf(j) = -0.65d0*df(j)/1000.d0
    tdd=dexp((EbarD)*(t-298.0d0)/(t*298.0d0))
    df(j)=df(j)*tdd
    ddf(j)=ddf(j)*tdd
    cd(j) = (ee**1.5d0)*(0.0911d0+1.9101d0*xx(1,j)/1000.0d0 -
   & 1.052d0*((xx(1,j)/1000.0d0)**2) +
   & 0.1554d0*((xx(1,j)/1000.0d0)**3))
    dcd(j) = (ee**1.5d0)*(1.9101d0/1000.0d0 -
   & 2.0d0*1.052d0*xx(1,j)/1000.0d0/1000.0d0
   & + 0.1554d0*3.0d0*((xx(1,j)/1000.0d0)**2)/1000.0d0)
    tdkap=dexp((Ebarkap)*(t-298.0d0)/(t*298.0d0))
    cd(j)=cd(j)*tdkap
    dcd(j)=dcd(j)*tdkap
    tm(j) =0.4d0
    dtm(j) = 0.0d0
    dfu(j) = 0.0d0
    d2fu(j) = 0.0d0
```

Above values are plotted which give concentration profiles across electrode



It can be concluded from above graph the concentration of Li-ions decrease as we move from anode to cathode during discharge.

Optimization Algorithm

The optimization algorithm that is used is Multiobjective Simulated Annealing, MOSA-aJG*
Multi-Objective Simulated Annealing-aJG is developed by SankararaoBoddupalli
The code for MOSA (developed by Sankararao B) is based on the work of Suppapitnarm (2000)

It takes following input files

- Nparam :number of parameters.
- Randomseed:value of random seed which lies between 0-1
- Iterations:numberof iterations to be done.
- Ri:value of theri
- Rb:value of therb
- B:parameter for temperature(used for t=b*std)
- C:parameter c(used forna=c*nt2)
- Ss:value of the step size
- Nt :number of iterations to be performed before initial annealing schedule
- nt2 :number of iterations to be performed for the next annealing schedule
- ns1 :no of iterations to be performed before changingstep size
- pjump:jumping gene probability.

Values of above parameter are taken from txt files:

- ✓ Nparam= 6
- ✓ Randomseed= 0.888876
- ✓ Iterations=35000
- ✓ Ri= 0.9d0
- ✓ Rb=0.9d0
- ✓ B=1
- ✓ C=0.4d0
- ✓ Ss=0.5d0
- ✓ Nt=5000
- ✓ nt2=900
- ✓ ns=1200
- ✓ pjump= 0.5

2. The objective function:specific energy segment (power)

It is to be maximized using MOSA algorithms.

Code:

```
realheat,pow
double precision aobj
common heat, pow


if((x(1).le.800.01).and.(x(1).ge.800.0)) x(1)=800.0
if((x(1).ge.1099.99).and.(x(1).le.1100.0)) x(1)=1100.0

if((x(2).le.80.01d-06).and.(x(2).ge.80.0d-06)) x(2)=80.0d-06
if((x(2).ge.119.99d-06).and.(x(2).le.120.0d-06)) x(2)=120.0d-06

if((x(3).le.20.01d-06).and.(x(3).ge.20.0d-06)) x(3)=20.0d-06
if((x(3).ge.29.99d-06).and.(x(3).le.30.0d-06)) x(3)=30.0d-06

if((x(4).le.80.01d-06).and.(x(4).ge.80.0d-06)) x(4)=80.0d-06
if((x(4).ge.119.99d-06).and.(x(4).le.120.0d-06)) x(4)=120.0d-06


if((x(5).le.20.01d-06).and.(x(5).ge.20.0d-06)) x(5)=20.0d-06
if((x(5).ge.29.99d-06).and.(x(5).le.30.0d-06)) x(5)=30.0d-06


if((x(6).le.20.01d-06).and.(x(6).ge.20.0d-06)) x(6)=20.0d-06
if((x(6).ge.29.99d-06).and.(x(6).le.30.0d-06)) x(6)=30.0d-06


aobj = pow

 funct2 = 1.0/(1.0+aobj)

