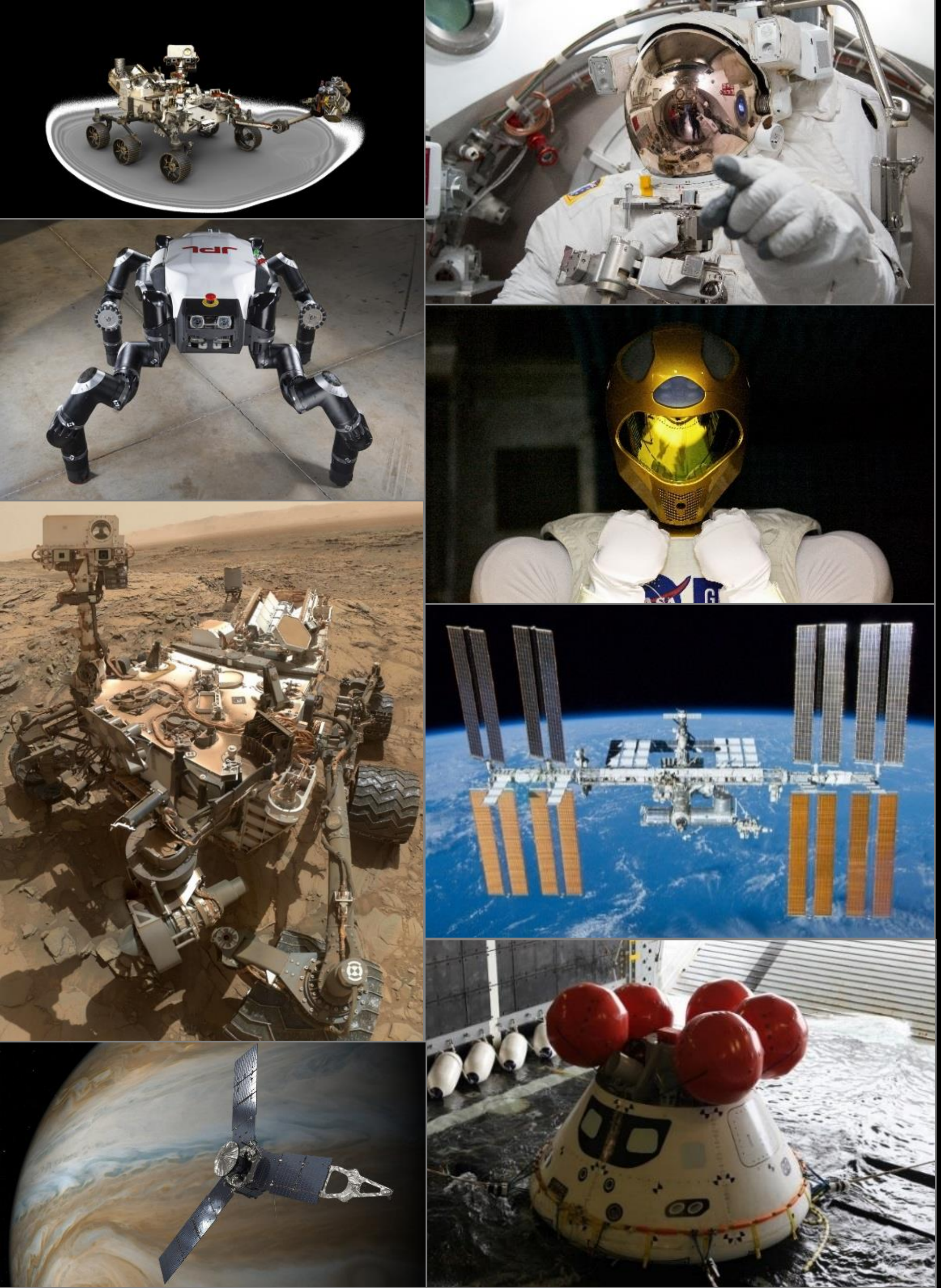

COMBINING FRACTIONAL CALORIMETRY WITH STATISTICAL METHODS TO CHARACTERIZE THERMAL RUNAWAY

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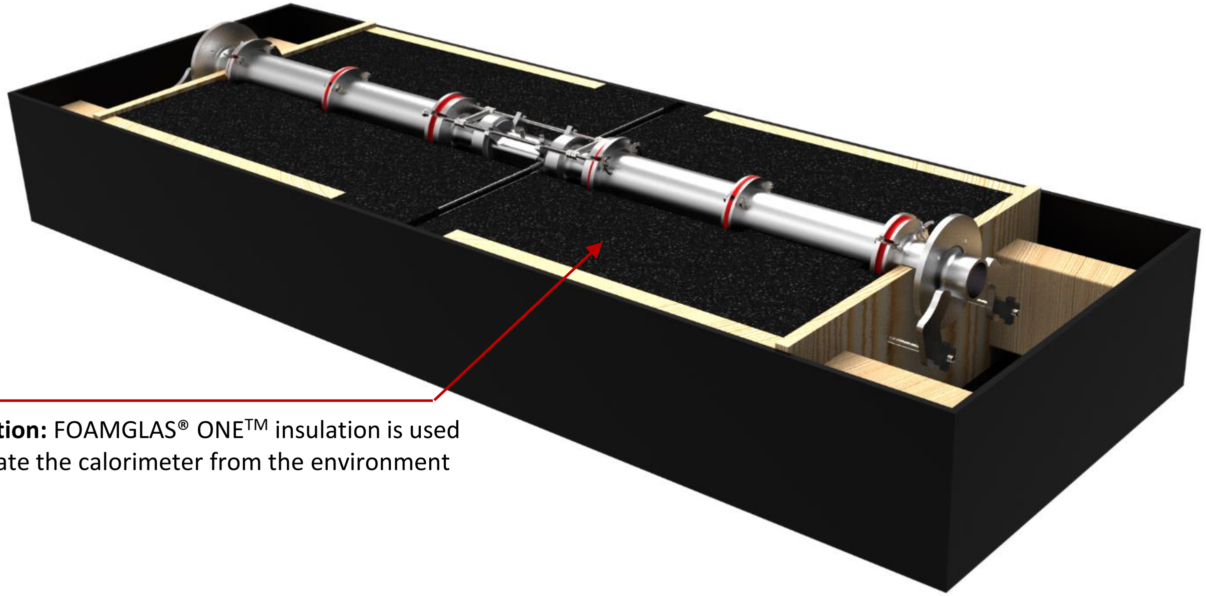
[5] Science Applications International Corporation (SAIC)
[6] NASA Engineering and Safety Center (NESC)

