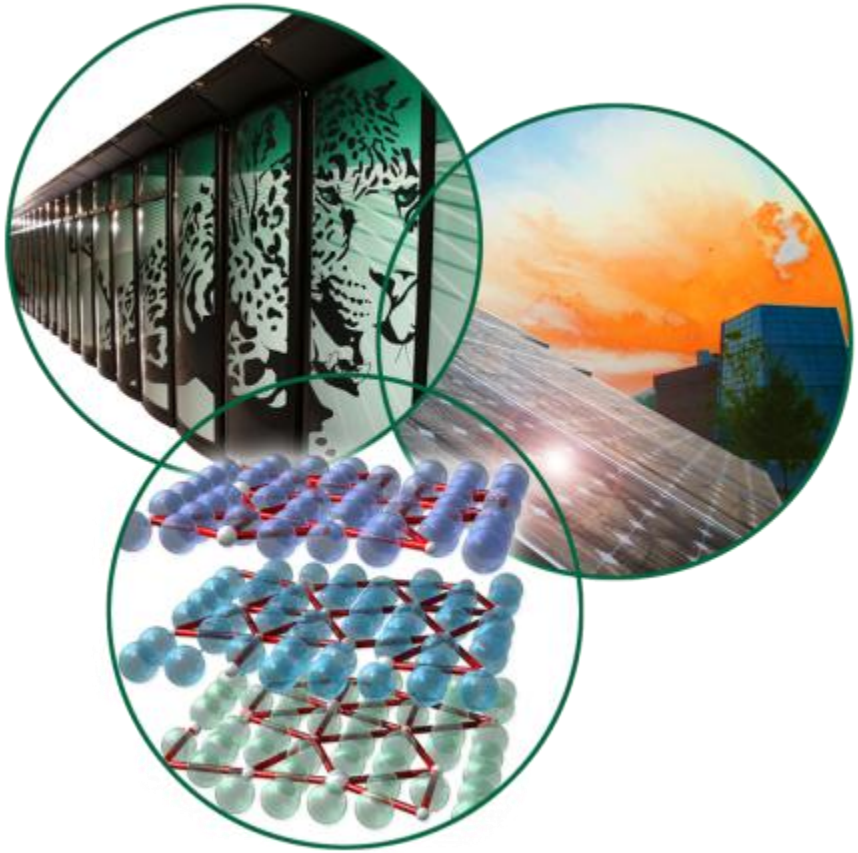
Thermo-electrochemical Modeling of Li-Ion Batteries – Demonstration Problem



ORNL OAS/CAEBAT Team

OAS Kick-off meeting

August 2, 2011

ORNL

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Volume Averaged Modeling Formulation in Li-Ion Batteries

Species Conservation

Electrolyte phase:

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \nabla \cdot \left(D_e^{eff} \nabla c_e\right) + \frac{1 - t_+^0}{F} j^{Li} - \frac{i_e \cdot \nabla t_+^0}{F}$$

Solid phase:

$$\frac{\partial(\varepsilon_s c_s)}{\partial t} = \nabla \cdot \left(D_s^{eff} \nabla c_s\right) - \frac{j^{Li}}{F}$$

Closures:

$$D_e^{eff} = D_e \varepsilon_e^{\xi} \qquad D_s^{eff} = D_s \varepsilon_s^{\zeta}$$

Charge Conservation

Electrolyte phase:

$$\nabla \cdot \left(\kappa^{eff} \nabla \phi_e\right) + \nabla \cdot \left(\kappa_D^{eff} \nabla \ln c_e\right) + j^{Li} = 0$$

Solid phase:

$$\nabla \cdot \left(\sigma^{eff} \nabla \phi_s\right) - j^{Li} = 0$$

Closures:

$$\kappa^{eff} = \kappa \varepsilon_e^{1.5} \qquad \kappa_D^{eff} = \frac{2RT\kappa^{eff}}{F}(t_+^0 - 1)\left(1 + \frac{d \ln f_{\pm}}{d \ln c_e}\right) \qquad \sigma^{eff} = \sigma \varepsilon_s^{m}$$

