



# THERMO-ELECTROCHEMICAL TESTING AND SIMULATION OF LITHIUM-ION BATTERIES OPERATING IN RADIATION DRIVEN SPACE ENVIRONMENTS

*~2015 International Conference and Exhibition on Satellite~*

PREPARED BY: WILLIAM Q. WALKER

NASA JOHNSON SPACE CENTER  
STRUCTURAL ENGINEERING DIVISION-ES  
THERMAL DESIGN BRANCH-ES3

PH.D. CANDIDATE MATERIALS SCIENCE AND ENGINEERING  
UNIVERSITY OF HOUSTON

WILLIAM.WALKER@NASA.GOV  
281.483.0434

## PRESENTATION OVERVIEW

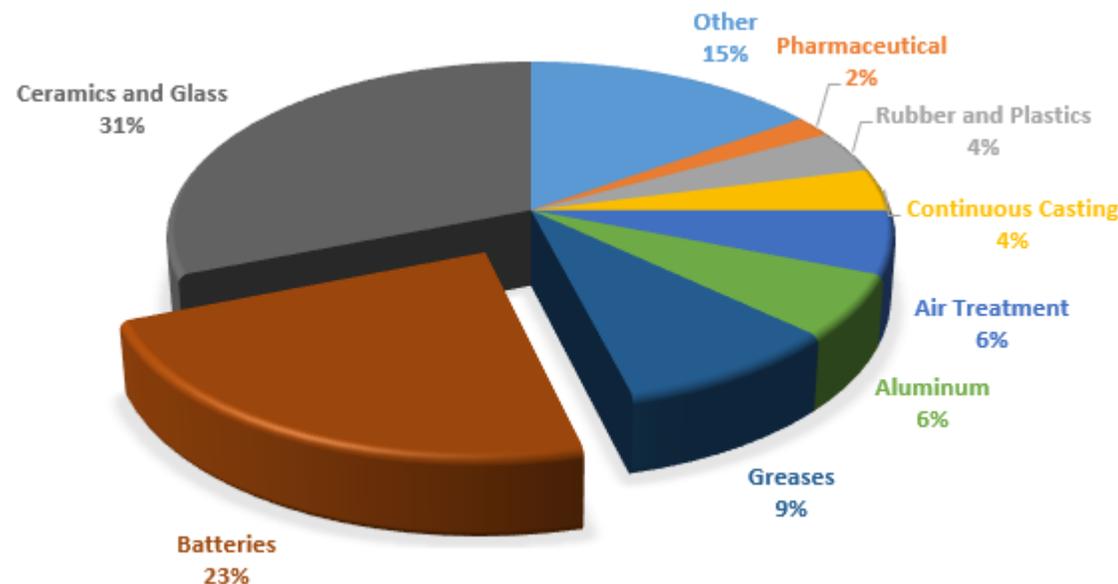
- **Section 1: Lithium-ion Battery Market Characteristics**
- **Section 2: Lithium-ion Battery Fundamentals**
- **Section 3: Understanding Battery Heat Generation**
- **Section 4: Computational Analysis Techniques Part 1: Charge-Discharge Operations**
- **Section 5: Computational Analysis Techniques Part 2: Thermal Runaway Mechanisms**



# SECTION 1: LITHIUM-ION BATTERY MARKET CHARACTERISTICS

## LITHIUM-ION BATTERY MARKET CHARACTERISTICS

- **Global energy crisis drives the battery market**
- **Lithium (Li) provides energy dense and low mass solutions for a wide array of applications**
- **Growing demand for advanced energy storage (AES) and power management systems drives the Li-ion battery market today [1]**
  - Strong growth for use of Li-ion batteries could strain the available supply for other industries
- **The Li-ion battery market (2012) was \$11.7 billion United States Dollar (USD) globally [2]:**
  - Medical and industrial
  - Railway and automobile
  - Aerospace and defense
- **Based on current and past performance, predictions indicate exponential growth in the total Li-ion battery market [1-4]:**
  - Double to \$22.5 billion USD by 2016
  - Triple to \$43 billion USD by 2020



Lithium battery end use breakdown based on data from Roskill Information Services LTD. 2009 estimates [1]



Various battery Li-ion battery manufacturers. Note that the presence of any logo in no way indicates any preference of the presenter or their affiliation [5-15]

## LITHIUM-ION BATTERY MARKET CHARACTERISTICS: BATTERIES AND SPACE EXPLORATION

- **Aerospace and space exploration applications rely on AES and power management systems**
  - Mission longevity and success depends on lightweight, safe, reliable and efficient AES
- **Energy in space is limited to finite quantities of resources [20]:**
  - Fuel is limited by storage tank size and launch mass limits
  - Cost per pound to orbit ranges between \$10k to \$55k
- **Traditional alkaline based nickel cadmium (NiCd), nickel-metal hydride (NiMH) and nickel hydrogen (NiH<sub>2</sub>) batteries face replacement with Li-ion systems [2]:**
  - Li-ion batteries offer more the double the performance for half the mass of their alkaline counterparts
  - Li is the lightest metal with an atomic mass of 6.94 amu
  - The International Space Station (ISS) begins replacing NiH<sub>2</sub> batteries with Li-ion batteries in November 2016
- **The number of international partners and new private companies in the space industry are growing [21-32]**
- **Space industry growth equates to increased usage and development of advanced Li-ion batteries**

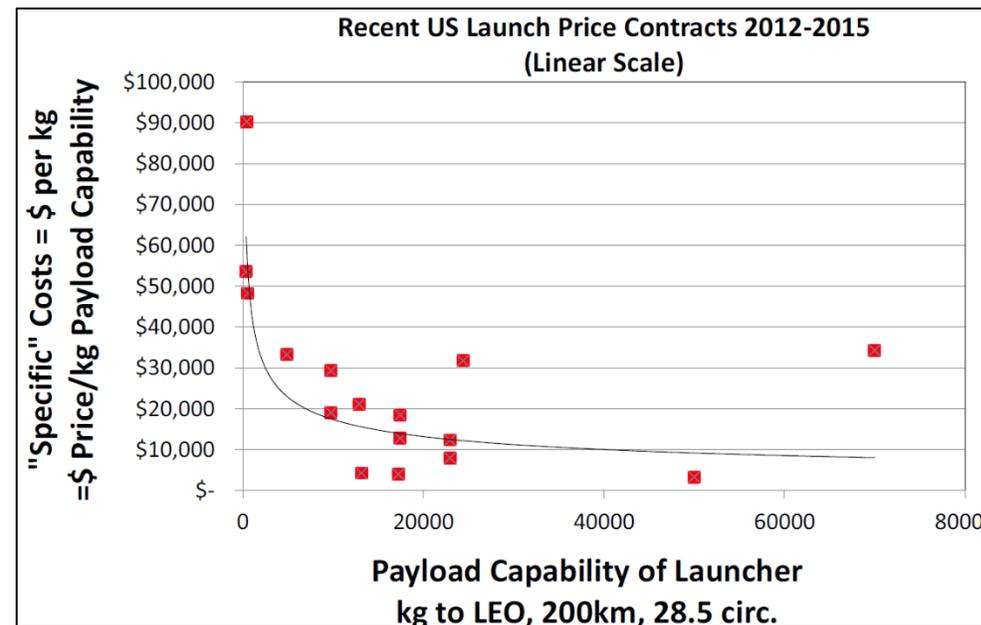
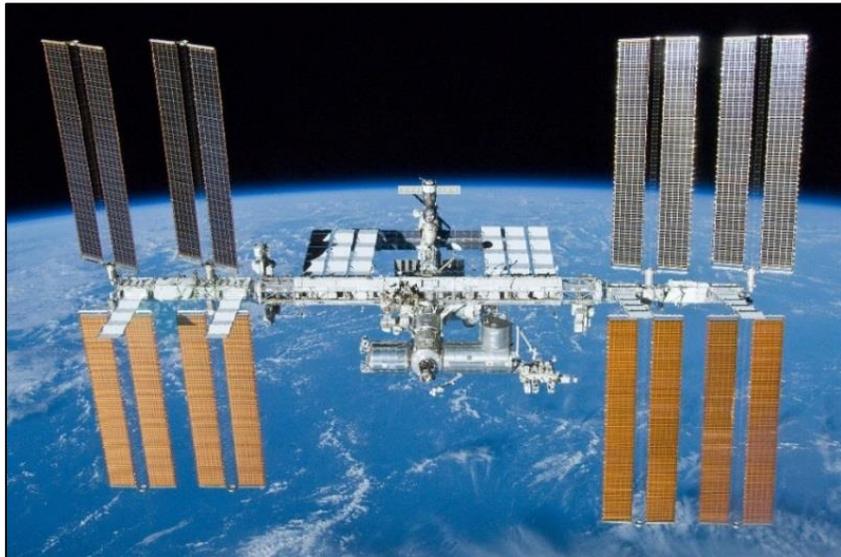


Chart from "An Analysis and Review of Measures and Relationships in Space Transportation Affordability" by E. Zapata and C. McCleskey [20]



Images retrieved online from company websites. Examples of national agencies and various companies involved in space exploration. This list is not comprehensive and does not indicate any opinion or preference of the presenter or his affiliation [21-32]