NASA STRATEGY TO PROTECT AGAINST THERMAL RUNAWAY

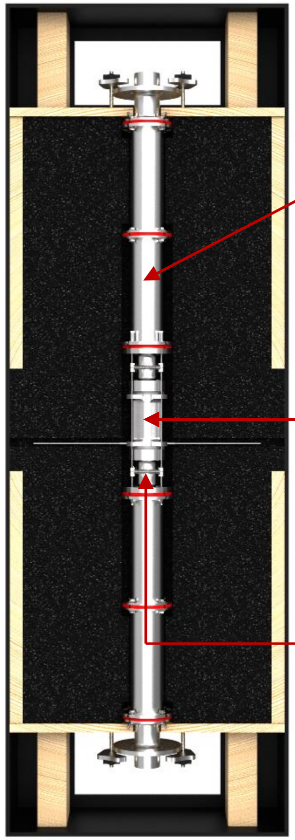
- **Following the 2013 Boeing 787 Dreamliner incident, NASA teams developed new definitions for battery design success criteria:**
  - Always assume thermal runaway (TR) will eventually happen
  - Design should ensure that TR event is not catastrophic
  - Demonstrate that propagation to surrounding cells will not occur
- **Thermal management systems designed to mitigate the effects of thermal runaway and prevent cell-to-cell propagation should consider the following:**
  - No runaway event is the same; even for the same manufacturer and state-of-charge; there is a range of possible outcomes
  - Onset temperature, acceleration temperature, trigger temperature, trigger cell peak temperature and neighbor cell peak temperature
  - Total energy released through sides and top of the cell body
  - Cell failure type (e.g. side wall vs. top), system pressure increase, gases released and ejecta material
- **Optimization of Li-ion battery assemblies that satisfy the aforementioned strategies requires knowledge of the following:**
  - Total energy output range during TR for a single Li-ion cell
  - Fraction of TR energy transferred through the cell casing
  - Fraction of TR energy ejected through cell vent/burst paths

FRACTIONAL THERMAL RUNAWAY CALORIMETRY

- **As an NESC assessment, NASA developed a new fractional TR calorimetry (FTRC) method for 18650-format Li-ion cells:**
  - Collaborators included NESC, NASA JSC, and SAIC
  - Allows discernment between (1) total heat output and (2) fraction of heat released through the cell casing vs. ejecta material
  - The energy distributions are determined by post processing temperature vs. time for each calorimeter sub-assembly (i.e. $\sum m_i C_{p_i} dT_i$)
  - Ambidextrous configuration accommodates cell designs with bottom vents (BVs)
  - Uses high flux heaters to initiate TR quickly (i.e. relevant to field failure)
  - Simple operation enables multiple experiments per day
  - Compatible with high speed X-ray videography [9]
  - Optional interface for measuring the gas exhaust heat



Insulation: FOAMGLAS® ONE^{TM} insulation is used to isolate the calorimeter from the environment



Ejecta Bore Assemblies: Slow down and extract heat from escaping flames and gas

Cell Chamber Assembly: Includes heating system for thermally induced failure and mounting point for nail penetration system

Ejecta Mating Assemblies: Captures ejected solids such as the electrode winding

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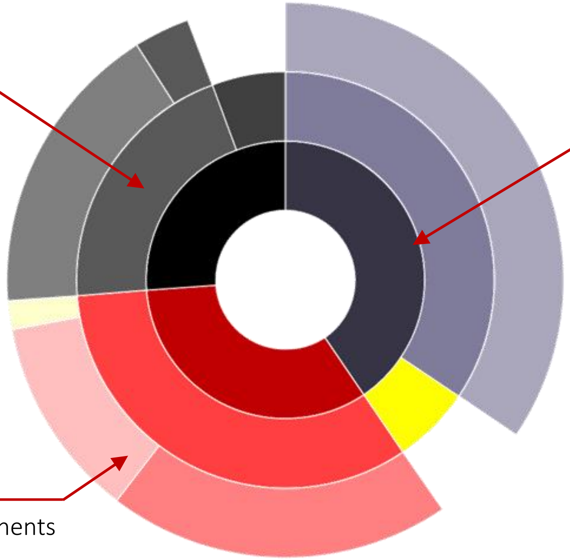
FRACTIONAL THERMAL RUNAWAY CALORIMETRY

- **The calculated energy fractions are traceable to every calorimeter assembly, sub-assembly, and individual component**
- **The primary assemblies used for fractional calculations are the following:**
  - Cell Chamber Assembly (Red)
  - Positive Ejecta Mating Assembly (Indigo)
  - Positive Ejecta Bore Assembly (Indigo)
  - Negative Ejecta Mating Assembly (Black)
  - Negative Ejecta Bore Assembly (Black)



Middle Ring: Indicates calorimeter sub-assemblies

Outer Ring: Corresponds to components of the calorimeter sub-assemblies

Inner Ring: Characterizes the division of total TR energy release where red corresponds to the cell casing, indigo to the positive ejecta and gases, and black to the negative ejecta and gases