return
end
```

Optimization Parameters

The chosen parameters and their ranges for the current result sets are:

- **h1, thickness of negative electrode (m)**
  - ✓ Upper Range Limit – 120.0d-06
  - ✓ Lower Range Limit – 80.0d-06
- **h2, thickness of separator (m)**
  - ✓ Upper Range Limit – 30.d-06
  - ✓ Lower Range Limit – 20.d-06
- **h3, thickness of positive electrode (m)**
  - ✓ Upper Range Limit – 120.0d-06
  - ✓ Lower Range Limit – 80.0d-06
- **hcn, thickness of negative current collector (m)**
  - ✓ Upper Range Limit – 30.d-06
  - ✓ Lower Range Limit – 20.d-06
- **hcp, thickness of positive current collector (m)**
  - ✓ Upper Range Limit – 30.d-06
  - ✓ Lower Range Limit – 20.d-06
- **xi(1,1), initial salt concentration (mol/m3)**
  - ✓ Upper Range Limit – 1100
  - ✓ Lower Range Limit – 800

LINKING DUALFOIL AND OPTIMIZATION ALGORITHM

In order for the optimization to run successfully we should be able to access and use the values of the outputs given by DualFoil. We should also be able to create dynamic input parameters (which are given by the optimization algorithm), which are read by DualFoil.

MODIFICATION OF DUALFOIL FOR OPTIMIZATION

In order to optimize, DualFoil was modified in order to take inputs from the optimization algorithm, within the specified range of parameters. We first make the optimization algorithm create a temporary file called param.in, which contains a random value of all the parameters (as discussed above). The randomly generated parameter values are then written to this file.This is basically achieved by the following code:

```
open (22, file='param.in', status='old')
write(22,*) x(3)
write(22,*) x(4)
write(22,*) x(5)
write(22,*) x(6)
write(22,*) x(1)
close(22)
```

Now we should have DualFoil read the required parameters from this input file param.in instead of the default input file dualfoil.in. Hence the following modification is done to DualFoil.

```
open (8, FILE='param.in', status='old')
read (1,*) lim !limit on number of iterations
read (8,*) h1  !thickness of negative electrode (m)
read (8,*) h2  !thickness of separator (m)
read (8,*) h3  !thickness of positive electrode (m)
read (8,*) hcn !thickness of negative electrode current collector (m)
read (8,*) hcp !thickness of positive electrode current collector (m)
```

Next the optimization algorithm should be able to read the output of DualFoil before the next iteration. Hence we shall create a second output file into which the outputs that are optimization objectives are written into and saved. The optimization algorithm will access these before the next iteration of input parameters is created.

Code:

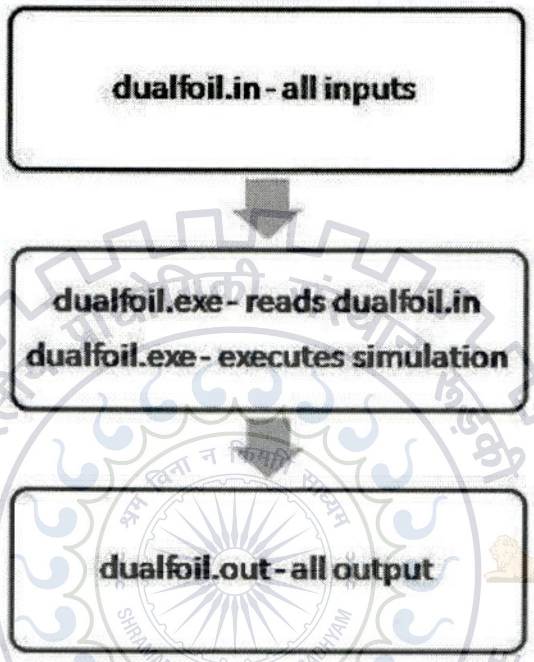
```
open (9, FILE='opti_temp.out', status='unknown')
write (2,47) heat
write (9,*) heat
write (9,*) pow
close (9)
```

Now the final step being that the optimization algorithm should be able to read this output and apply **multi-objective optimization** on it. This is done by a simple read command and then a call to DualFoil inside the optimization subroutine. Therefore all we need to do is finally run only the Optimization Program and wait for the results