# LITHIUM-ION BATTERY MARKET CHARACTERISTICS: BATTERIES AND SPACE EXPLORATION



International Space Station



Orion



SpaceX Dragon



Resource Prospector



Extra-Vehicular Mobility Unit



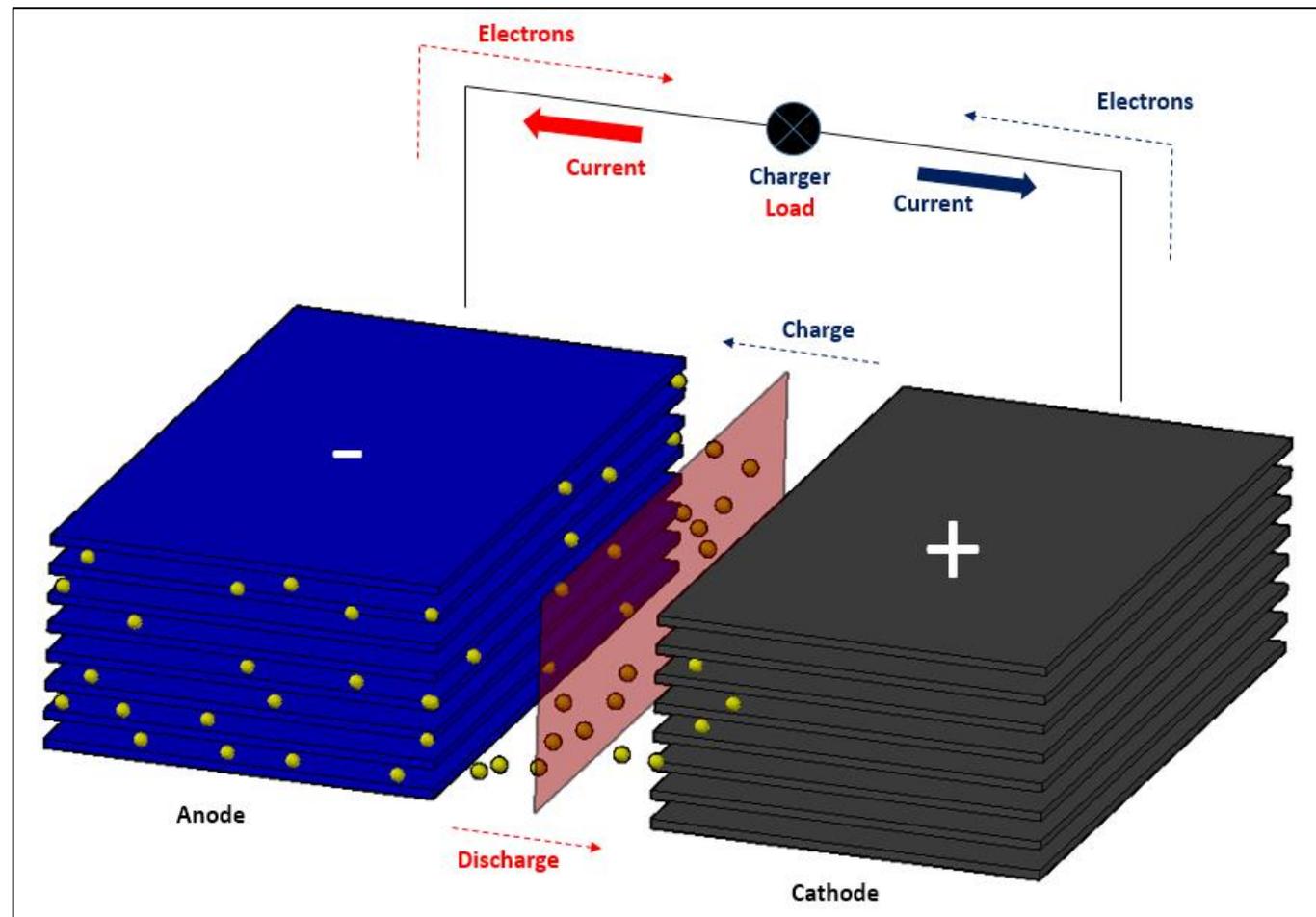
Robonaut 2



## SECTION 2: LITHIUM-ION BATTERY FUNDAMENTALS

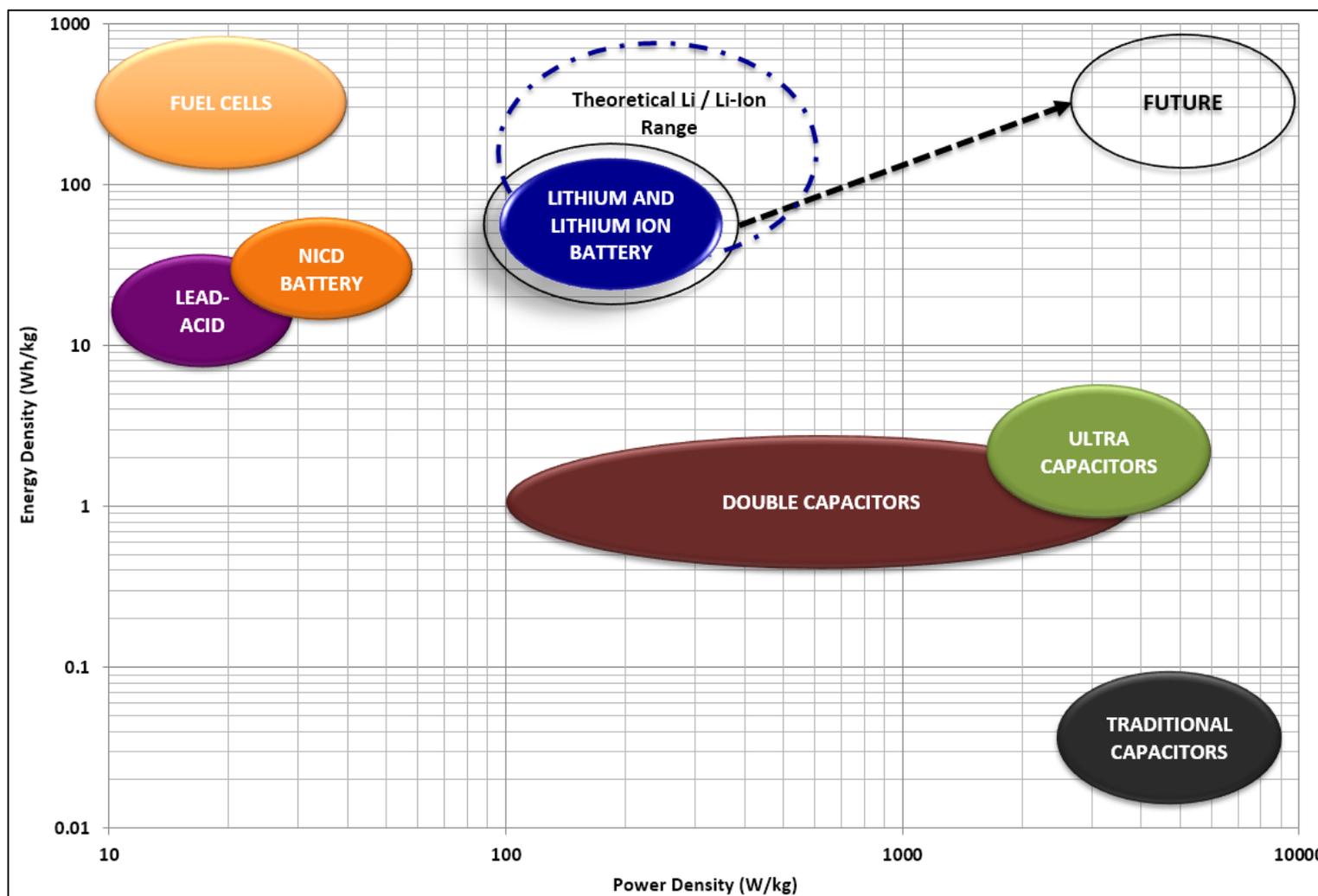
## LITHIUM-ION BATTERY FUNDAMENTALS

- The primary components of Li-ion batteries are the anode, cathode, electrolyte and separator
- Li ions intercalate/de-intercalate between the anode and cathode (i.e. electrodes) during discharge/charge respectively
  - Intercalation refers to the insertion and extraction of ions between the layers of cathode/anode materials
- Need an ion-conductive and electrically insulative separator to prevent shorting
  - Thin polymer film
- Electrons flow through an external circuit
- Coulomb (C-Rate): charge/discharge rate based on total capacity
- Example for a 1 Amp-hour battery:
  - 2 C = 2 A for 30 minutes (min)
  - 1 C = 1 A for 1 hour (hr)
  - C/2 = 0.5 A for 2 hours (hrs)



Schematic of battery charge (blue) and discharge (red) processes

## LITHIUM-ION BATTERY FUNDAMENTALS: ADVANTAGES

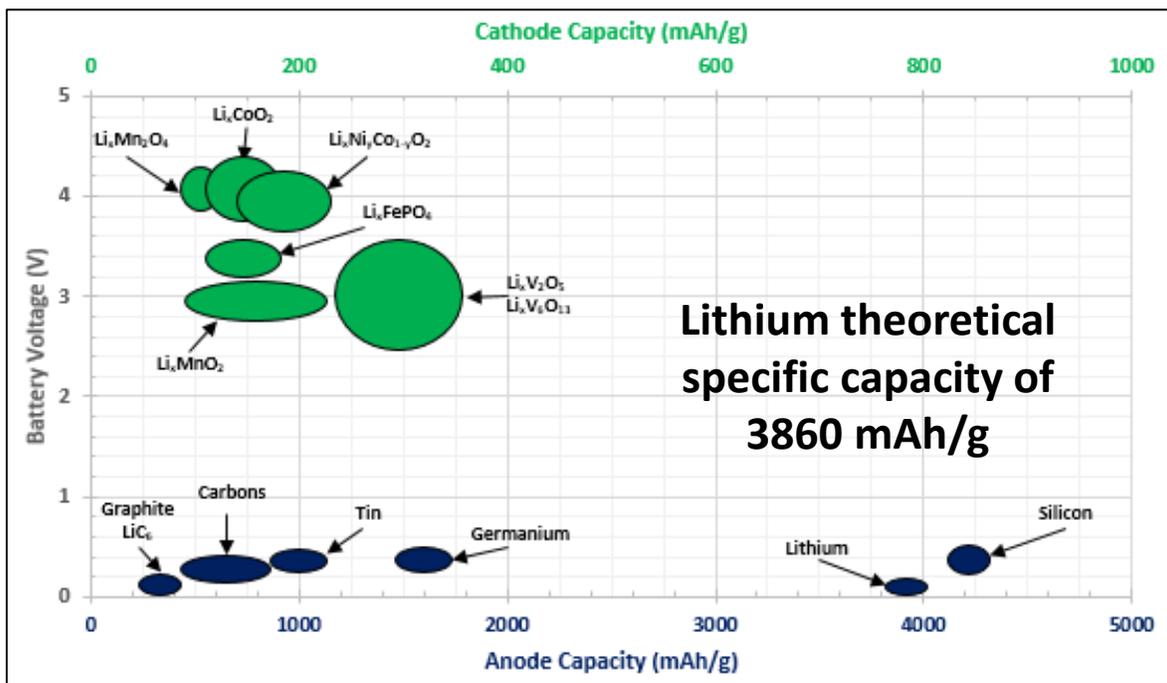


Ragone plot based on United States Defense Logistics Agency [33]



## LITHIUM-ION BATTERY FUNDAMENTALS: ADVANTAGES

- Mass reduction, Li is the lightest metal with 6.94 amu
- Charge capacity (mAh) is the amount of energy stored in the battery (specific capacity is mAh/g)
- Cycling behavior and memory effect refer to the loss in capacity through cycling



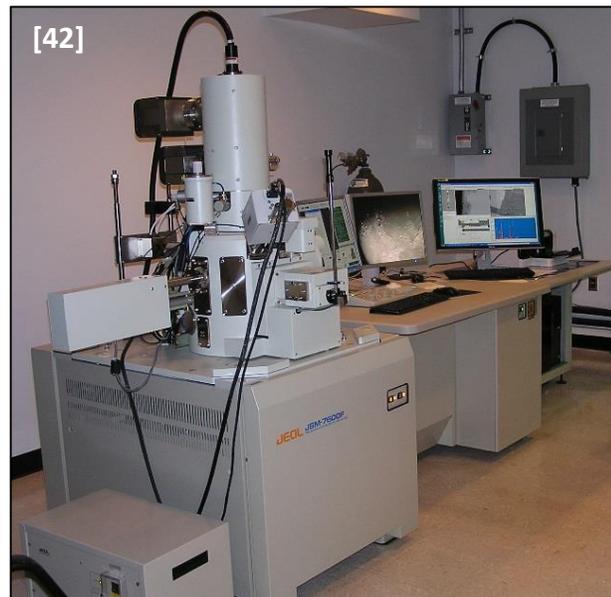
Data adapted from Landi et. al. 2009 [62]

Characteristic	Lead Acid	Ni-Cd	Ni-MH	Li-Ion	Li-Poly	LiFe
Voltage	2V	1.2V	1.2V	3.6-3.7V	3.6-3.7V	3.3V
Energy Density (Wh/kg)	35	45	70	167	110	100
Cycle Life	400	500-1000	400-1000	300-1000	300-1000	>1000
Life (Yrs) @ one charge/day	1	2	2	1+	1+	3
Self Discharge Rate (%/month)	10%	30%	30%	3%	3%	3%
Charging Time	8 hrs	1.5 hrs	4 hrs	2-6 hrs	2-6 hrs	1-3 hrs
Safety	No BMS	Good	Good	Poor	Average	Good
High Temp Performance	Good	Good	Good	Average	Average	Good
Cold Temp Charge (0°F)	Good	Fair	Fair	0-45°C	0-45°C	0-45°C
Cold Temp Discharge (0°F)	Good	Good	Poor	Avg-Good	Avg-Good	Good
Memory Effect	No	Yes	Little	No	No	No

Battery performance characteristics comparison [40]

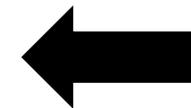
## LITHIUM-ION BATTERY FUNDAMENTALS: DISADVANTAGES