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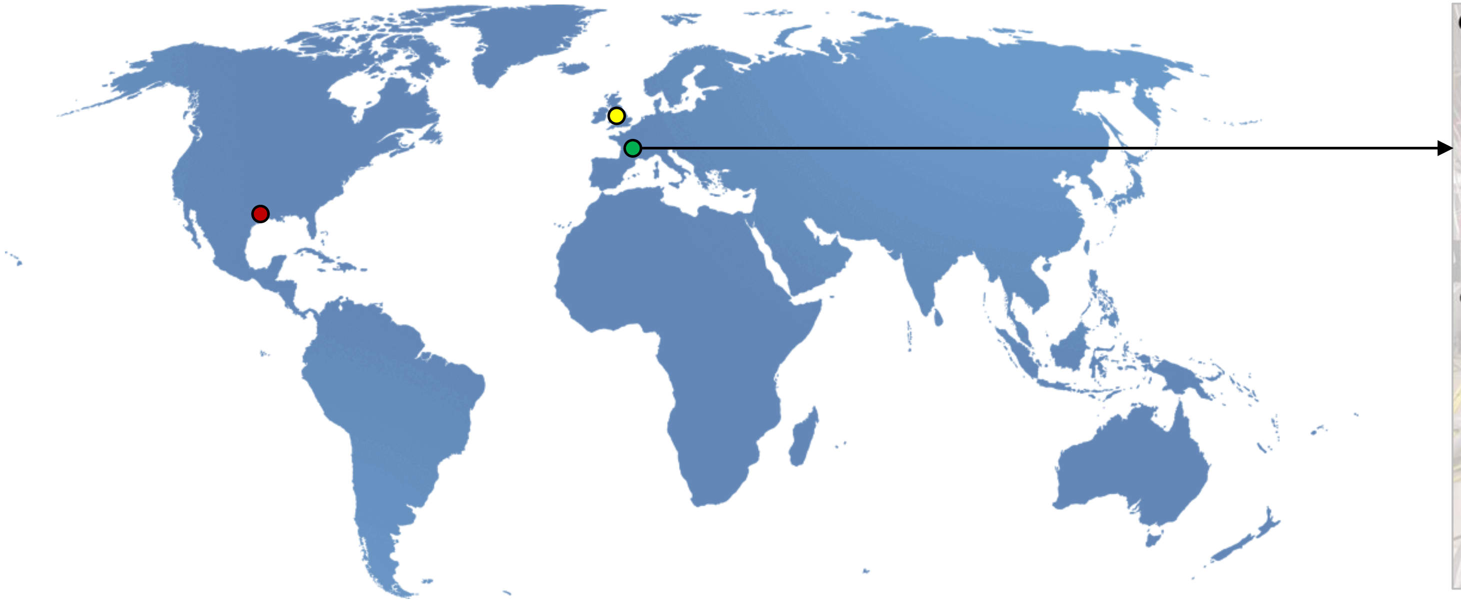
FRACTIONAL THERMAL RUNAWAY CALORIMETRY

- **Images below depict the global testing capability of the device:**
  - FTRC testing at the NASA JSC Energy Systems Test Area (Red Dot)
  - FTRC testing at the European Synchrotron Radiation Facility (ESRF) for in-situ high speed tomography (Green Dot)
  - FTRC testing at the Diamond Light Source (DLS) Facility for in-situ high speed tomography (Yellow Dot)



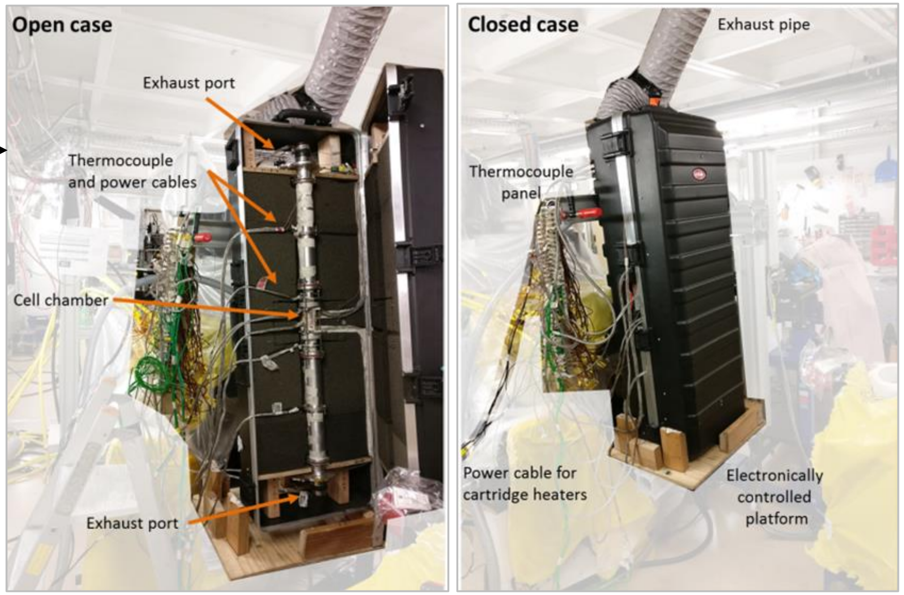


Image courtesy of Dr. Donal Finegan and ESRF

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FRACTIONAL THERMAL RUNAWAY CALORIMETRY

Cell type: Li-ion 18650
Capacity: 3.5 Ah
State of Charge: 100 % (4.2 V)
Bottom vent: No
Wall thickness: Not known
Separator: Polymer
Orientation of cell: Positive end up
Location of ISCD radially: N/A
Location of ISCD longitudinally: N/A
Side of ISCD in image: N/A

Location of FOV longitudinally: Top
Frame rate: 2000 Hz
Frame dimension (Hor x Ver): 1280 x 800 pixels
Pixel size: 17.8 µm

Video courtesy of Dr. Donal Finegan (NREL) and ESRF

DESCRIPTION OF CELL TYPES AND VARIABLES TESTED

- **The TR behavior of a variety of cell types, with varying chemistries and safety features, has been characterized:**
  - 3.35 Ah LG 18650 control groups consider the effects of bottom vent mechanisms (BV) vs. non-bottom vent (non-BV) mechanisms and the cell casing thickness (220 vs. 250 µm);
  - Molicel 18650-J control groups consider standard polymer separators and Dreamweaver gold and silver separators
  - Some of the 3.35 Ah LG 18650 cells and Molicel 18650-J cells had the NASA/NREL developed internal short circuiting (ISC) devices installed to examine TR behavior at lower temperatures (i.e. closer to field failure conditions); image below depicts the device
  - All cells were tested at 100% state of charge
- **Most experiments are conducted with high flux heaters for a trigger mechanism:**
  - For select cells, some of the FTRC experiments were conducted with nail penetration as well