Electrode Kinetics

$$\bar{j} = a i_0 \left[\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta\right)\right] \qquad \eta = \phi_s - \phi_e - U$$

Volume Averaged Modeling Formulation in Li-Ion Batteries (2)

Thermal Energy Conservation

$$\frac{\partial(\rho c_p T)}{\partial t} = \nabla\cdot(\lambda\nabla T) + q$$

$$\rho c_p = \sum_k \varepsilon_k \rho_k c_{p,k}$$

$$\lambda = \sum_k \varepsilon_k \lambda_k$$

Heat Source:

$$q = \sum_j a_{sj} i_{nj}(\phi_s - \phi_e - U_j) + \sum_j a_{sj} i_{nj} T \frac{\partial U_n}{\partial T} + \sigma^{eff}\nabla\phi_s\cdot\nabla\phi_s + \kappa^{eff}\nabla\phi_e\cdot\nabla\phi_e + \kappa_D^{eff}\nabla\ln c_e\cdot\nabla\phi_e$$

Irreversible Heat | Reversible Heat | Ohmic Heat in Matrix Phase | Ohmic Heat in Solution Phase

Note on Solid Phase Diffusion Modeling:

Volume averaged approach:

$$\frac{\partial(\varepsilon_s c_s)}{\partial t} = \nabla\cdot(D_s^{eff}\nabla c_s) - \frac{j^{Li}}{F}$$

- Duhamel superposition method (Doyle *et al.*, *JES* 1993, 1994)
- Polynomial approximation (Subramanian *et al.*, *JES* 2005)
- Pseudo steady state approach (Liu, *Solid State Ionics* 2006)

Pseudo-2D approach:

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_s \frac{\partial c_s}{\partial r}\right)$$

at $t = 0$ for $0 \le r \le R_s$ $c_s = c_{s0}$

$$\left.\frac{\partial c_s}{\partial r}\right|_{r=0} = 0$$

$$j(t) = -D_s \left.\frac{\partial c_s}{\partial r}\right|_{r=R_s}$$

Operator splitting approach:
*(Wang *et al.*, *JES* 1998, *JPS* 2002)

$$c_s(t) = c_{avg}(t) + \frac{i(t) l_s}{nFD}\left[1 - e^{-4\sqrt{Dt}/3l_s}\right]$$

$$\frac{\partial(\varepsilon_s c_s)}{\partial t} = \frac{j^{Li}}{F}$$

$$\frac{D_s}{l_{se}}(\bar{c}_{se} - c_s) = \frac{j^{Li}}{a_s F}$$

Thermal-Electrochemical Coupling

Heat Generation Rate:

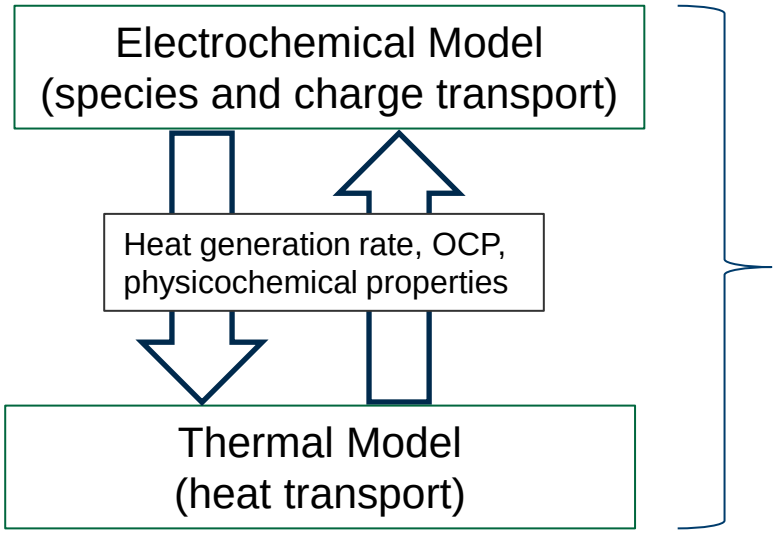
$$q = \sum_j a_{sj} i_{nj} \left(\phi_s - \phi_e - U_j\right) + \sum_j a_{sj} i_{nj} T \frac{\partial U_n}{\partial T} + \sigma^{eff} \nabla \phi_s \cdot \nabla \phi_s + \kappa^{eff} \nabla \phi_e \cdot \nabla \phi_e + \kappa_D^{eff} \nabla \ln c_e \cdot \nabla \phi_e$$