- **Solid Electrolyte Interphase (SEI) formation**
  - A passive layer consisting of organic and inorganic electrolyte decomposition products
  - Forms over anode surface during first charge cycle
  - Ion conducting, electrically insulating
  - Negative effects on safety, cyclability, rate capability and there charge retention
- **Volumetric expansion**
  - Too much volumetric change during insertion and de-insertion of Li ions can damage electrodes and detrimentally affect battery life and performance
- **Other disadvantages center around thermal related safety concerns:**
  - Thermal runaway (TR), which occurs due to mechanical failure, electrochemical failure or thermal failure
  - Single cell TR energy can propagate to surrounding Li-ion cells causing a chain-reaction event
  - Ejected materials and gases during runaway events are flammable, toxic, acidic and highly dangerous



Top image displays the Boeing 787-A Dreamliner failed APU battery compared to a non-damaged APU battery; images retrieved from the National Transportation Safety Board Interim Factual Report

Bottom image (left) displays a scanning electron microscope (SEM) commonly used for battery materials analysis. Image taken in the NASA ARES laboratory





## **SECTION 3: UNDERSTANDING BATTERY HEAT GENERATION**

## UNDERSTANDING BATTERY HEAT GENERATION: OHMIC HEATING

➤ **Li-ion batteries dissipate heat during charge-discharge operations due to:**

- Differences in open circuit and working voltages
- Enthalpy
- Changes in heat capacity

➤ **Bernardi et. al. [46] developed a general energy balance to represent the local heat generated in a Li-ion cell (Equation 4):**

- Voltage and current
- Enthalpy of reaction (enthalpy voltage of reaction)
- Enthalpy of mixing
- Phase change
- Heat capacity change

➤ **Bernardi's derivation is often simplified to only include Ohmic losses which are the primary thermal driver (Equation 5)**

$$\frac{\partial(\frac{\Delta G}{T})}{\partial T} = -\frac{\Delta H}{T^2} \tag{1}$$

$$Q_{Local} = -IV - \sum_k I_k T^2 \frac{d\frac{U_{k,avg}}{T}}{dT} + \sum_j \frac{d}{dt} \left( \int_{v_i} \sum_i c_{ij} RT^2 \frac{\partial}{\partial T} \ln\left(\frac{y_{ij}}{y_{ij}^{avg}}\right) dv_j \right) + \sum_{jjm} \sum_i \left[ \left( \Delta H_{ij \rightarrow m}^* - RT^2 \frac{d}{dT} \ln\left(\frac{\gamma_{i,m}^{avg}}{\gamma_{ij}^{avg}}\right) \right) \frac{dn_{ij}}{dt} \right] \tag{2}$$

$$Q_{Cell} = I \left( E - E_{Working} - T \frac{\partial E}{\partial T} \right) \tag{3}$$

G: Gibbs Free Energy  
 n: Number of Electrons per Mol  
 F: Faraday Constant  
 E: Potential  
 R: Gas Constant

T: Temperature  
 Q<sub>R</sub>: Reaction Quotient  
 Q<sub>Conv</sub>: Convective Heat  
 Q<sub>Cond</sub>: Conductive Heat  
 Q<sub>Rad</sub>: Radiative Heat

h: Convective Heat Transfer Coefficient  
 A: Surface Area  
 k: Thermal Conductivity  
 ε: Surface Emissivity  
 σ: Stefan Boltzmann Constant

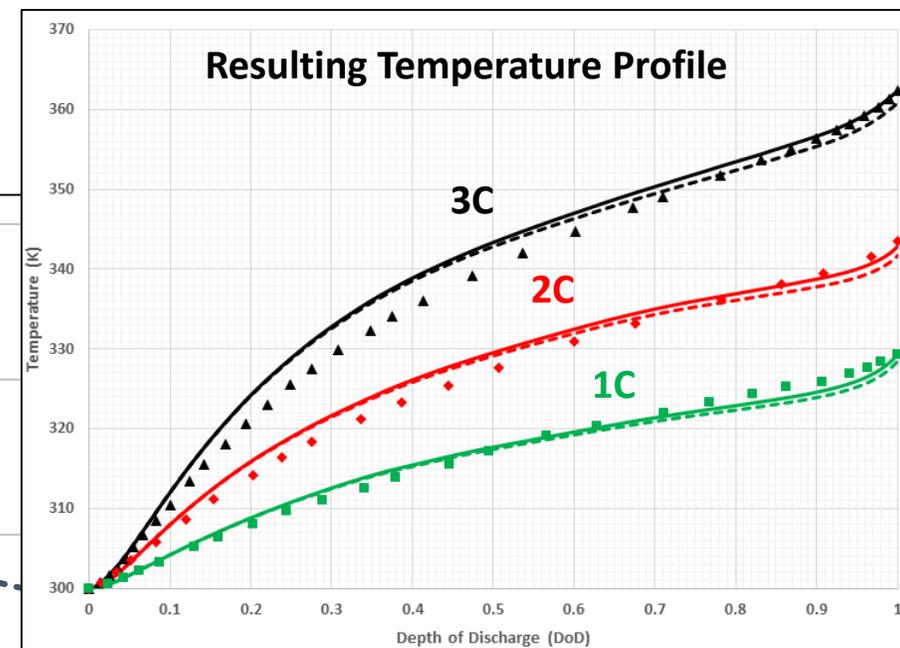
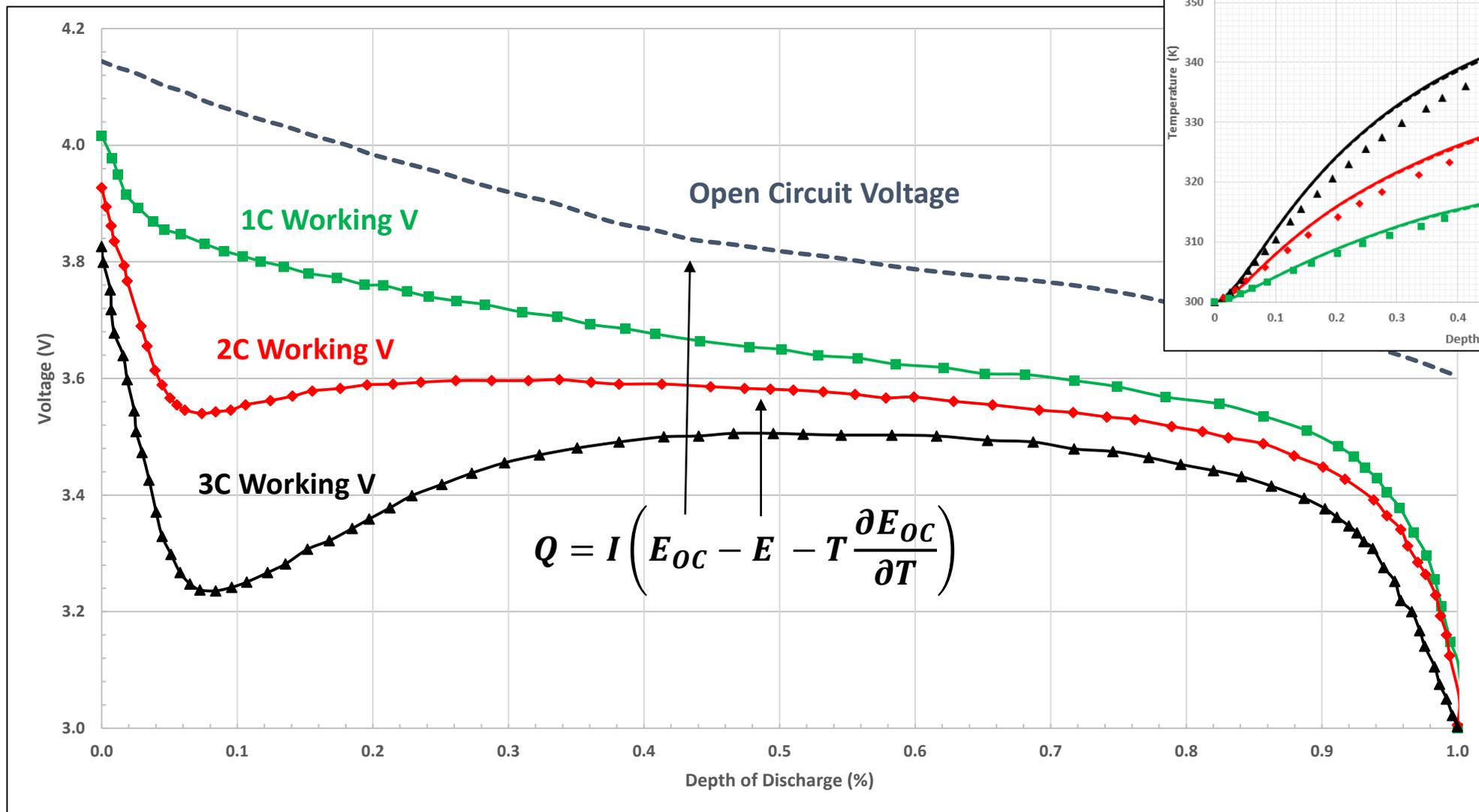
V: Radiation View Factor  
 A: Surface Area  
 Q<sub>Local</sub> (i.e. Q<sub>cell</sub>): Cell Heating  
 I: Current  
 E<sub>Working</sub>: Working Voltage

k<sub>R</sub>: Rate Constant  
 X: Pre-Exponential Factor (Pre-Factor)  
 E<sub>a</sub>: Activation Energy  
 H: Enthalpy  
 y, γ: Activity Coefficients

# UNDERSTANDING BATTERY HEAT GENERATION: OHMIC HEATING

## DISCHARGE OPERATIONS

- Discharge data from large format 185 Ah LiCoO<sub>2</sub> electric vehicle battery