Variable	Unit	LG 18650	Sony 18650	LG 18650	Panasonic 18650	LG 18650	Samsung 18650	LG 18650	Molicel 18650
Model	-	MJ1	VC7	Test Cell	BE	HG2	30Q	HE2	J
Capacity at 100% SOC	**Ah**	3.5	3.5	3.35	3.2	3.0	3.0	2.5	2.3
Nominal Voltage	**V**	3.6	3.6	3.67	3.6	3.6	3.6	3.6	3.78
Nom. Energy	**Wh**	12.7	12.7	12.4	11.5	10.8	10.8	10.8	8.7
Venting Mechanism	-	Non-BV	BV	BV and Non-BV	BV	Non-BV	Non-BV	Non-BV	Non-BV
Casing Thickness	**µm**	150	-	220 and 250	125	150	170	-	203
Internal Short Circuit [1]	-	No	No	Yes	No	No	No	No	Yes
Trigger Mechanism	-	Heat/Nail	Heat	Heat/Nail	Heat	Heat	Heat	Heat	Heat/Nail
Separator Material	-	-	-	-	-	-	-	-	Poly, Ag, Au
Count [2]	-	15	9	40	2	10	5	3	15

[1] The ISC device was only installed in some of the cells

[2] The count refers to the total number of cells tested per cell type

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Separator Material	-	-	-	-	-	-	-	-	Poly, Ag, Au
Count [2]	-	15	9	40	2	10	5	3	15

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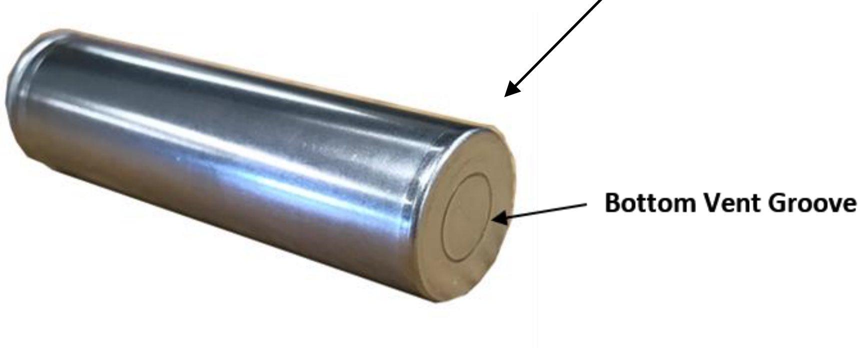

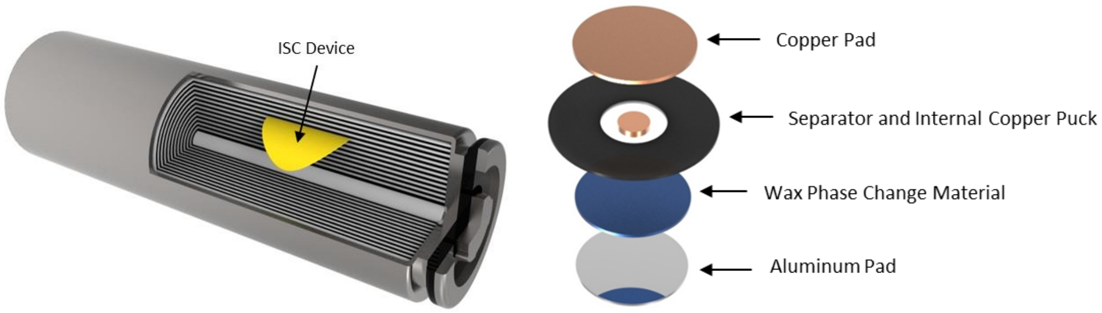

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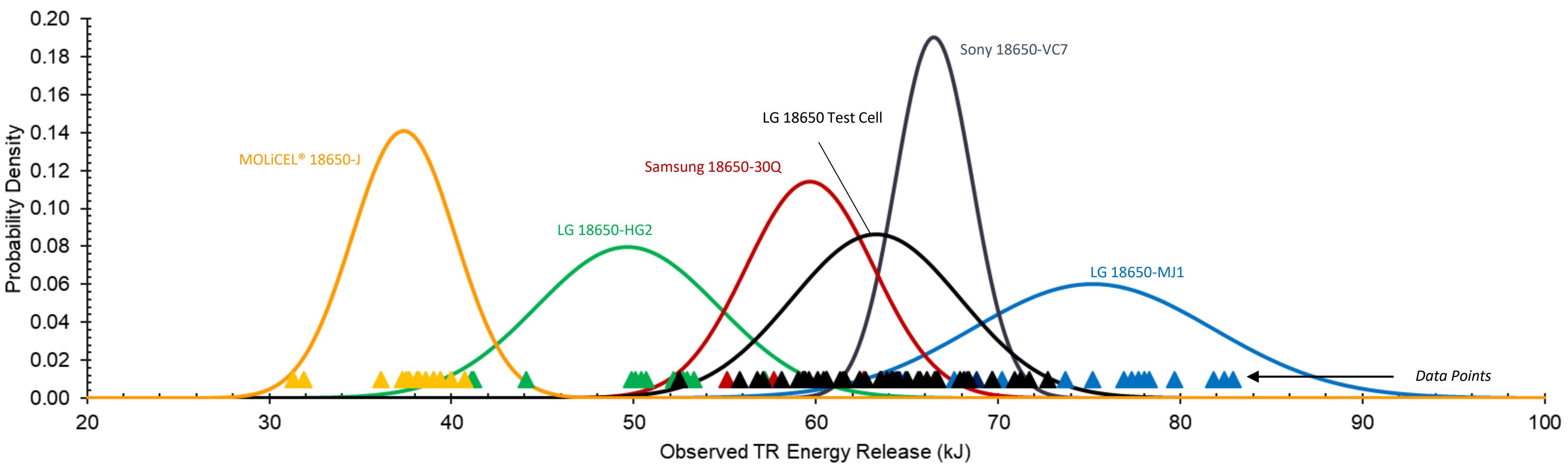
DIRECT COMPARISON OF TOTAL ENERGY RELEASE