Temperature dependent physicochemical properties

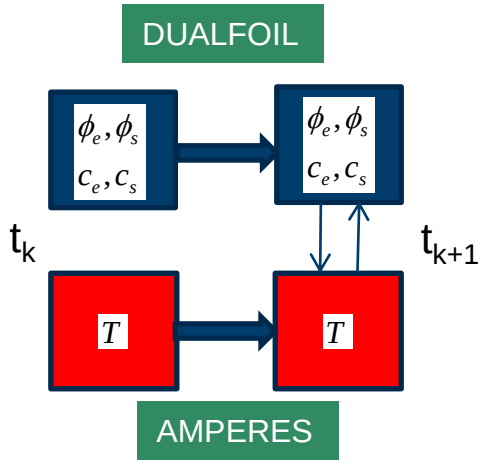
$$\Gamma = \Gamma_{ref} \exp\left[\frac{E_{act,\Gamma}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$

Temperature dependent open circuit potential (OCP)

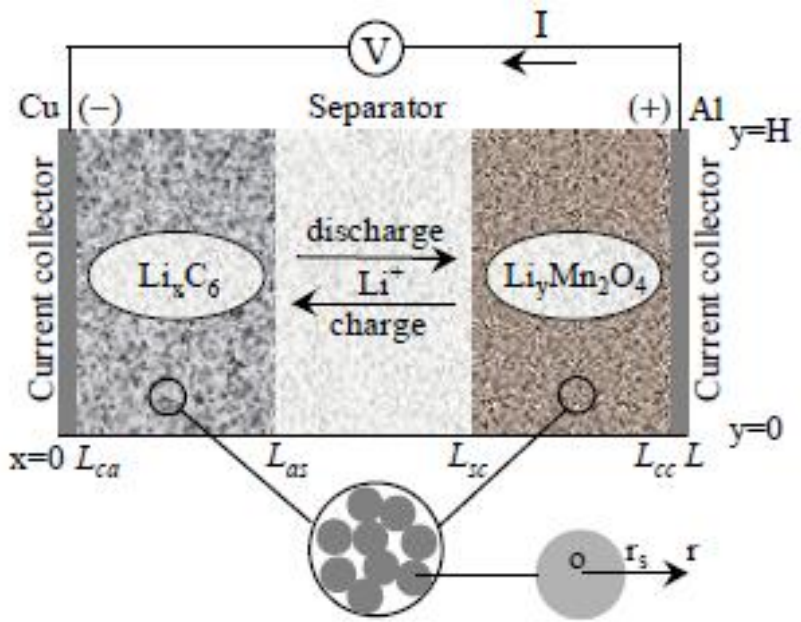
$$U_j = U_{j,ref} + \left(T - T_{ref}\right)\frac{\partial U_j}{\partial T}$$