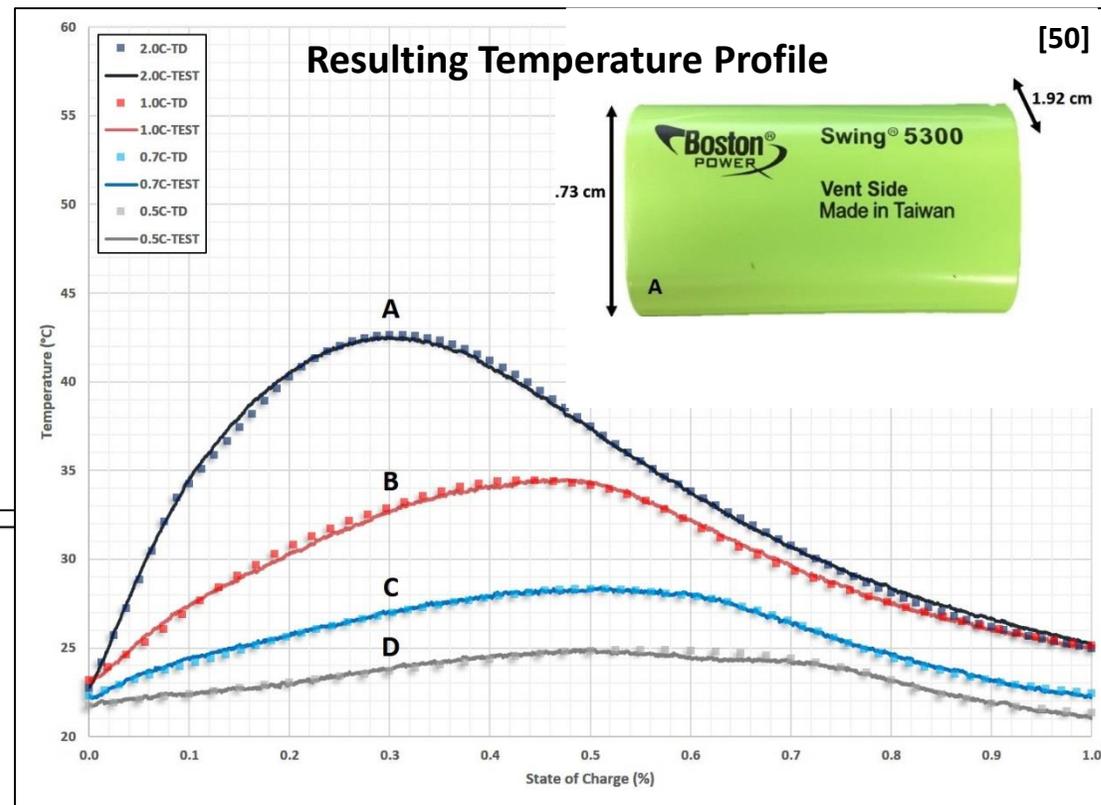
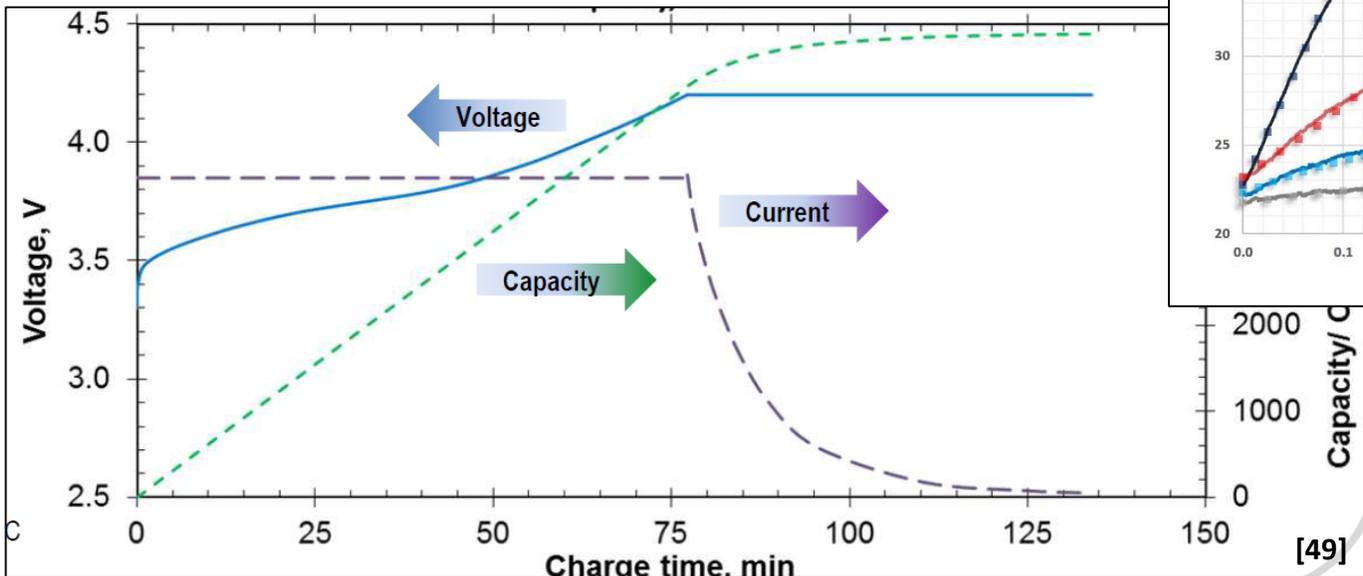


Discharge voltage profile (left) for open circuit, 3C, 2C and 1C and related temperature profiles (top) for a large format 185 Ah LiCoO<sub>2</sub> electric vehicle battery [47-48]

# UNDERSTANDING BATTERY HEAT GENERATION: OHMIC HEATING

## CHARGE OPERATIONS

- **0.7 C charging profile for Boston Power Li-ion cell shown below in 23 °C environment**
  - Charge profile is for constant current until 90% charge is reached
  - Occurs after approximately 80 min
- **Ohmic heat generation greatly reduces after 90% charge is reached which results in the curve shown below**



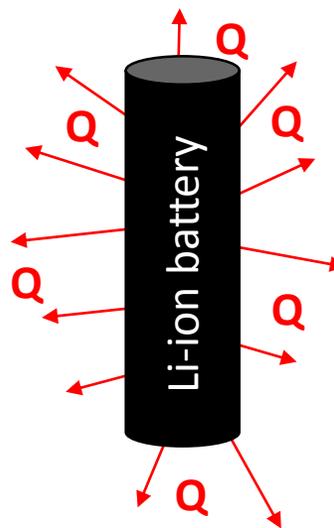
General charge operations voltage/current profile (left) for the Boston Power Swing 5300 Li-ion cell (top) and related temperature profile (top) for 0.5C, 0.7C, 1.0C and 2.0C rates [49-50]

## UNDERSTANDING BATTERY HEAT GENERATION: THERMAL RUNAWAY AND PROPAGATION

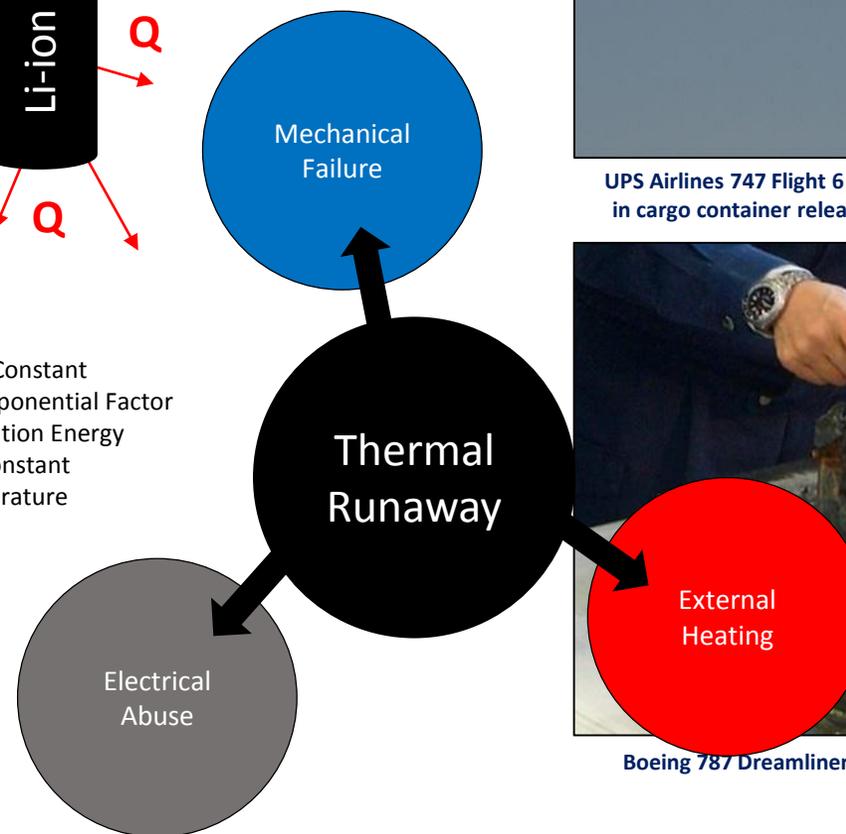
- TR is caused due to undesirable temperature increases from three failure mechanisms
- Exothermic decomposition reactions begin at certain critical threshold temperatures
- Self-heating begins when heat generation rates become greater than heat dissipation capability
- The rate of the exothermic reactions increase with temperature; Arrhenius equation

$$k_R = X e^{-E_a/(RT)} \quad (4)$$

- Eventually the exponential release of remaining energy in the cell occurs (i.e. thermal runaway)
- Propagation is when surrounding cells undergo thermal runaway due to energy released from the first cell



$k_R$ : Rate Constant  
 $X$ : Pre-Exponential Factor  
 $E_a$ : Activation Energy  
 $R$ : Gas Constant  
 $T$ : Temperature



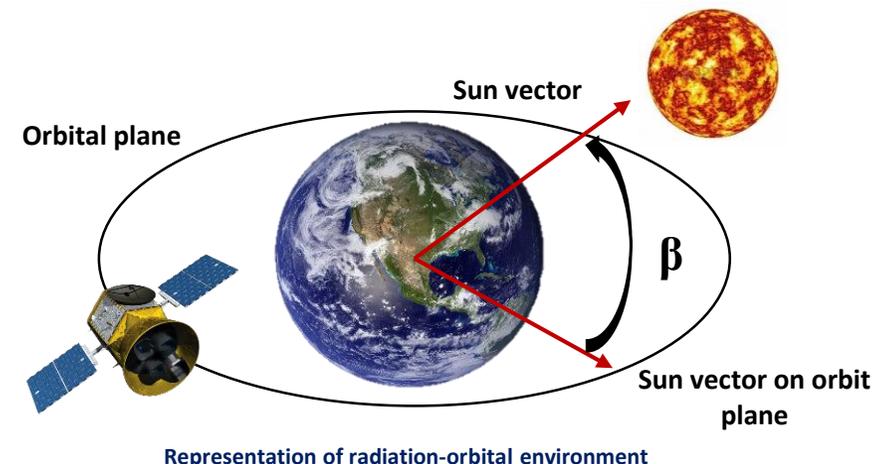
UPS Airlines 747 Flight 6 crashes on 09/03/2010 after Li batteries in cargo container release enough smoke to fill the cockpit [54]



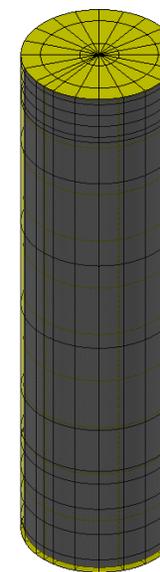
Boeing 787 Dreamliner Li-ion battery deconstruction post TR event [43]

## UNDERSTANDING BATTERY HEAT GENERATION: NEED FOR COUPLED ANALYSIS

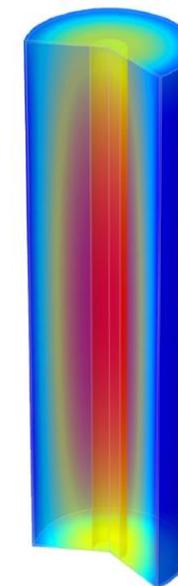
- **Li-ion battery performance, efficiency and safety are heavily influenced by cell temperature and surrounding temperature**
  - *Utilization for space applications exemplifies the need to predict thermal performance in radiation driven orbital environments*
- **Generally, the optimal way to perform thermo-electrochemical analysis is with a multi-physics methodology, however;**
  - Implementing complex thermal radiation space environments requires specialized software (e.g. CR Tech Thermal Desktop, SINDA and RadCAD)
- **A joint approach to representing nominal and off-nominal cell heating in a radiation environment is recommended**
  - Rather than providing user defined heat loads from testing for charge-discharge operation representation, make the load a function of the model
  - Employ concepts encompassed by multi-physics software (e.g. Bernardi's energy balance and thermal runaway theory) and couple with radiation software heat load logic thus removing user defined heating and providing a more accurate applied load
- **Presenter is not advocating specific software packages, but IS recommending the use of these techniques regardless of software**