- **Higher energy cells (e.g. the LG 18650-MJ1) release more TR energy, have more violent ejections, and lower remaining cell mass when compared to lower energy cells (e.g. the Molicel 18650-J):**
  - Note that the normal distributions (left image) shown below are created from the raw data and are generated to give an initial glance at the data
  - These plots do not break down the impacts of the aforementioned design variables on the thermal runaway behavior; hence the significant differences in standard deviations seen in the plot below
  - Although direct interpretation of the raw data is insightful, we recommend referring to the regression model results (next few slides) for final assessment of thermal runaway behavior



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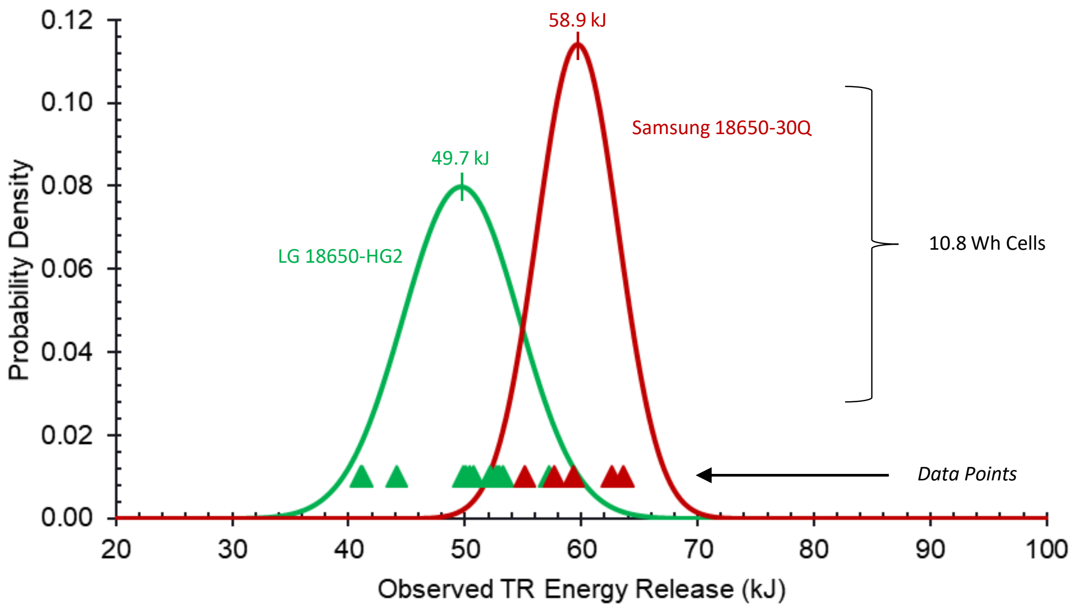
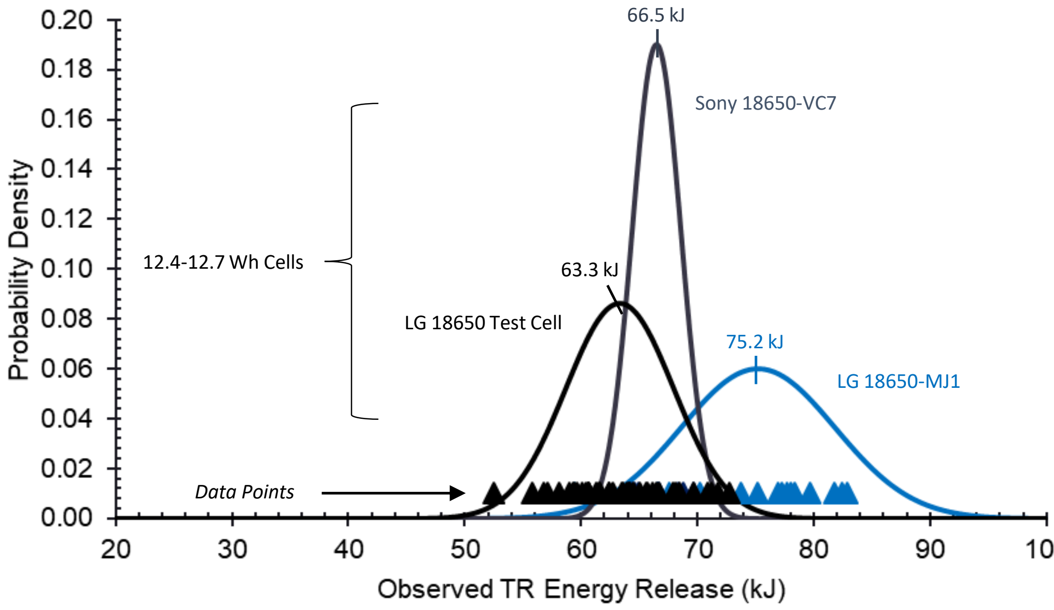
DIRECT COMPARISON OF TOTAL ENERGY RELEASE

- **There is not a linear relationship between stored electrochemical energy and the total energy released:**
  - The two 10.8 Wh cells have significantly different thermal runaway responses with the Samsung 18650-30Q average total energy release at 59.7 kJ and the LG 18650-HG2 average total energy release at 49.7 kJ
  - The three higher energy cells (12.4 to 12.7 kJ) also have differing thermal runaway responses with the LG 18650 Test Cell average total energy release of 63.3 kJ, the Sony 18650-VC7 average total energy release of 66.5 kJ, and the LG 18650-MJ1 average total energy release of 75.2 kJ
  - Again, we recommend referring to the regression model results (next few slides) for final assessment of thermal runaway behavior