Two-way, loose coupling



Thermo-Electrochemical Modeling in LIBs – Problem Definition



Composite positive electrode

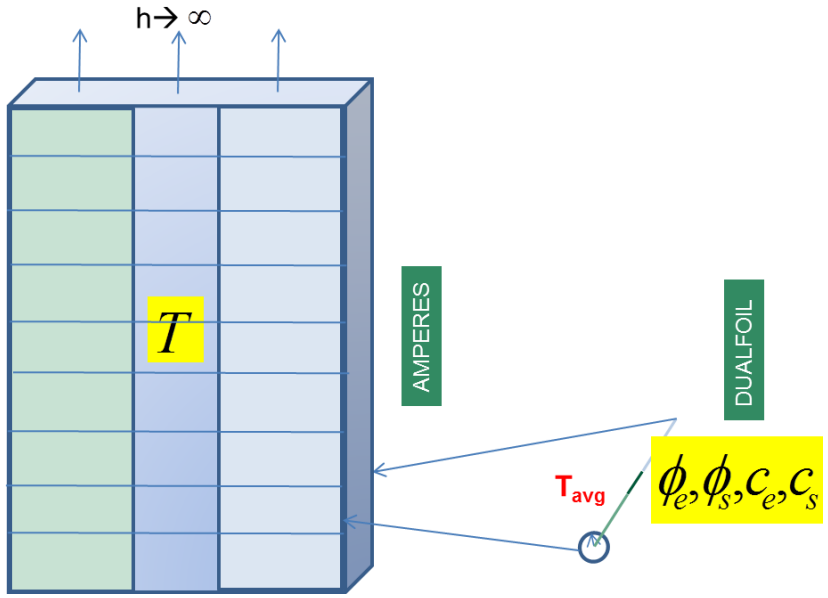
$$Li_{y-x}Mn_2O_4 + xLi^+ + xe^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Li_yMn_2O_4$$

Composite negative electrode

$$Li_xC_6 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Li_0C_6 + xLi^+ + xe^-$$

Initial test case configuration:

March 09, 2011 Meeting



Assumptions:

1. Concentrated binary electrolyte
2. No side reactions
3. No gas phase
4. Volume change negligible

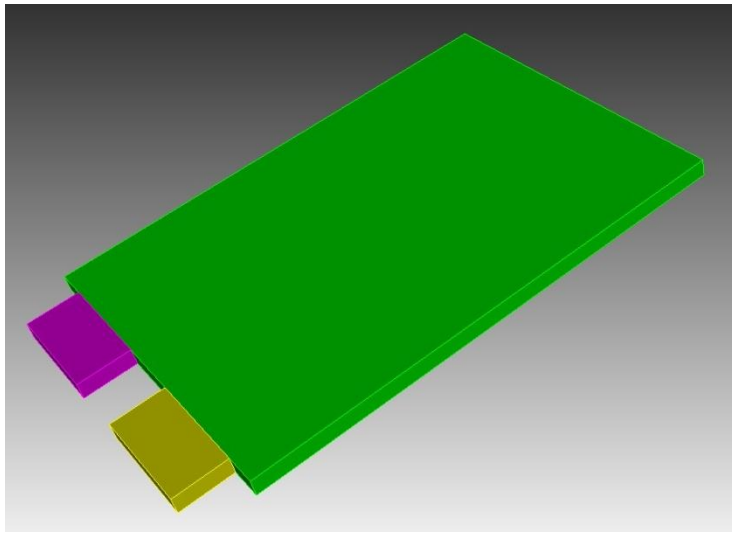
Thermal Sources:

$$q = \sum_j a_{sj} i_{nj} \left(\phi_s - \phi_e - U_j\right) + \sum_j a_{sj} i_{nj} T \frac{\partial U_n}{\partial T} + \sigma^{eff} \nabla\phi_s \cdot \nabla\phi_s + \kappa^{eff} \nabla\phi_e \cdot \nabla\phi_e + \kappa_D^{eff} \nabla \ln c_e \cdot \nabla\phi_e$$