```
open (23, file='opti_temp.out', status='old')
read (23, *) heat
read (23, *) pow
close(23)
```

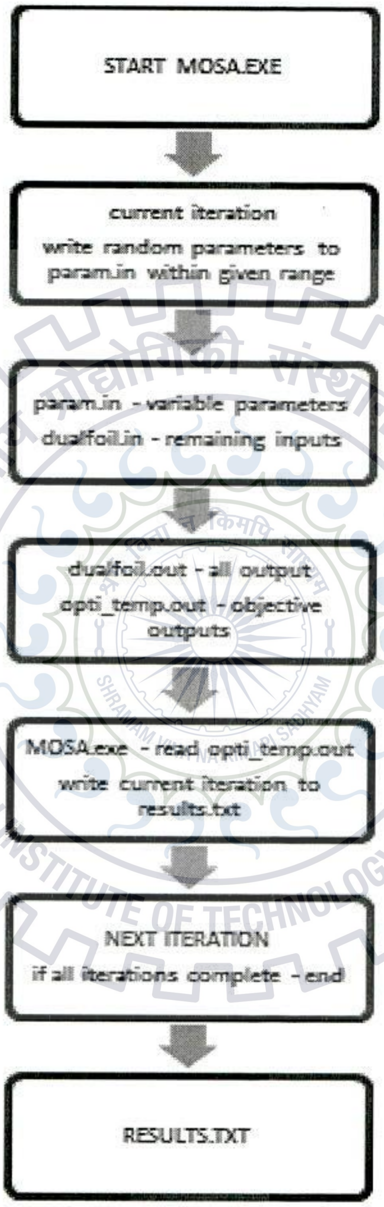
Flow Chart

Dualfoil simulation without optimization



The above flow chart clearly indicates working algorithms of code.Dualfoil code takes all properties of electrode and electrolytes from a input files. After compiling, dual foil generates output which contains detailed information of battery.

Dualfoil simulation with optimization



RESULT

After calling optimization algorithms, code takes 48-72 hours to run for 32000 iterations. MOSA code produces non-dominated files which contain both function values and solution values.

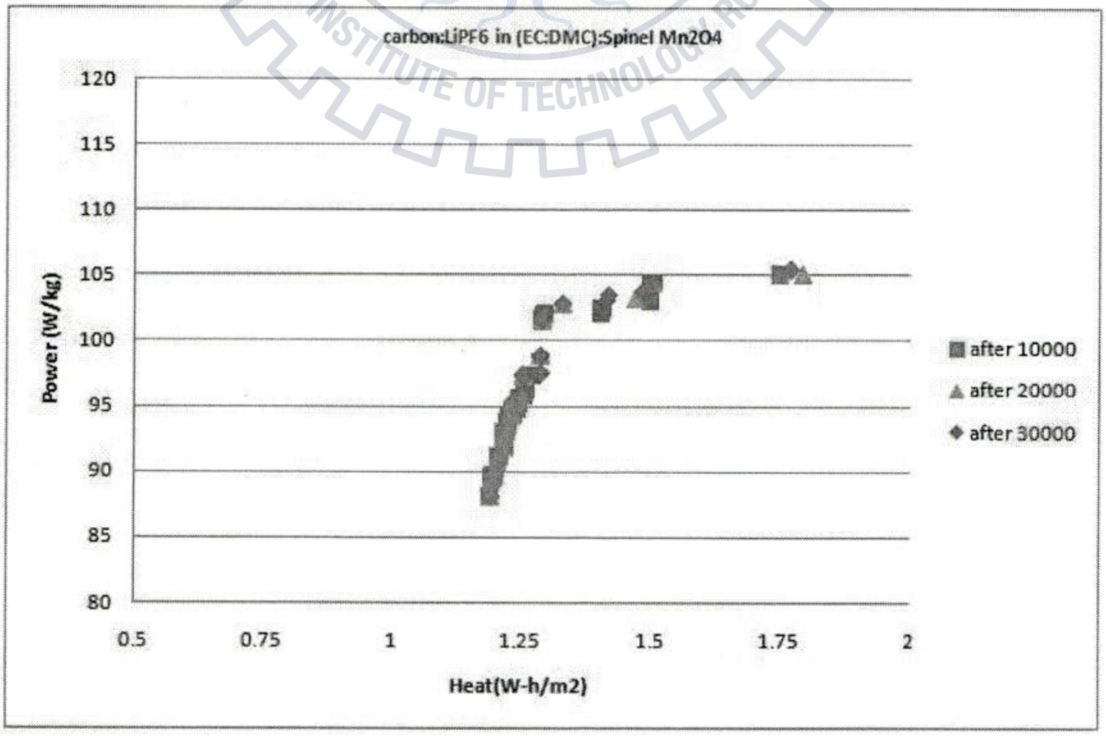