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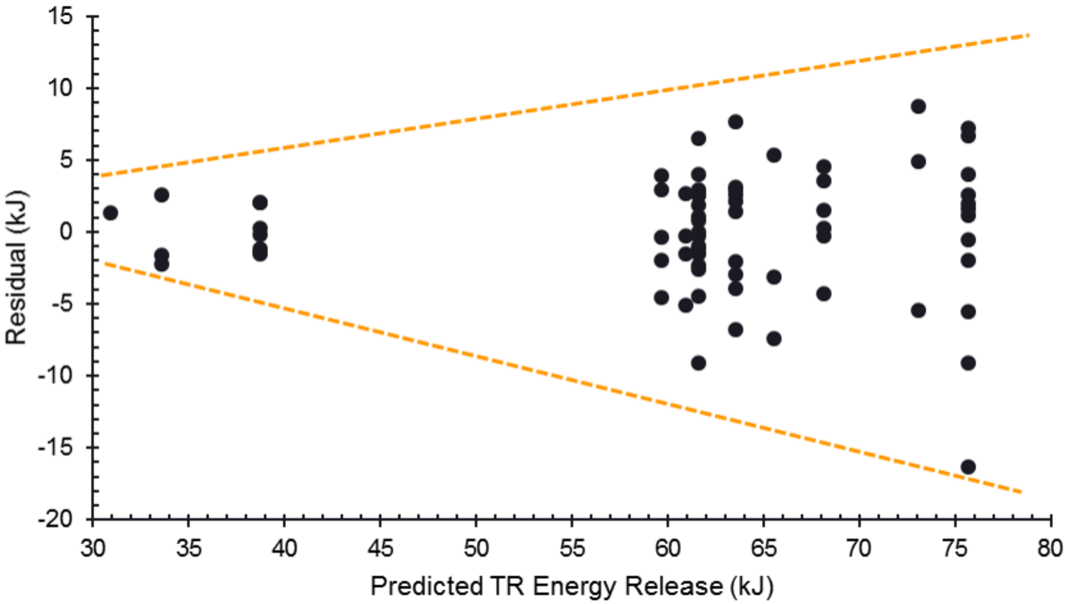
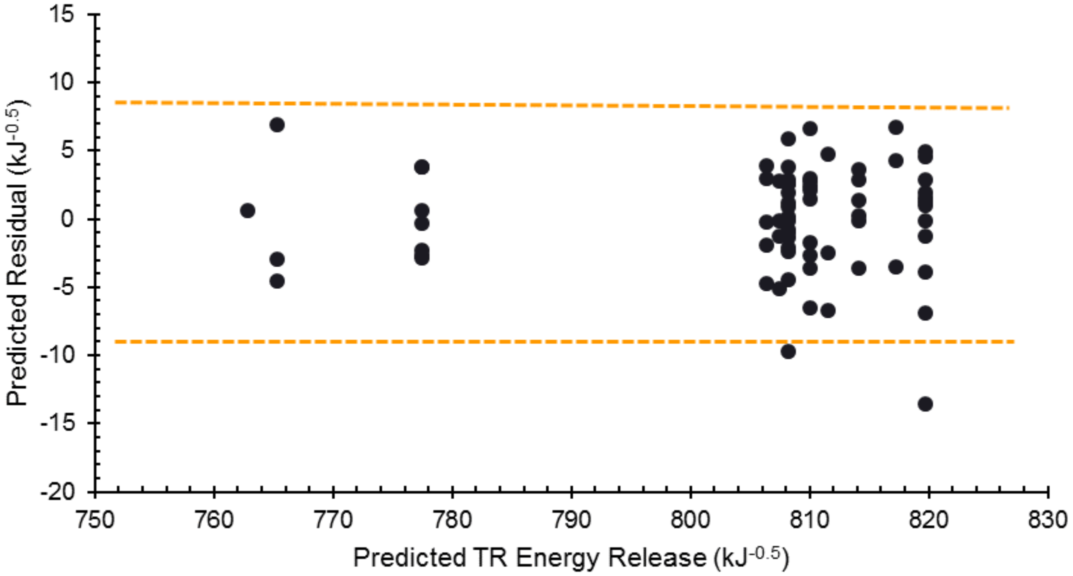
ENGINEERING STATISTICS METHODOLOGY

- **The TR results for each experiment are directly post-processed with primary consideration given to the following:**
  - Total TR energy yield
  - Fraction of energy released through the cell casing vs. through the ejecta materials and gases
  - Remaining cell mass following TR
  - The raw data derived versions of these values are referred to as the “observed” values and serve as inputs to a regression model
- **No two TR events are identical which results in variation of total TR energy release on a test-to-test basis:**
  - This variation is a function of various random and non-random factors associated with the experiments
  - A regression model was developed as a function of all of the FTRC results (e.g. cell type, failure mechanism, energy distribution, total energy release)
  - The completed regression model then uses the observed values for each experiment and outputs a corresponding predicted total energy release
  - The predicted energy release values are then used to recreate distributions to characterize the range of thermal runaway energy release
- **Note that the regression model can be used to predict energy fractions as well, but at this point we are only using it to predict total energy release:**
  - The predicted values and the associated distributions are shown on the next few slides

PREDICTED TOTAL ENERGY RELEASE

- **First it is important to examine how effective the regression model is at predicting total energy release:**
  - This effectiveness can be considered by looking at the residuals (differences between predicted and corresponding observed values)
- **A key assumption for the regression analysis was equal variability of the residuals across zero:**
  - Residual = difference between predicted value and corresponding observed value
  - Initial model, based on total energy release in kJ, did not satisfy this assumption (left image)
  - Performed inverse-square root translation of observed total energy release ($kJ^{-0.5}$) factor to achieve a better model (right image)