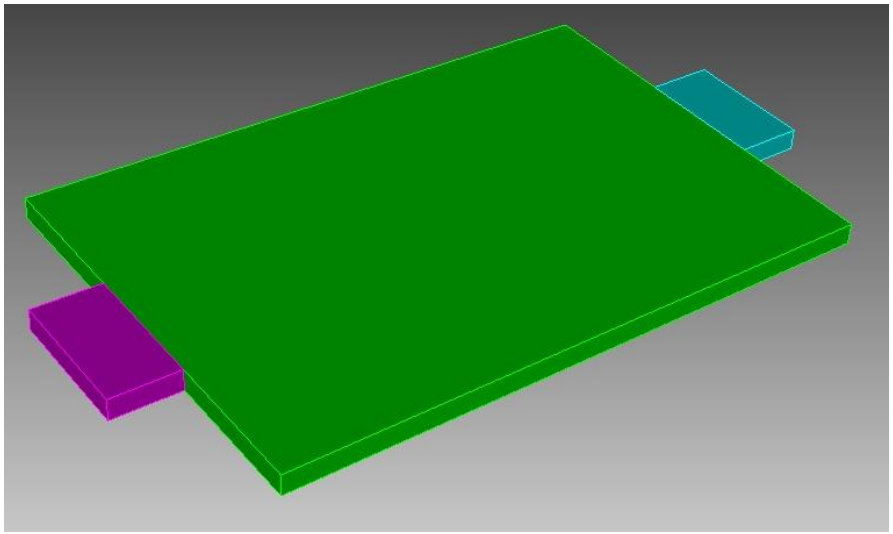
Irreversible Heat | Reversible Heat | Ohmic Heat in Matrix Phase | Ohmic Heat in Solution Phase

*Srinivasan and Wang, "Analysis of Electrochemical and Thermal Behavior of Li-Ion Cells," *Journal of the Electrochemical Society*, **150**, A98 (2003).