The results for different battery systems are calculated for 35000 iterations.

- ✓ **Positive electrode: carbon**
- ✓ **Electyoltes:LiPF6 in (EC:DMC)**
- ✓ **Negative electrode:Spinel Mn2O4**

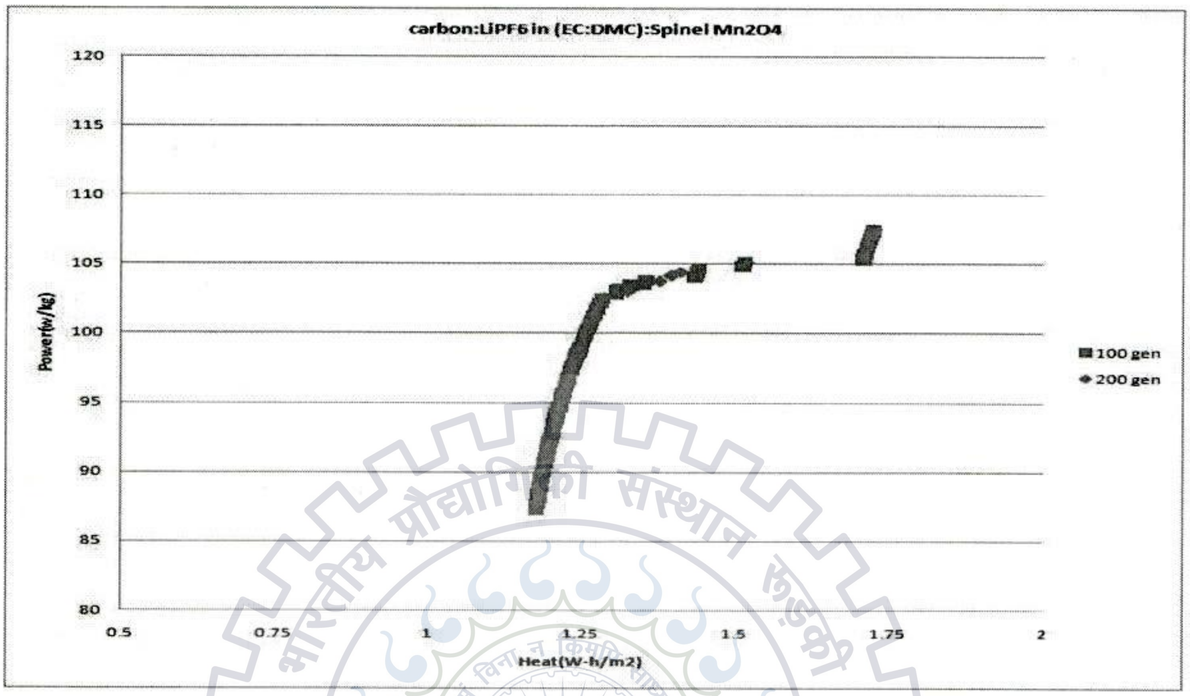
Non-dominating function values are (after 100 iterations)

HEAT	POWER
1.489590525627136	99.815921213845220
1.420394539833069	97.888957749755720
1.207918643951416	81.317205935432550
1.316052436828613	96.062127239203990
1.311259150505066	91.387703934437640
1.208947777748108	91.112481389152830
1.312312841415405	94.894644622483910

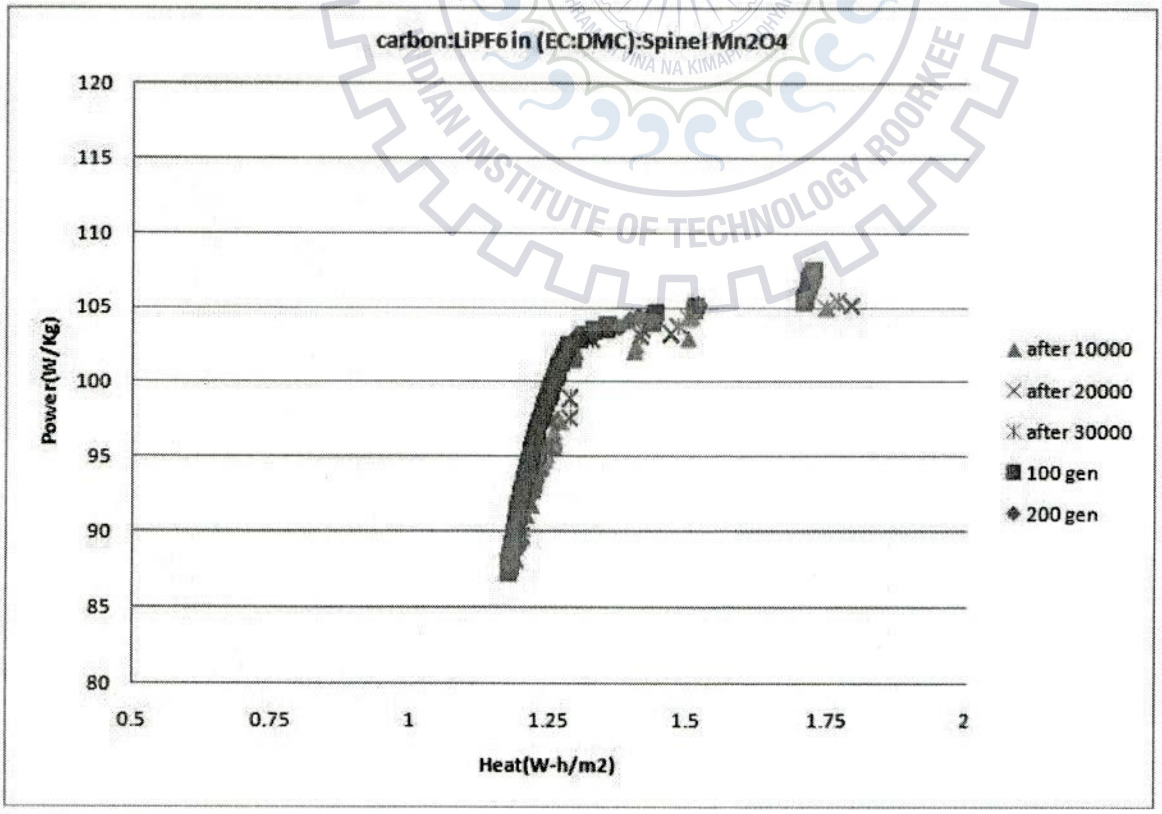
Similar values are obtained after 10000, 20000 and30000 iteration .When it is plotted give following curves.



The same battery is optimized using NSGA-II,we get following curve