18650 Cell [59]



TD 18650 Cell



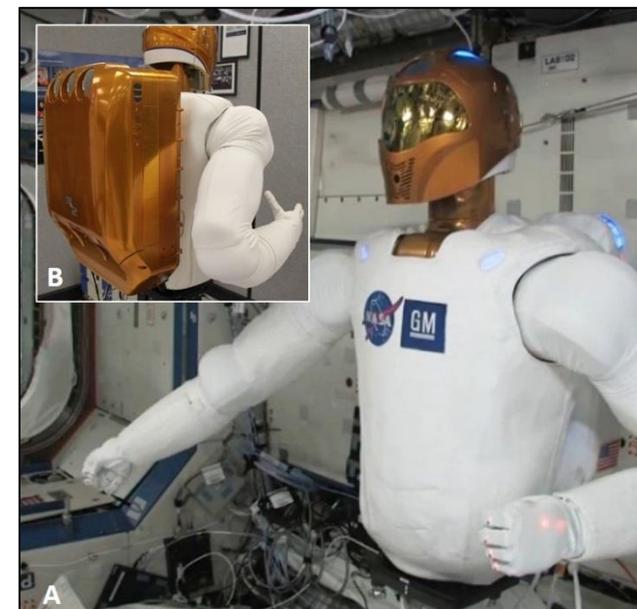
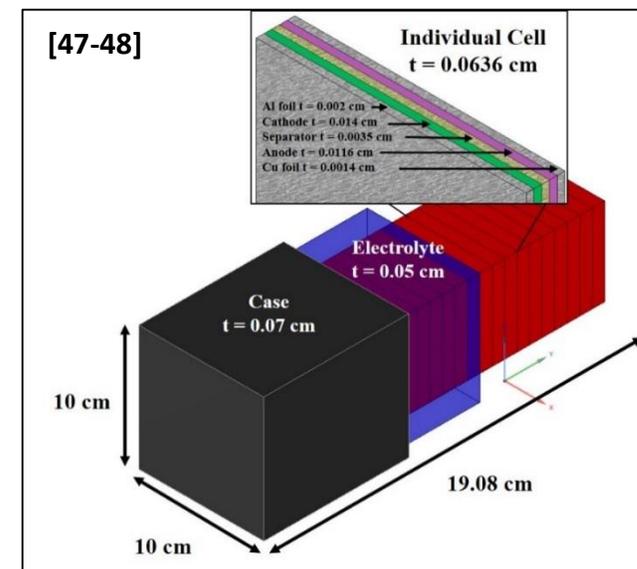
COMSOL 18650 Cell [60]



# **SECTION 4: COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS**

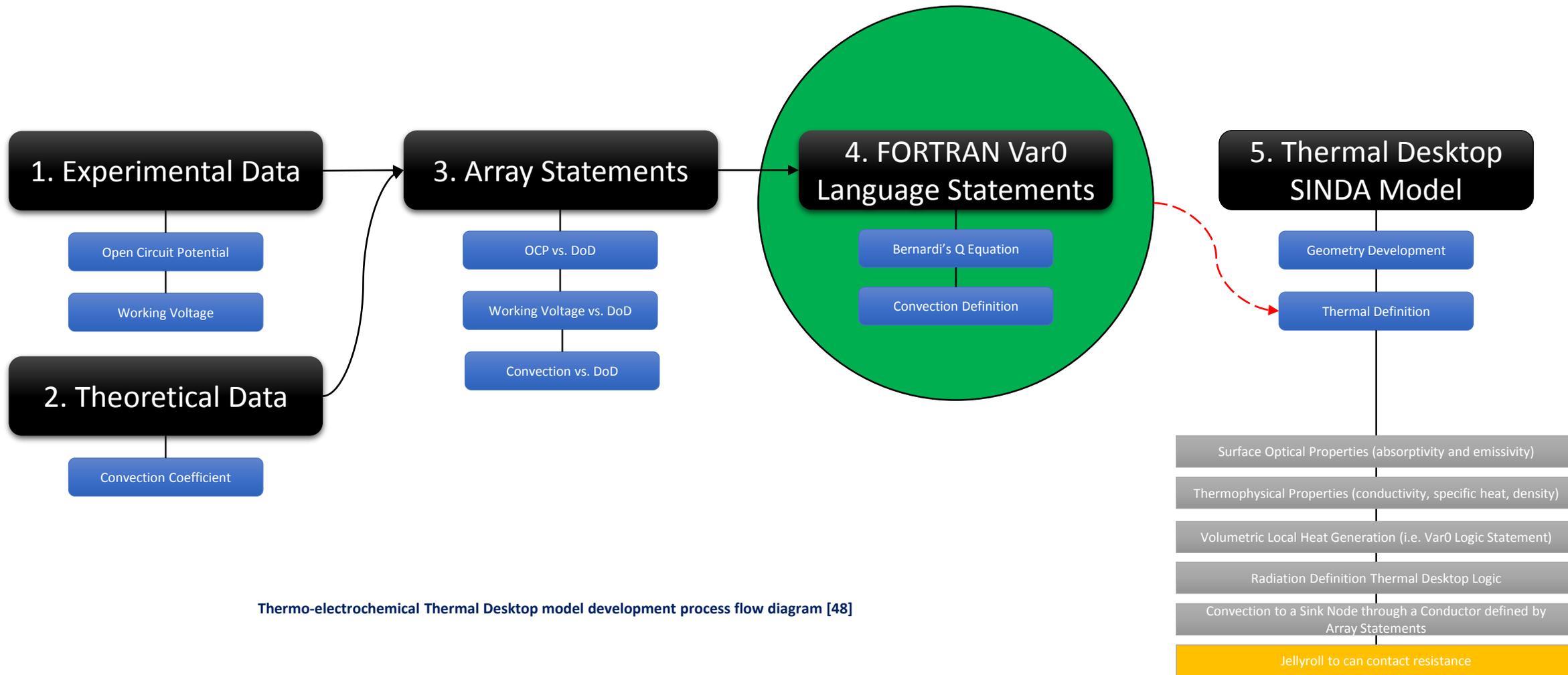
## COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS

- **Performed two studies examining thermo-electrochemical analysis in a Thermal Desktop environment (Proof-of-Concept and Validation-of-Concept):**
  - Both studies focused on Ohmic heat generation simulations
  - “Thermo-electrochemical analysis of lithium ion batteries for space applications using Thermal Desktop.” Walker, W.; Ardebili, H.; JPS 2014.
  - “Thermo-electrochemical evaluation of lithium ion batteries for space applications.” Walker, W.; Yayathi, S.; Shaw, J.; Ardebili, H. (pending JPS 2015)
- **Proof-of-Concept study recreated test and analysis results of a large format 185 Ah LiCoO<sub>2</sub> battery designed for electric vehicles in Thermal Desktop**
  - Original work (Chen et. al. 2005) focused on Ohmic heating in a convection-radiation environment for discharge operations only
- **Validation-of-Concept employed and improved Thermal Desktop techniques developed in the first study to support Robonaut 2 (R2) thermal requirements**
  - R2 simulations represented both charge and discharge Ohmic heat generation
  - Demonstrated R2 battery thermal performance in example orbital-radiation environments



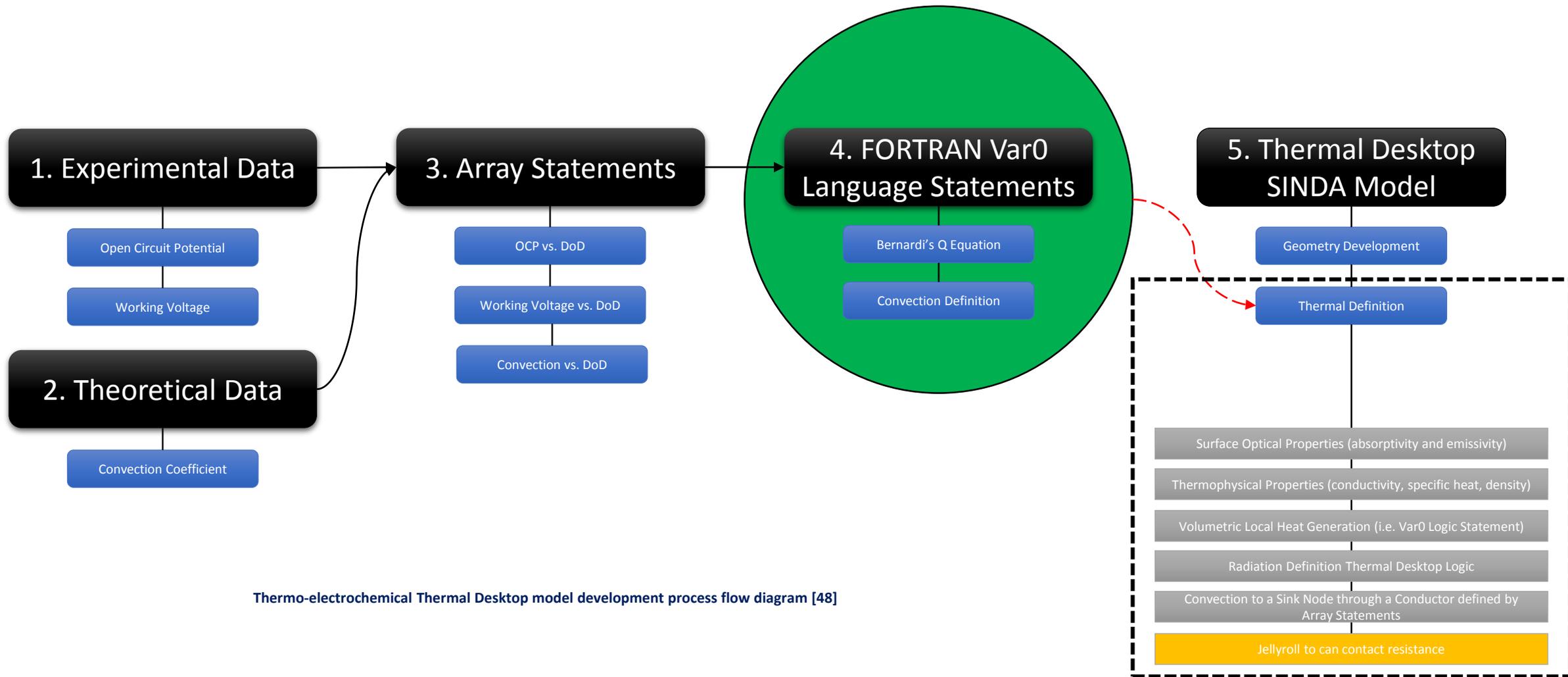
[50]

# COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS



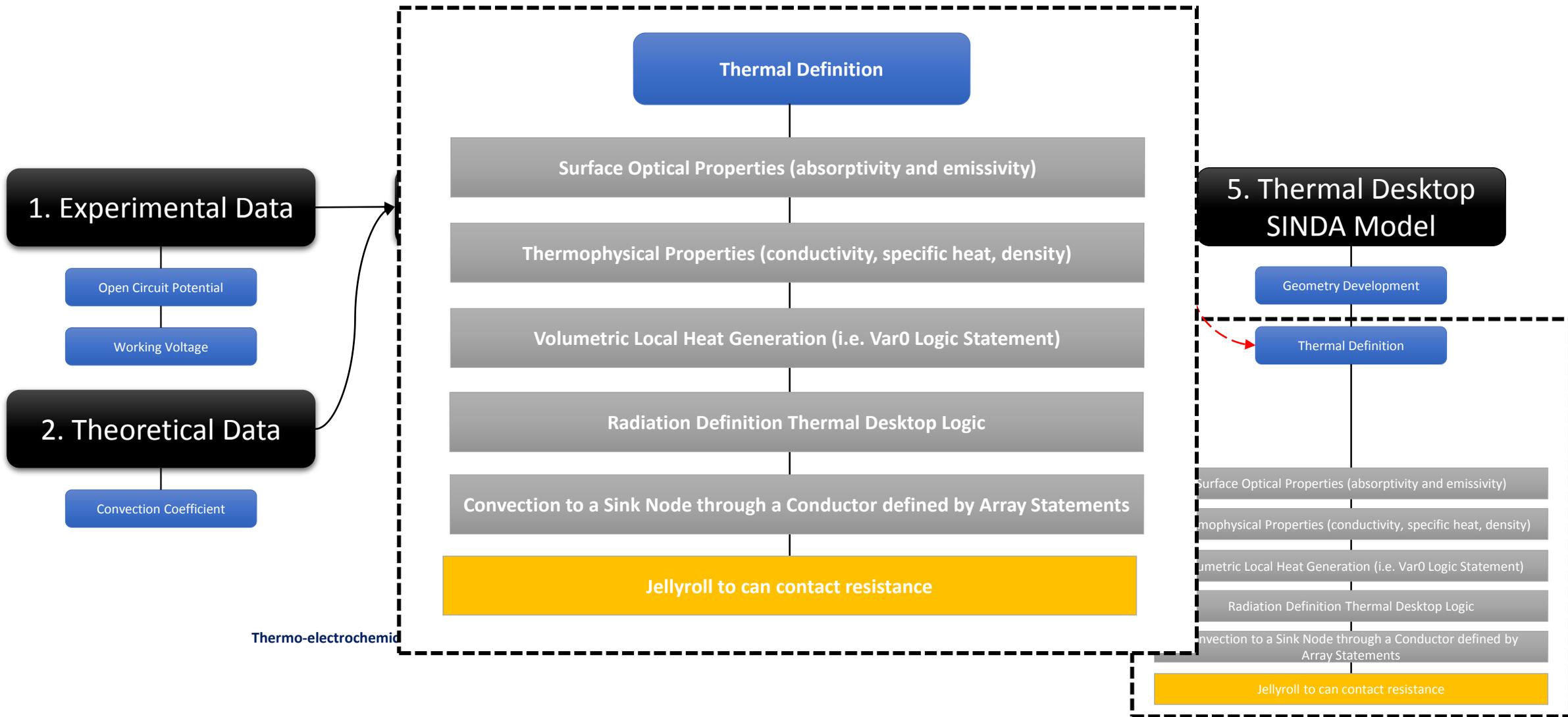
Thermo-electrochemical Thermal Desktop model development process flow diagram [48]

# COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS

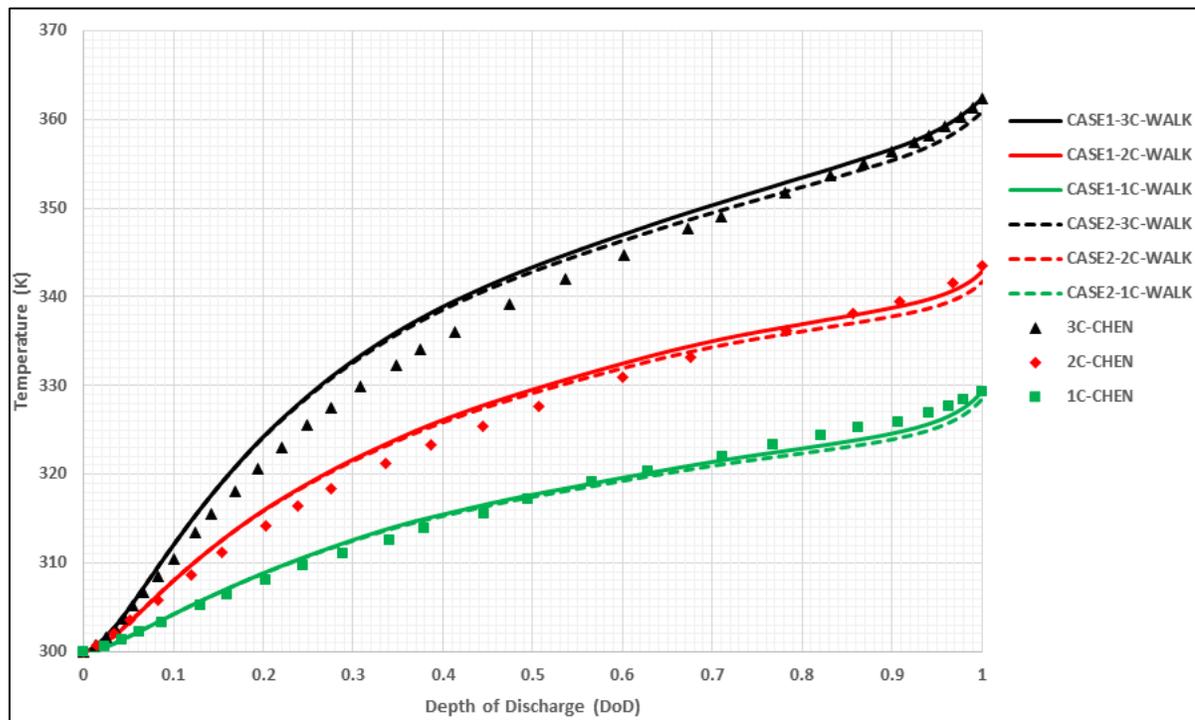


Thermo-electrochemical Thermal Desktop model development process flow diagram [48]

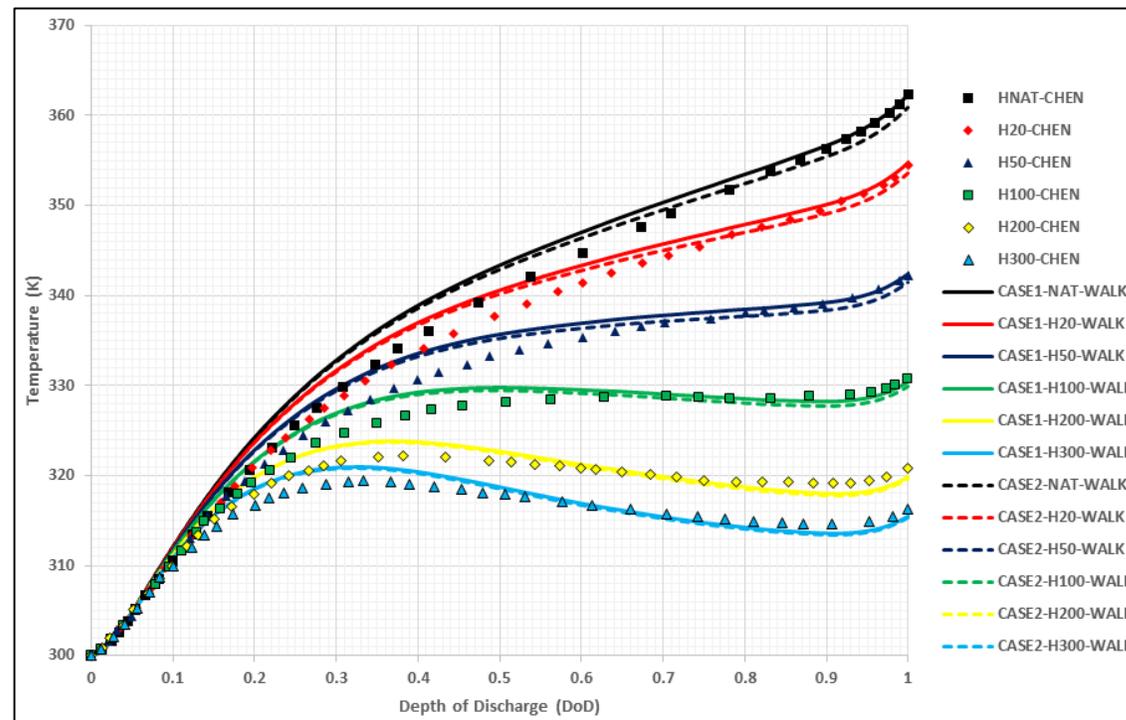
# COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS



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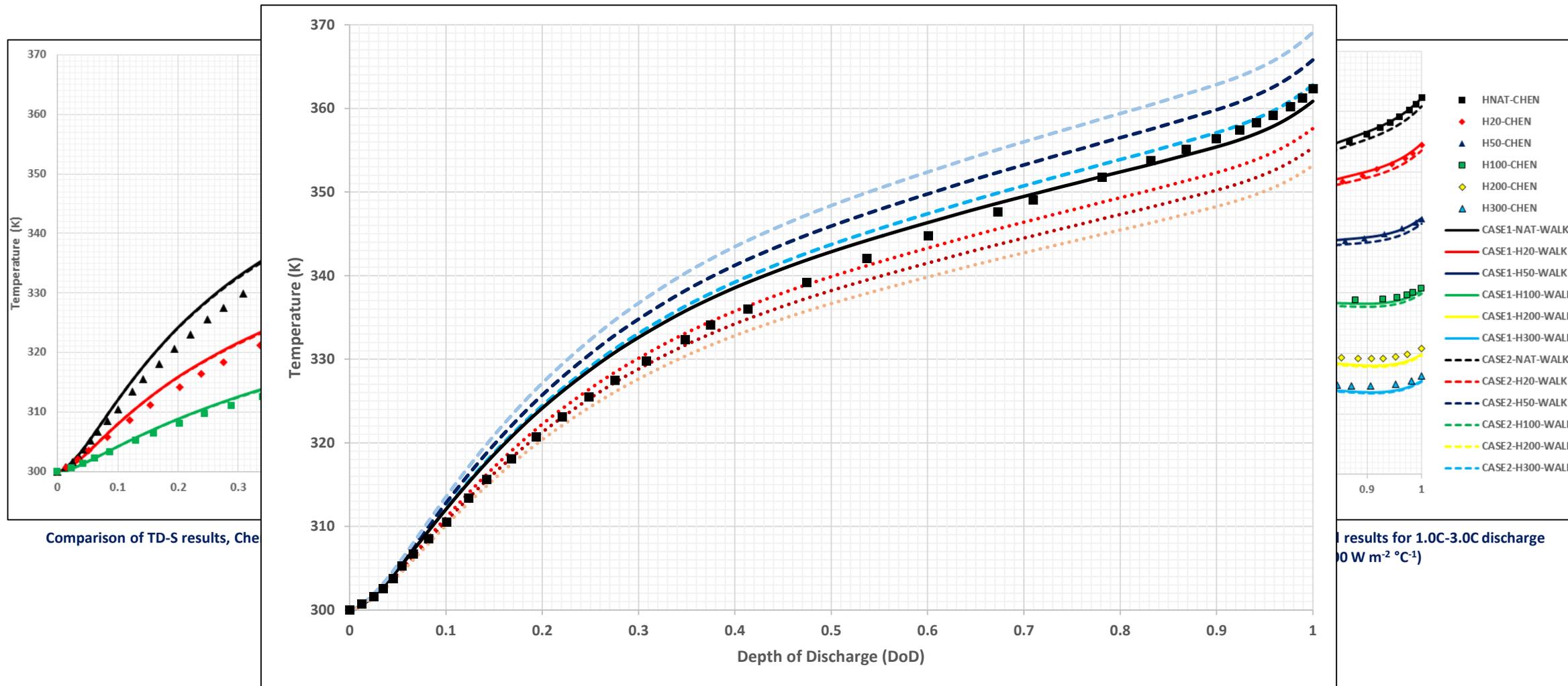


Comparison of TD-S results, Chen's results and experimental results for 1.0C-3.0C discharge rates in a natural convection environment [47-48]



Comparison of TD-S results, Chen's results and experimental results for 1.0C-3.0C discharge rates in varied forced convection environments (20-300 W m<sup>-2</sup> °C<sup>-1</sup>) [47-48]

# COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS

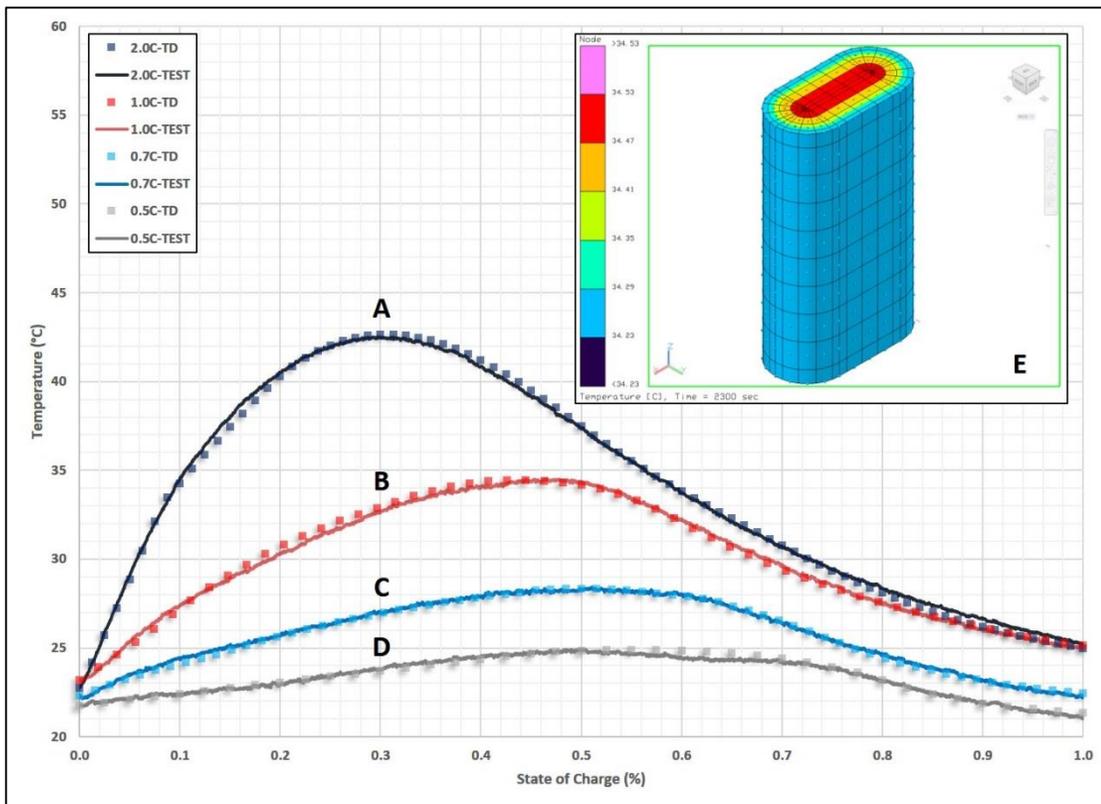


Comparison of TD-S results, Che

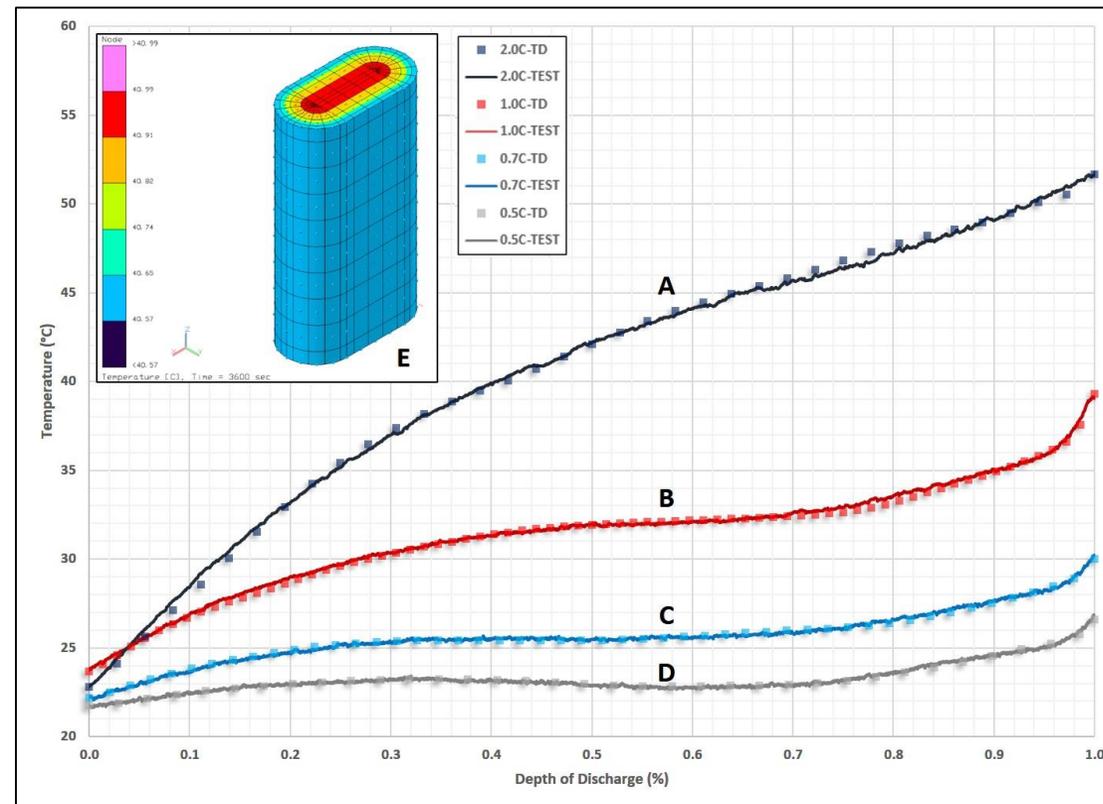
Re-run of 3.0C case with varied specific heat to determine the impact of induced error through incorrect thermophysical property calculations [47-48]

Results for 1.0C-3.0C discharge  
 $10 \text{ W m}^{-2} \text{ } ^\circ\text{C}^{-1}$

# COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS



Comparison of TD-S results to experimental results for 0.5C to 2.0C discharge testing [50]

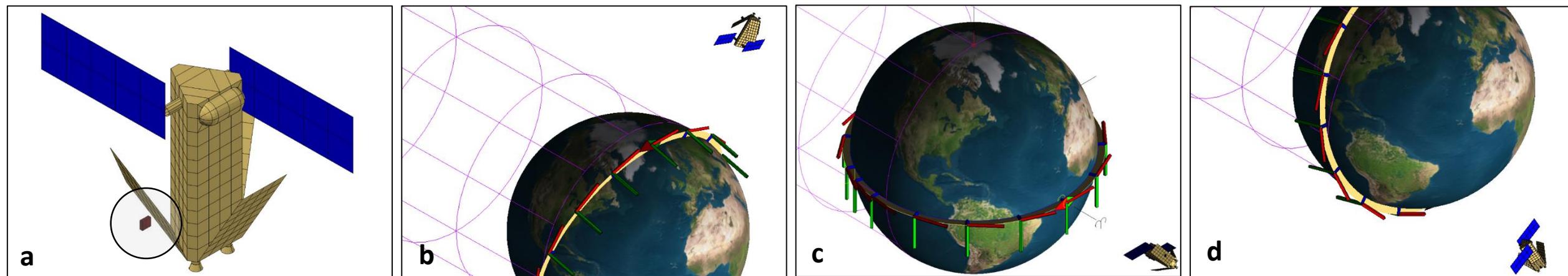


Comparison of TD-S results to experimental results for 0.5C to 2.0 C charge testing [50]

- Simulated constant current charging and discharge as a function of state-of-charge/depth-of-discharge, working voltage, open circuit voltage and temperature (simulation-squares, experimental-line)

## COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS

- **Results in both the “Proof-of-Concept” study and “Validation-of-Concept” study demonstrate capability for accurate thermo-electrochemical analysis of charge-discharge operations in a Thermal Desktop environment**
  - $Q_{Cell}$  is a function of model temperature predictions
  - For the R2 demonstration,  $Q_{Cell}$  is a function of each orbital environment
  - TD-S model predictions compared to test data provide excellent correlation
- **Developed TD capability provides unique method for  $Q_{Cell}$  input parameters which provides designers the ability to assess battery thermal and electrical performance for any orbital configuration as a function of said orbit**



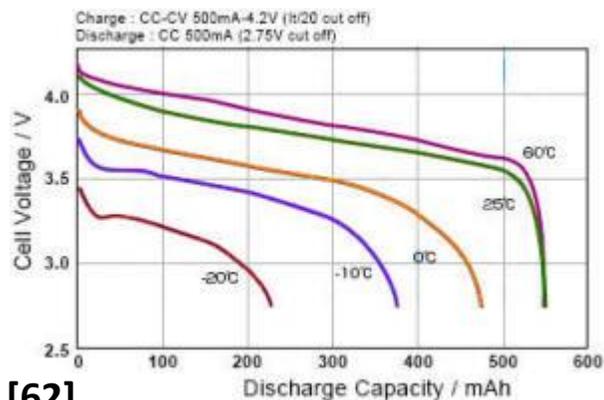
R2 300 cell system level model simulated (a) exterior to an example satellite in a (b) -75 beta orbit, (c) 0 beta orbit and (d) +75 beta orbit [50]

## COMPUTATIONAL ANALYSIS TECHNIQUES PART 1: CHARGE-DISCHARGE OPERATIONS

- Results in both the “Proof-of-Concept” study and “Validation-of-Concept” study demonstrate capability for accurate thermo-electrochemical analysis of charge-discharge operations in a Thermal Desktop environment
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$$Q_{Cell} = Current \times [OCV \text{ Bivariate Array}]$$

$$— Working \text{ Voltage Bivariate Array}$$



	-45°C	-25°C	0°C	+25°C	+45°C
0min	#	#	#	#	#
10min	#	#	#	#	#
20min	#	#	#	#	#
30min	#	#	#	#	#
40min	#	#	#	#	#
50min	#	#	#	#	#
60min	#	#	#	#	#
70min	#	#	#	#	#

	-45°C	-25°C	0°C	+25°C	+45°C
0min	#	#	#	#	#
10min	#	#	#	#	#
20min	#	#	#	#	#
30min	#	#	#	#	#
40min	#	#	#	#	#
50min	#	#	#	#	#
60min	#	#	#	#	#
70min	#	#	#	#	#

[62]

Example of current work using bivariate arrays to incorporate temperature based efficiency



# SECTION 5: COMPUTATIONAL ANALYSIS TECHNIQUES PART 2: THERMAL RUNAWAY MECHANISMS

## COMPUTATIONAL ANALYSIS TECHNIQUES PART 2: THERMAL RUNAWAY MECHANISMS

### ➤ Collaborated with C&R Technologies and the NASA Engineering and Safety Center (NESC) to develop FORTRAN logic that simulates the energy released during TR

- Disclaimer: these simulations are still in development and are not test correlated, but do demonstrate the capability we will gain once completed

### ➤ FORTRAN logic considers:

- Jellyroll trigger temperature (**TTRIG**)
- Length of the runaway event (**TEVENT**)
- Energy released per second (**QEVENT**)
- Ensures runaway only happens once (**RUNAWAY01**)
- Deactivates exterior heater (**END\_TRIGGER01**)

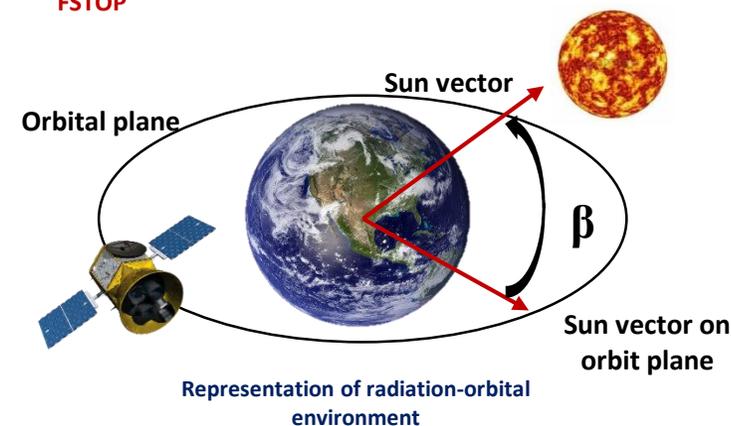
### ➤ Using Thermal Desktop for battery design certification