Battery Geometry



Co-tab prismatic cell



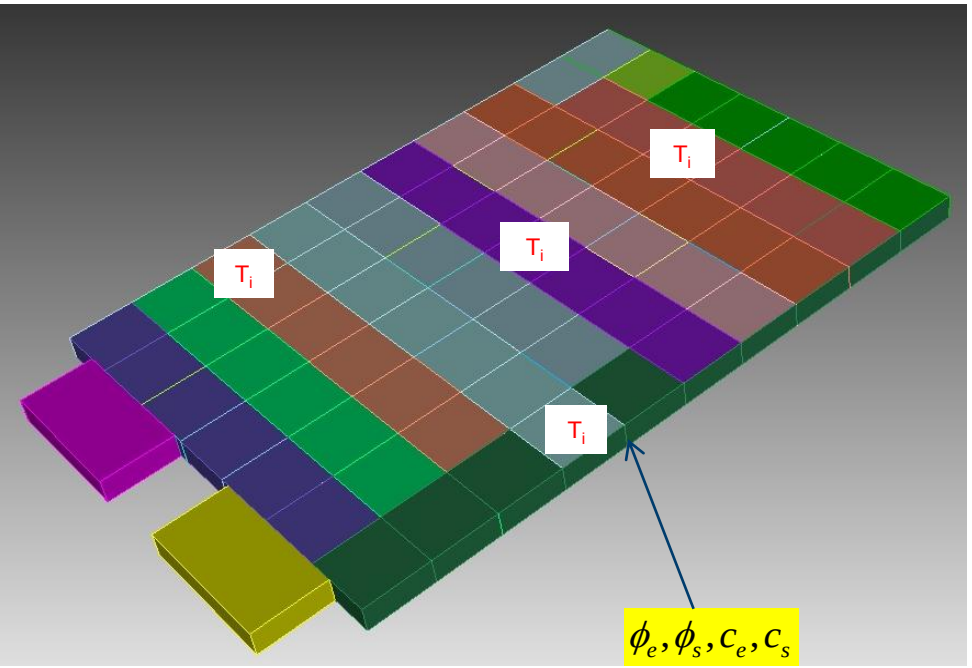
Counter-tab prismatic cell

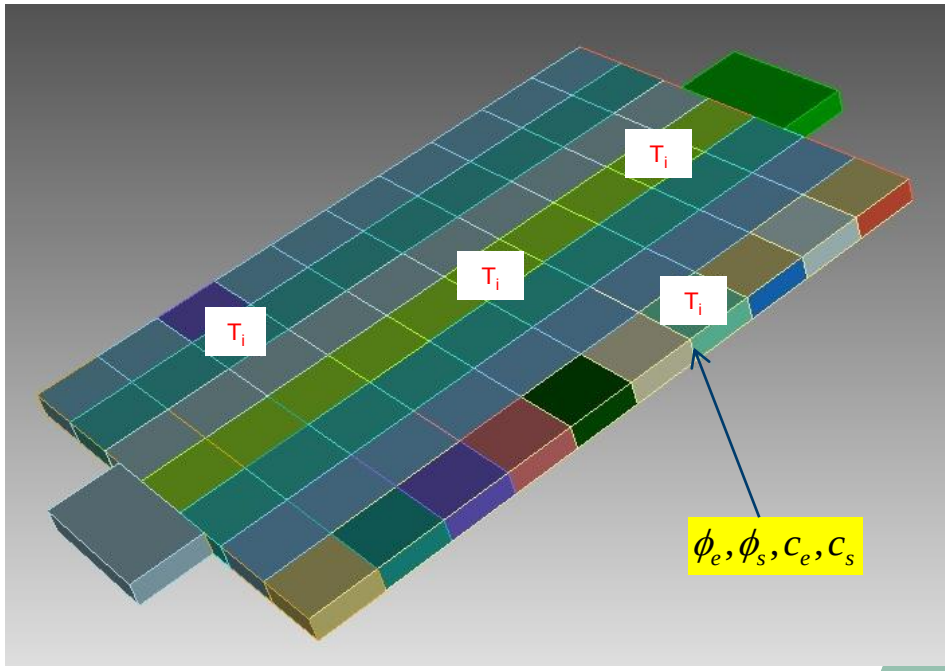
- Co-tabbed and Counter-tabbed design
  - Cooling condition on top surface, adiabatic condition on all other surfaces
- Geometry and mesh created using CUBIT
  - CUBIT → Geometry and mesh generation toolkit from Sandia (http://cubit.sandia.gov/)
- Parametric journal file (or Python script) can be used to automate the geometry and mesh generation for typical battery configurations

*Kim *et al*., "Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales," *Journal of the Electrochemical Society*, **158**, A955 (2011).

Solution Methodology

- Zonal segmentation
- DUALFOIL solves for potential and concentration in the cell sandwich direction
- AMPERES solves for temperature in the segmented blocks with heat source terms calculated from potential and species distributions from DUALFOIL
- Two-way, loose coupling approach





Solution Methodology (2)