Both the curve on



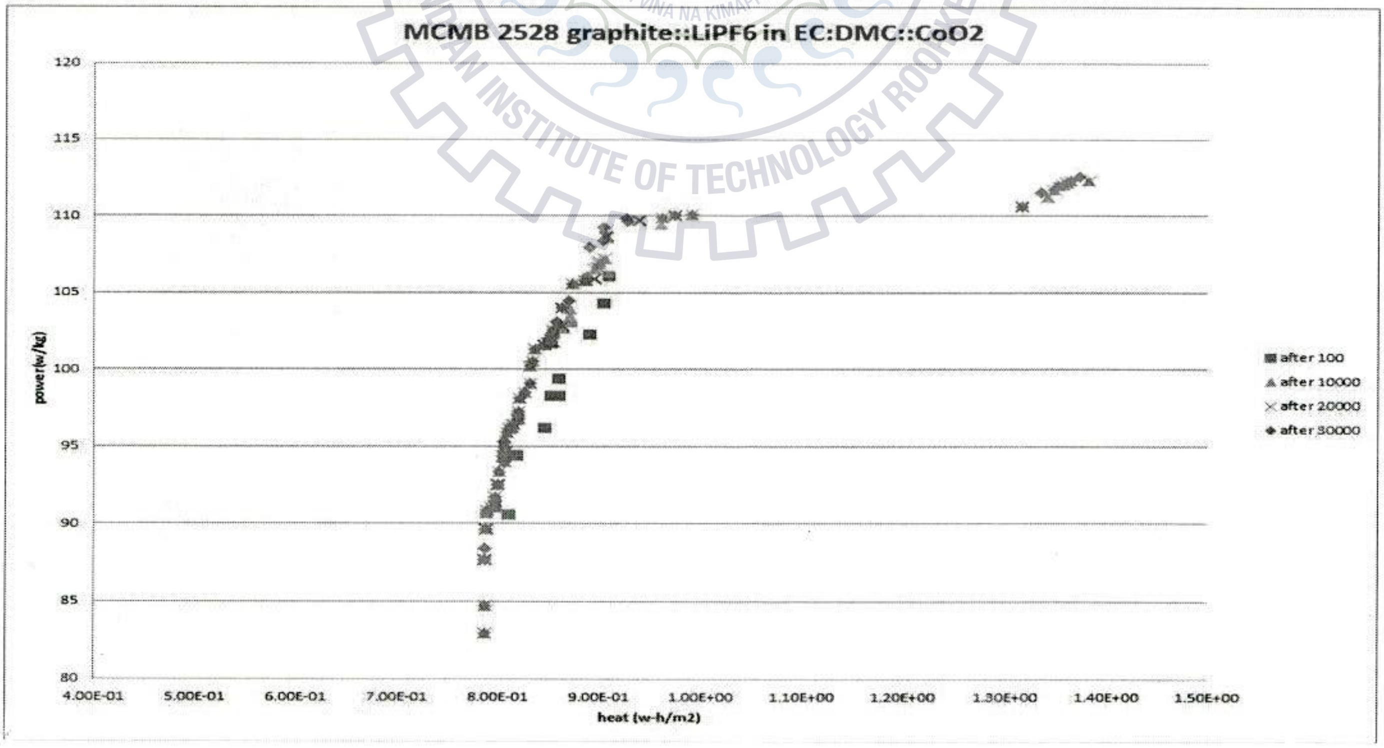
Both curves clearly indicate Power and Heat are optimizing and we are getting pareto curve.

- ✓ **Negative electrode:MCMB 2528 graphite**
- ✓ **Electrolytes: LiPF6 in EC:DMC**
- ✓ **Positive electrode: CoO2**

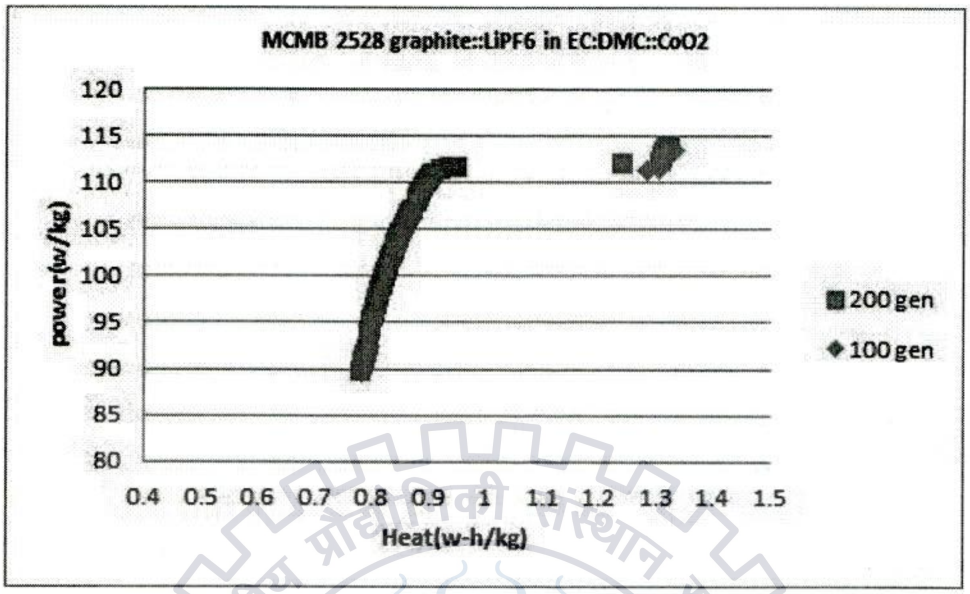
Non-dominating function values are (after 100 iterations)

Heat	POWER
8.60E-01	99.37307
8.60E-01	98.24367
8.91E-01	102.2334
9.05E-01	104.2941
8.18E-01	94.39208
8.53E-01	98.2387
8.46E-01	96.14845
9.10E-01	106.0285
8.11E-01	90.5434

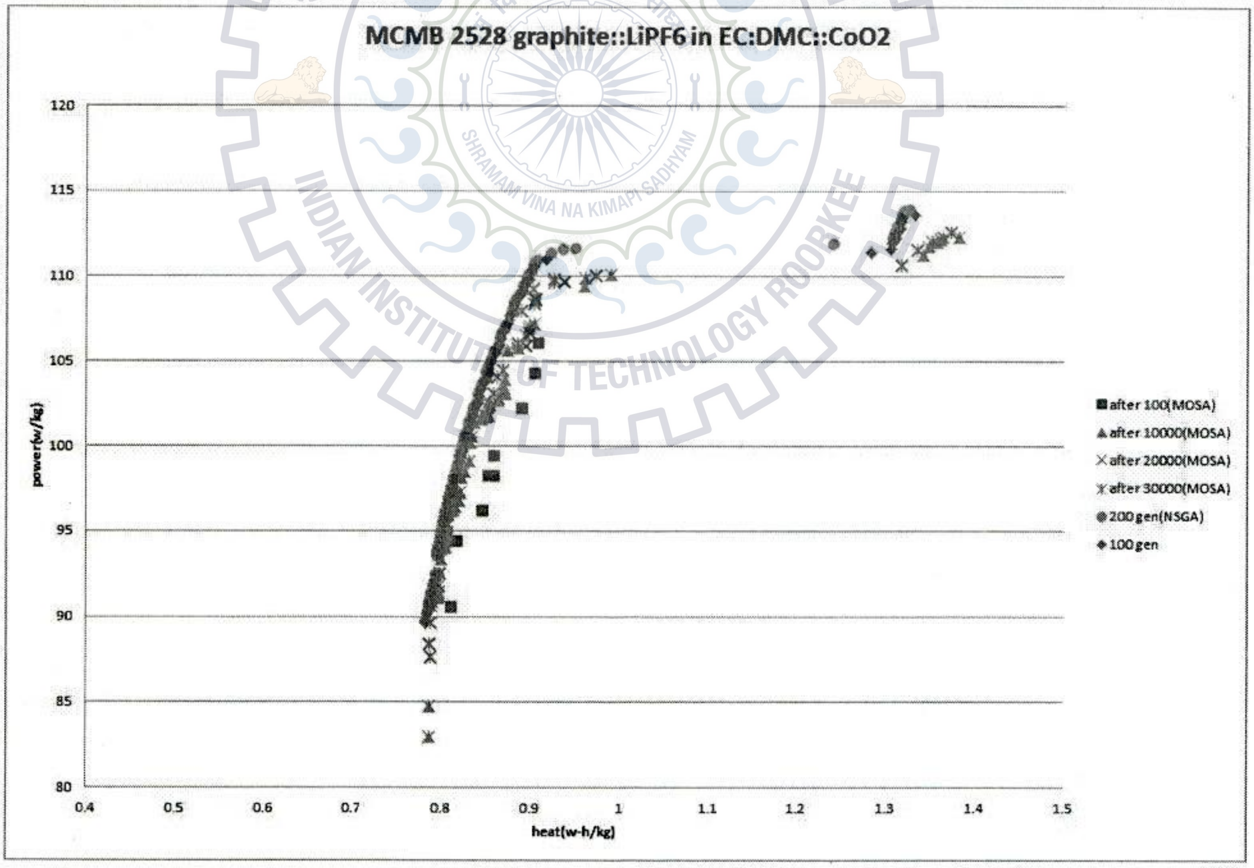
Similar values are obtained after 10000, 20000 and30000 iteration .When it is plotted give following curves.



The same battery is optimized using NSGA-II,we get following curve