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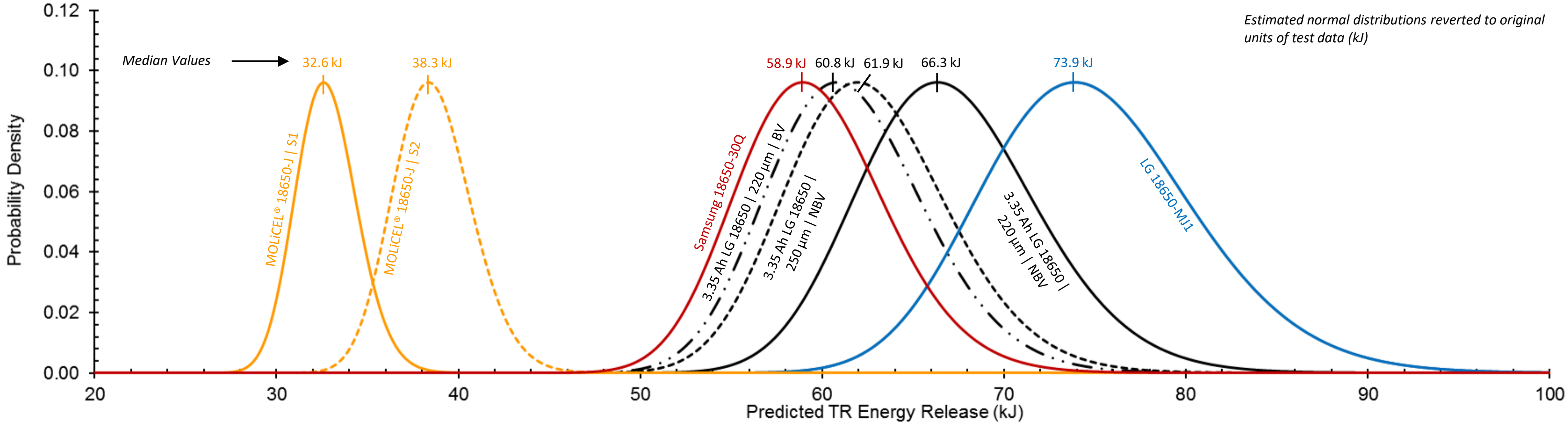
PREDICTED TOTAL ENERGY RELEASE

- **Final regression model results for total energy release were in inverse square root units (kJ $^{-0.5}$) as seen on the previous slide:**
  - These predictions were then translated back into the original units (kJ) for final interpretation
- **Distributions based on the final predicted values (in kJ) were then created:**
  - Think of the distribution curves below, plus the previously shown fractional pie charts, as the end goal for every cell, cell configuration, and cell variable that we attempt to characterize
  - The power of the regression model becomes apparent as we are now able to analyze the impacts of the random and non-random variables on thermal runaway behavior



Estimated normal distributions reverted to original units of test data (kJ)

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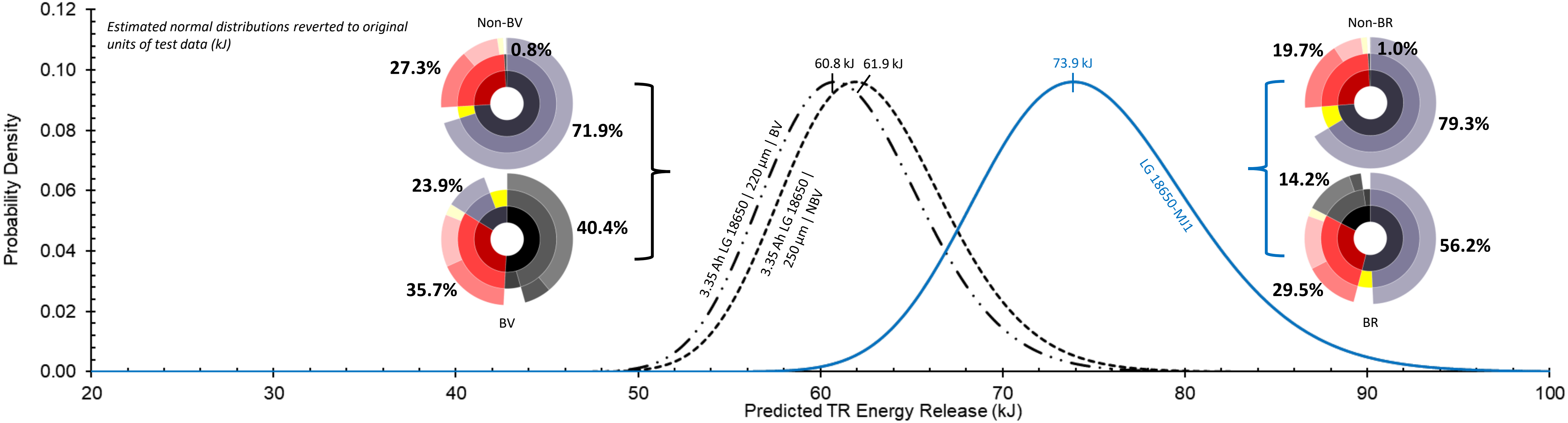
THERMAL RUNAWAY ENERGY FRACTIONS

- **The thermal runaway energy release fractions are determined for every cell configuration:**
  - Fractions can be determined from an average of all results for a given cell type or can be an average based on nominal vs. off nominal failure mechanism (e.g. difference between top vent vs. bottom rupture)
  - Fractional analysis is particularly helpful in comparing the distribution of standard vent cells to bottom vent cells
  - Standard cells typically release 20-30% through the cell casing and the remainder through the ejecta material
  - Bottom vent cells tend to release the energy in a three-way split between the casing and the top and bottom ejecta materials
- **The fractions provide test verification of how much energy is directly impended on neighbor cells during runaway events**