- Pre-determine the thermal environment a permanently mounted Li-ion battery must operate in and design to that environment
- Determine attitudes and environments which would induce thermal runaway and propagation

#### FSTART

```

C find submodel reference ID
  call modtrn('jell1',mtest)
C loop through all diffusion nodes in the submodel
C assumes nodes are sequentially numbered
  do itest = 1, nmdif(mtest)
C look up node storage location
    call nodtrn('jell1',itest,mtest)
C perform runaway logic
    if ((T(ntest) .ge. TTRIG) .and. (runaway01 .ge. 0)) then
      if (runaway01 .eq. 0.) then
        end_trigger01 = TIMEN + TEVENT
        runaway01 = 1
      end if
    if (TIMEN .le. end_trigger01) then
C use capacitance fraction to proportion the heat load
C battery_mCp can be calculated in advance
      Q(ntest) = Q(ntest) + QEVENT*C(ntest)/JELLMCP
    else
      Q(ntest) = Q(ntest) + 0.
      runaway01 = -1
    end if
  end if
end do
FSTOP
  
```

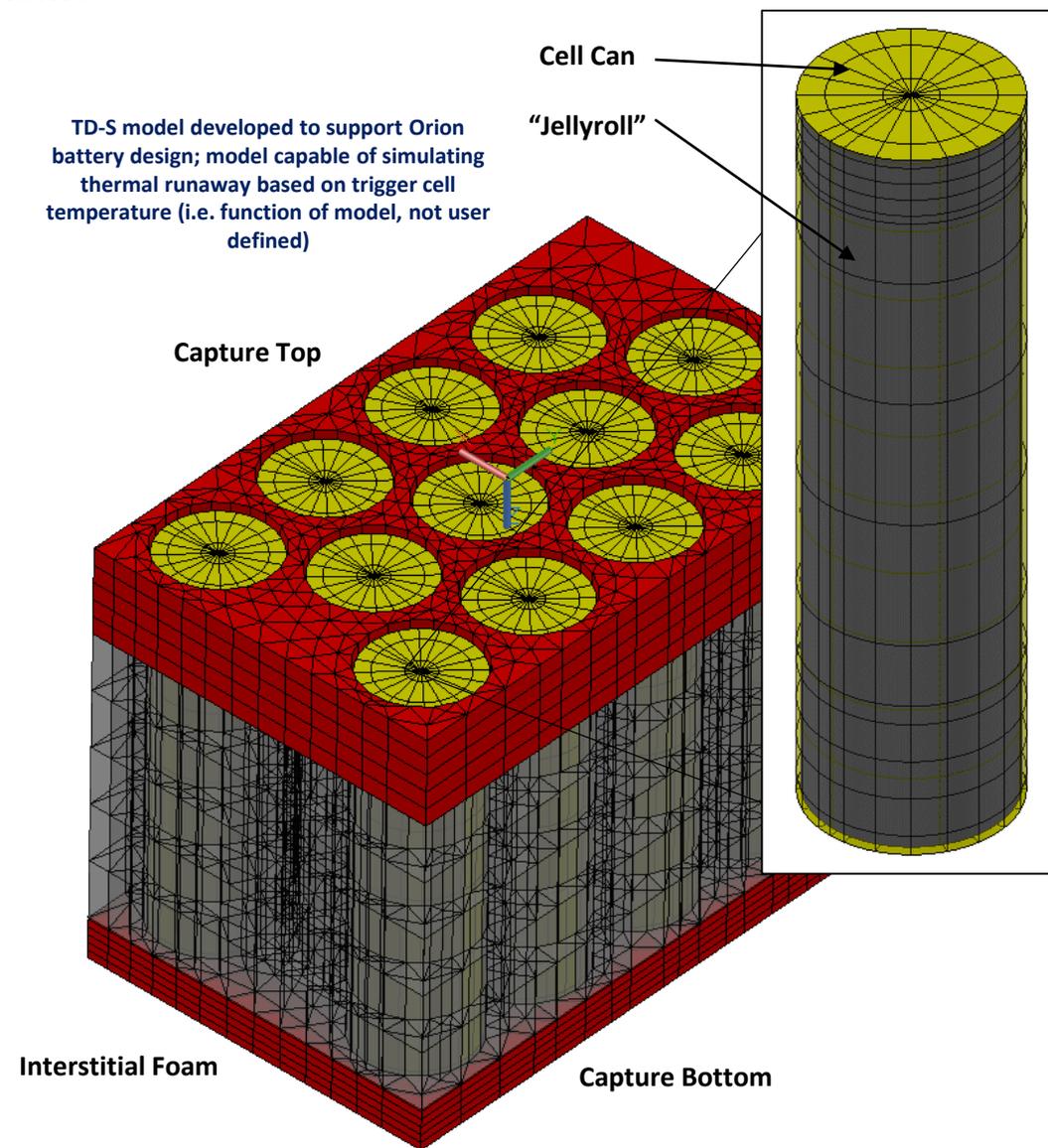


## COMPUTATIONAL ANALYSIS TECHNIQUES PART 2: THERMAL RUNAWAY MECHANISMS

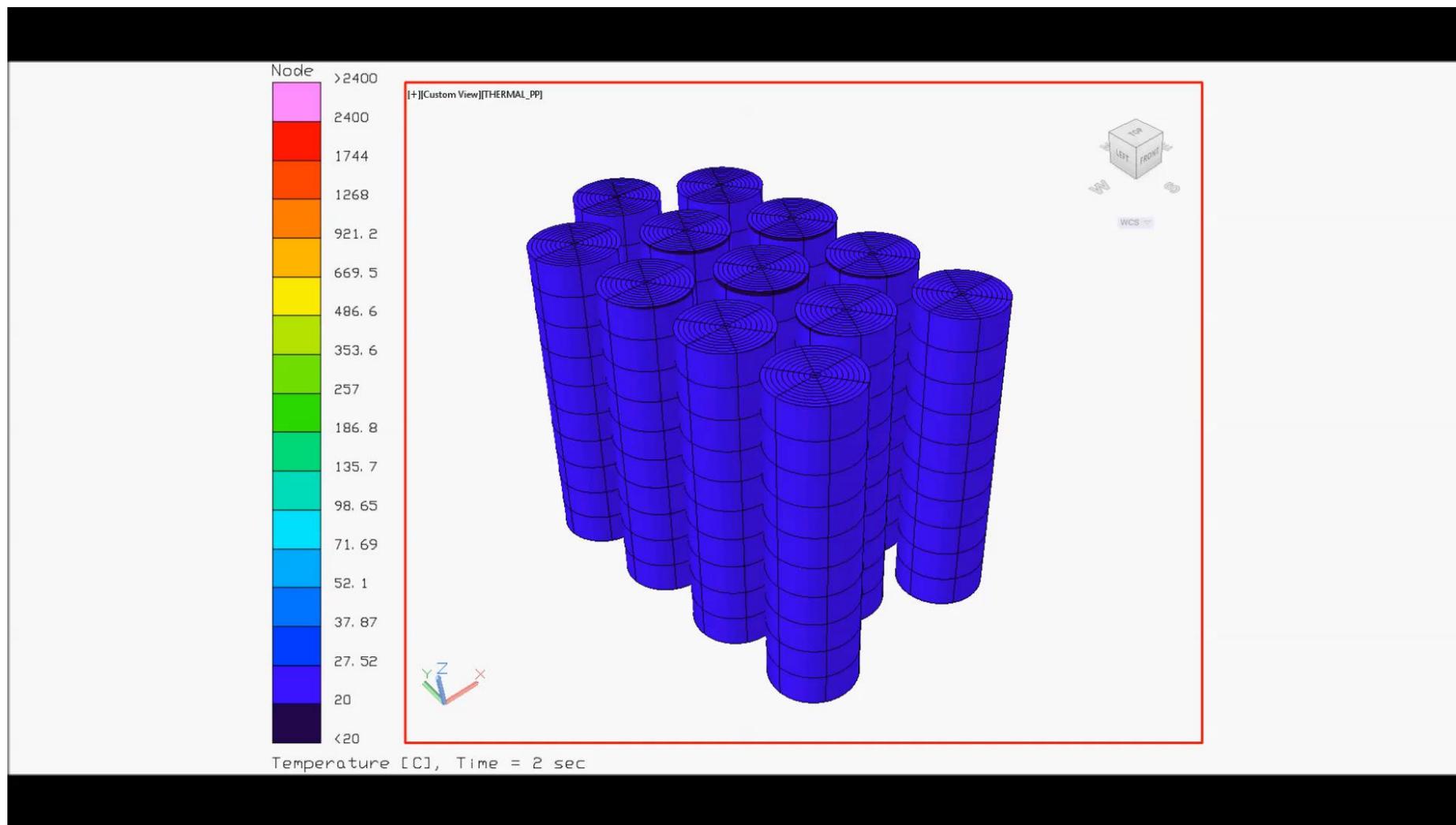
- Understanding and preventing thermal runaway and propagation is vital to spaceflight battery design and safety
- TD-S model techniques improved to represent basic thermal runaway mechanisms:
  - Developed FORTRAN logic which simulates thermal runaway energy release if “jellyroll”  $T_{Trigger}$  is achieved (160 °C)
- TD-S model considers x12 18650 cells as shown to the right
- “Jellyroll” logic is set to release 3500 W/s for 20 seconds
- 35W heater power is applied to the surface of the mild-steel can to force jellyroll to  $T_{Trigger}$

Component	Thermal Conductivity	Specific Heat	Density	Conductance
Capture Plates	167 W/m/°C	900 J/kg/°C	2700 kg/m <sup>3</sup>	10 W/m <sup>2</sup> /C to cell can
Foam	0.05-0.25 W/m/°C	1600 J/kg/°C	600 kg/m <sup>3</sup>	10 W/m <sup>2</sup> /C to cell can
Cell Can	43 W/m/°C	500 J/kg/°C	8000 kg/m <sup>3</sup>	10 W/m <sup>2</sup> /C to foam/capture plate
Jellyroll	ANISO W/m/°C	823 J/kg/°C	2776 kg/m <sup>3</sup>	50 W/m <sup>2</sup> /C to cell can

TD-S model characteristics for 18650 cell TR and propagation simulations



## COMPUTATIONAL ANALYSIS TECHNIQUES PART 2: THERMAL RUNAWAY MECHANISMS





## SECTION 6: WRAP-UP

## WRAP-UP: CONCLUSIONS

- **Provided lithium-ion battery market characteristics and overview**
- **Discussed battery fundamentals relevant to space thermal applications**
- **Presented theory for battery heat generation during nominal/off-nominal scenarios**
- **Techniques presented for simulating battery heat generation in radiation-driven space environments**



## WRAP-UP: QUESTION AND ANSWER

# QUESTIONS?

## WRAP-UP: ACKNOWLEDGEMENTS

- **NASA JSC Engineering Directorate (EA), Structural Engineering Division (ES) and Thermal Design Branch (ES3) Management**
- **NASA Engineering and Safety Center (NESC)**
- **Laurie Carrillo, Ph.D. Rice University, NASA JSC/EA/ES/ES3**
- **Eric Darcy, Ph.D. University of Houston, NASA JSC ESTA**
- **Haleh Ardebili, Ph.D. University of Houston**
- **Taylor Dizon, Ph.D. Candidate, University of Houston**

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