Both the curve on



CONCLUSION

The basic operating principles and applications of Li-ion batteries were understood. An idea of the current status and design methodology of Li-based batteries was also studied. We have successfully carried out the multi-objective optimization of an industrially accepted model of the Lithium Ion Battery, using the Multi Objective Simulated Annealing. As per as our expectation we are getting pareto curve.

FUTURE RESEARCH PROSPECTS

There seems to be great scope in the use of various Polymer Based blends, gels and nano-composites as the electrolytic medium in various Li-based battery systems. Using the DualFoil program, one can simulate these systems for industrial or research oriented use. Also using different algorithms like neural network, it can be optimized.

The new electrodes and electrolytes can be added in the main program in the subroutines nneg, npos and nprop respectively. For electrolytes, four parameters are needed i.e diffusion coefficient of salt, conductivity of the salt, transference number of lithium and activity factor for the salt.

REFERENCES

DualFoil

- Original Source Code - www.cchem.berkeley.edu/jsngrp/fortran.htm
- Introduction to DualFoil 5 www.cchem.berkeley.edu/jsngrp/fortran_files/Intro_Dualfoil5.pdf

Mosa code

http://www.iitk.ac.in/che/faculty/skgupta/MOSA_aJG.txt

Theory

Design and Simulation of Lithium Rechargeable Batteries

- C. M. Doyle, University of California (PHD Thesis)