DUALFOIL Inputs

```
.true.   ! restart, set to true when this is a restart
50       ! lim,  limit on number of iterations
128.0d-06 ! h1,   thickness of negative electrode (m)
76.d-06  ! h2,   thickness of separator (m)
190.0d-06 ! h3,   thickness of positive electrode (m)
10.d-06  ! hcn,  thickness of negative current collector (m)
15.d-06  ! hcp,  thickness of positive current collector (m)
40       ! n1,  number of nodes in negative electrode(set=0 if in foil mode)
20       ! n2,   number of nodes in separator
40       ! n3,   number of nodes in positive electrode
100      ! n4,   number of nodes in solid particle
0                    ! mvdc1, flag for variable solid diff coeff in anode
0        ! mvdc3, flag for variable solid diff coeff in cathode
20                   ! lims, number of iterations for solid phase convergence
298.15d0   ! T,    temperature (K)
2000.0   ! xi(1,1), initial salt concentration (mol/m3),
0.5635     ! x,    initial stoichiometric parameter for neg. (ignored if n1=0)
0.1705     ! y,    initial stoichiometric parameter for pos.
30.0d0   ! tmmax, maximum time step size (s)
3.9d-14  ! dfs1, diffusion coef. in negative solid (m2/s)
1.0d-13  ! dfs3, diffusion coef. in positive solid (m2/s)
12.5d-6   ! Rad1, radius of negative particles (m) (ignored in Foil mode)
8.5d-6   ! Rad3, radius of positive particles (m)
0.357    ! ep1,  volume fraction of electrolyte in negative electrode
0.146d0    ! epp1, volume fraction of polymer in negative electrode
0.026    ! epf1, volume fraction of inert filler in negative electrode
0.0d0    ! epg1, volume fraction of gas in negative
1.0      ! ep2,  ep2+epp2=1.0  volume fraction of electrolyte in separator
0.0d0    ! epp2, volume fraction of polymer in separator
0.0d0    ! epg2, volume fraction gas in separator
0.444    ! ep3,  volume fraction of electrolyte in positive electrode
0.186d0    ! epp3, volume fraction of polymer in positive electrode
0.073    ! epf3, volume fraction of inert filler in positive electrode
0.0d0    ! epg3, volume fraction of gas in positive
100.0d0  ! sig1, conductivity of negative matrix (S/m) (ignored in Foil mode)
3.8d0    ! sig3, conductivity of positive matrix (S/m)
1.0d-5   ! rka1, rate constant for negative reaction
3.d-11   ! rka3, rate constant for positive reaction
0.000d0  ! ranode, anode film resistance (ohm-m2)
0.000d0  ! rcathde, cathode film resistance (ohm-m2)
1324.0   ! re,   density of electrolyte (kg/m3)
1800.0   ! rf,   density of inert filler (kg/m3)
1780.0   ! rpl,  density of polymer material (kg/m3)
0.0d0    ! rc,   density of inert separator material (kg/m3)
9000.0   ! rcn,  density of negative current collector (kg/m3) [copper foil]
2700.0   ! rcp,  density of positive current collector (kg/m3) [aluminum foil]
0.0d0    ! htc,  heat-transfer coefficient at ends of cell stack (W/m2K)
2000.0d0 ! Cp,   heat capacity of system (J/kg-K)
298.15d0   ! Tam,  ambient air temperature (K)
1        ! ncell, number of cells in a cell stack
2        ! lht,  0 uses htc,  1 calcs htc,  2 isothermal
1        ! il1,  1 for long print-out  0 for short print-out
1        ! il2,  prints every il2 th node in long print-out
1        ! il3,  prints every il3 th time step in long print-out
0        ! imp,  0 for no impedance, 1 for impedance
0.0d0    ! capp1, capacitance of negative material (F/m2)
0.0d0    ! capp3, capacitance of positive material (F/m2)
0        ! jsol,  calculate solid profiles if 1 < jsol < nj
0        ! nside, flag to turn on (1) or off (0) side reactions
0.0d0    ! rksa1, rate constant side reaction 1 negative (ignored if nside=0)
0.0d0    ! rksc1, rate constant side reaction 1 positive (ignored if nside=0)
0.0d0    ! rksa2, rate constant side reaction 2 negative (ignored if nside=0)
0.0d0    ! rksc2, rate constant side reaction 2 positive (ignored if nside=0)
0.0d0    ! rksa3, rate constant side reaction 3 negative (ignored if nside=0)
0.0d0    ! rksc3, rate constant side reaction 3 positive (ignored if nside=0)
2        ! nneg,  see below
5        ! nprop, see below
3        ! npos,  see below
1        ! lcurs, number of current changes
10.d0 1.0d0 1 2.d0 4.3d0 !Discharge for 5.0 min or to a cutoff of 3 V at 10 A/m2
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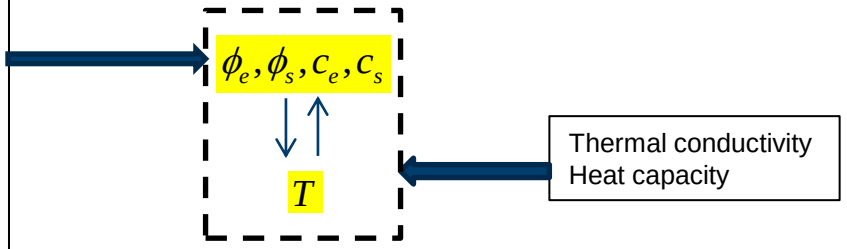

AMPERES Inputs

Thank You!