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CONCLUSIONS

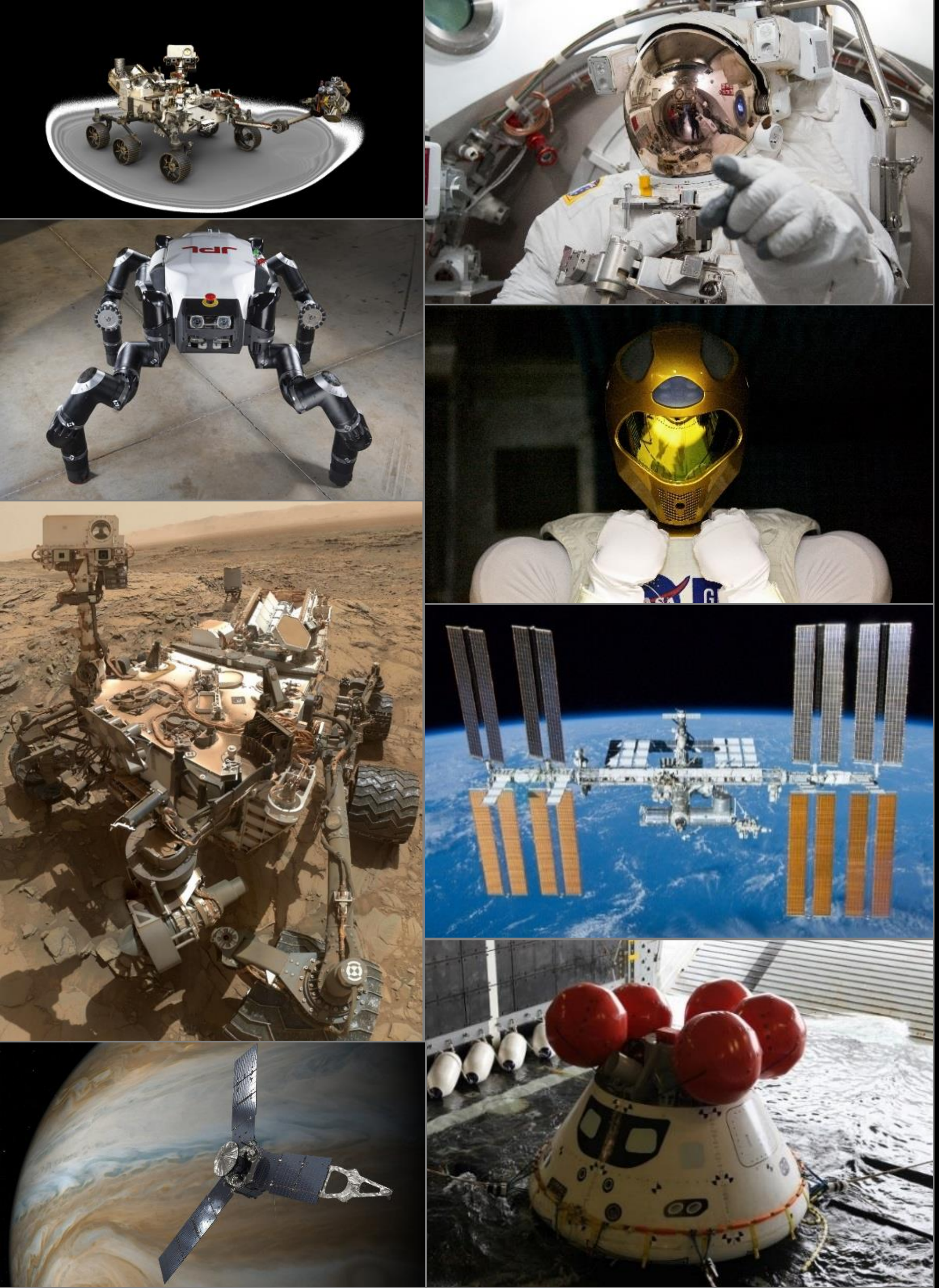
- **Results provide the means to develop optimized Li-ion batteries while also maintaining safety and margin**
- **FTRC, and the associated results, enables the discernment of the fractions of thermal runaway energy released through the cell casing and through the ejecta material:**
  - Due to the variability in thermal runaway responses, we recommend at least 10 runs to establish statistically defendable results
  - Can analyze the spread of heat sources when cells rupture and compare to when they remain intact
- **Higher energy cells produce more heat and eject more material during thermal runaway:**
  - Higher magnitudes of total energy released and more violent ejections
  - Less energy associated with the cell body and more energy associated with the ejecta
  - The correlation is not very linear because cell enclosure design impacts the results
- **BV cells released less energy (~4 kJ for 3.35 Ah LG cell) and have higher post runaway cell mass than non-BV cells:**
  - BV cells produce less and more localized heat, hence a less severe and more predictable thermal runaway event as an effect of the BV feature
  - Battery designers should be ready to accommodate and take advantage of cell designs with the BV feature in the future
- **There is not a linear relationship between stored electrochemical energy and total thermal runaway energy release**
- **Shapiro-Wilks goodness of fit tests, quantile-quantile plotting, residual analysis, and the shape of the normal distribution curves, for all cell types, indicate that a normal distribution is an appropriate assumption**

CURRENT FOCUS OF FTRC EFFORTS

- **The current focus of the FTRC efforts is on characterizing thermal runaway behavior for like cells as a function of three trigger mechanisms; i.e. thermal, nail, and ISC (combined with thermal)**
- **Examining the effects of failure location on rupture behavior using the ISC device**
- **Development of accommodations for small format cells beyond 18650 cells including the following:**
    - 21700 cells
    - D-Cells
    - Pouch cells
    - These three (plus the 18650 calorimeter) are referred to as small format FTRC or S-FTRC
- **Development of FTRC capability for >100 Ah Li-ion cells; this is referred to as large format FTRC or L-FTRC**
- **Improvement of regression modeling techniques**

ACKNOWLEDGEMENTS

- **NASA Engineering and Safety Center**
  - Steve Rickman and Christopher Iannello
- **NASA JSC Engineering Directorate (EA):**
  - Power and Propulsion Division (EP)
  - Structural Engineering Division (ES)
- **FTRC Team Members**
- **NASA JSC Energy Systems Test Area (ESTA)**



QUESTIONS?