Trends in Safety with State-of-Charge for Lithium-ion Cells and Batteries

Judith Jeevarajan, Ph.D., Saad Azam, Tapesh Joshi, Ph.D.,
Underwriters Laboratories

Carlos Lopez, Steve Kinyon, Ph.D.
Stress Engineering Services Inc.

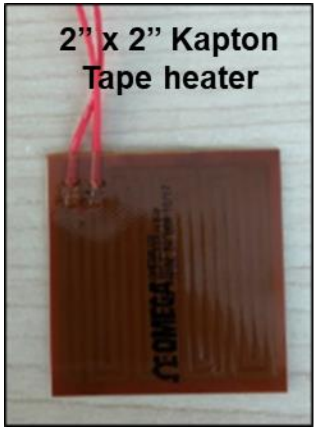
Space Power Workshop 2021
April 20, 2021

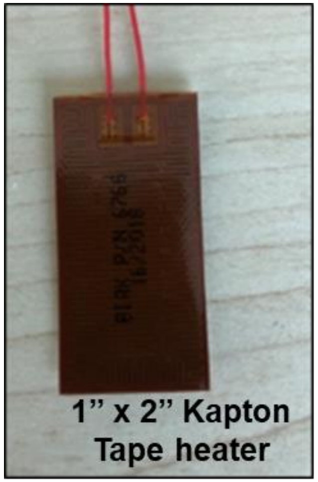
Background / Overview

- Lithium-ion cells and batteries today, provide power in a wide variety of applications from consumer electronic, automotive and aerospace to stationary grid energy storage.
- With the increase in demand, millions of cells and thousands of batteries are manufactured every month and the challenge of confirming the quality of every cell and battery manufactured has become a major factor in determining the safety, creating a significant concern especially for the shipping and transportation industry.
  - IATA estimates approximately 3 billion cells (Li-ion and Li-metal) and over one billion batteries are shipped by air each year
- This led the International Civil Aviation Organization (ICAO) to set temporary bans in transporting Li-based cells and batteries as cargo in passenger and cargo aircraft, with a restriction on the state-of-charge (SOC) of a lithium-ion cell or battery to not exceed 30%.
- The safety of li-ion cells and batteries at various states of charge have not been studied comprehensively in the past and hence the goal of this study was to determine if the result of an off-nominal condition would vary with varying SOC.
- Cells of different form factors (18650, 26650, and pouch), cathode chemistries (NCA, NMC, and LFP), capacities (2.5-10Ah), and quality (based on nominal price and inexpensive) were studied under this program. Battery designs were also studied.
- To characterize the behavior under off-nominal conditions, cells and batteries were subjected to two types of tests: the heating method using a heating tape, and the low impedance external short.
- In addition to that, the charge retention characteristics of these cells and batteries was studied at the various SOCs.

Thermal Runaway using Heating Method

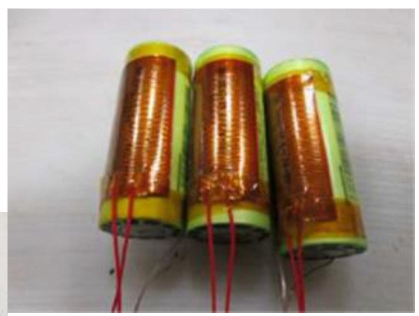
- 40 W Kapton heaters were used to initiate thermal runaway
  - 1” x 2” – 20W/in^2 **or** 2” x 2” – 10W/in^2
- Heating rate was maintained at 10 ºF/min until thermal runaway occurred or until the cell voltage fell to 0V
- Cells were subjected to thermal runaway test at 6 different SOCs
  - 100%, 50%, 40%, 30%, 15%, and 0% (3 samples under each test condition)
- Cells from 6 different manufacturers were tested
  - Manufacturer: A, B,C, D, E, and F
  - Label on cells indicate that manufacturer for A & B were the same, however, A was purchased at the nominal cost from a trusted vendor and B cells were inexpensive and purchased online (~$2/ cell)
- Pouch cells were restrained during the tests
- Two battery designs were also subjected to the same heating tests

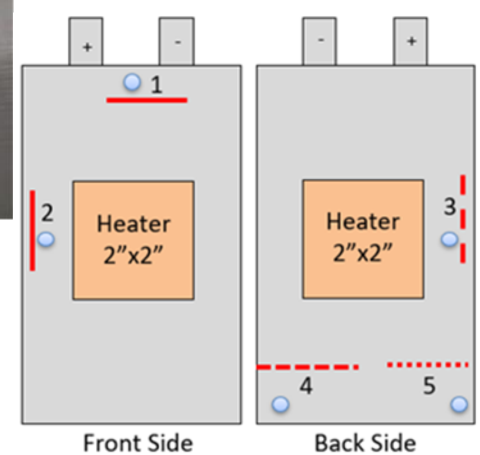


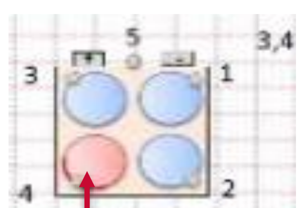


Test Samples Used in the Test Program

Manufacturer	Cell Design	Cathode Chemistry	Rated Capacity (mAh)	Actual Capacity (mAh)	Internal Resistance (mΩ)
A	18650	NCA	3200	3230	45
B	18650	NCA	3200	1810	35
C	26650	NMC	5000	5030	19
D	Pouch	NMC	3300	3180	18
E	26650	LFP	2500	2520	6
F	Pouch	LFP	10000	10400	8
G (Single cell low cost smart phone battery)	Pouch	Unknown	2915	2770	57
H (2P2S Camcorder battery)	18650	Unknown	4900	4950	111

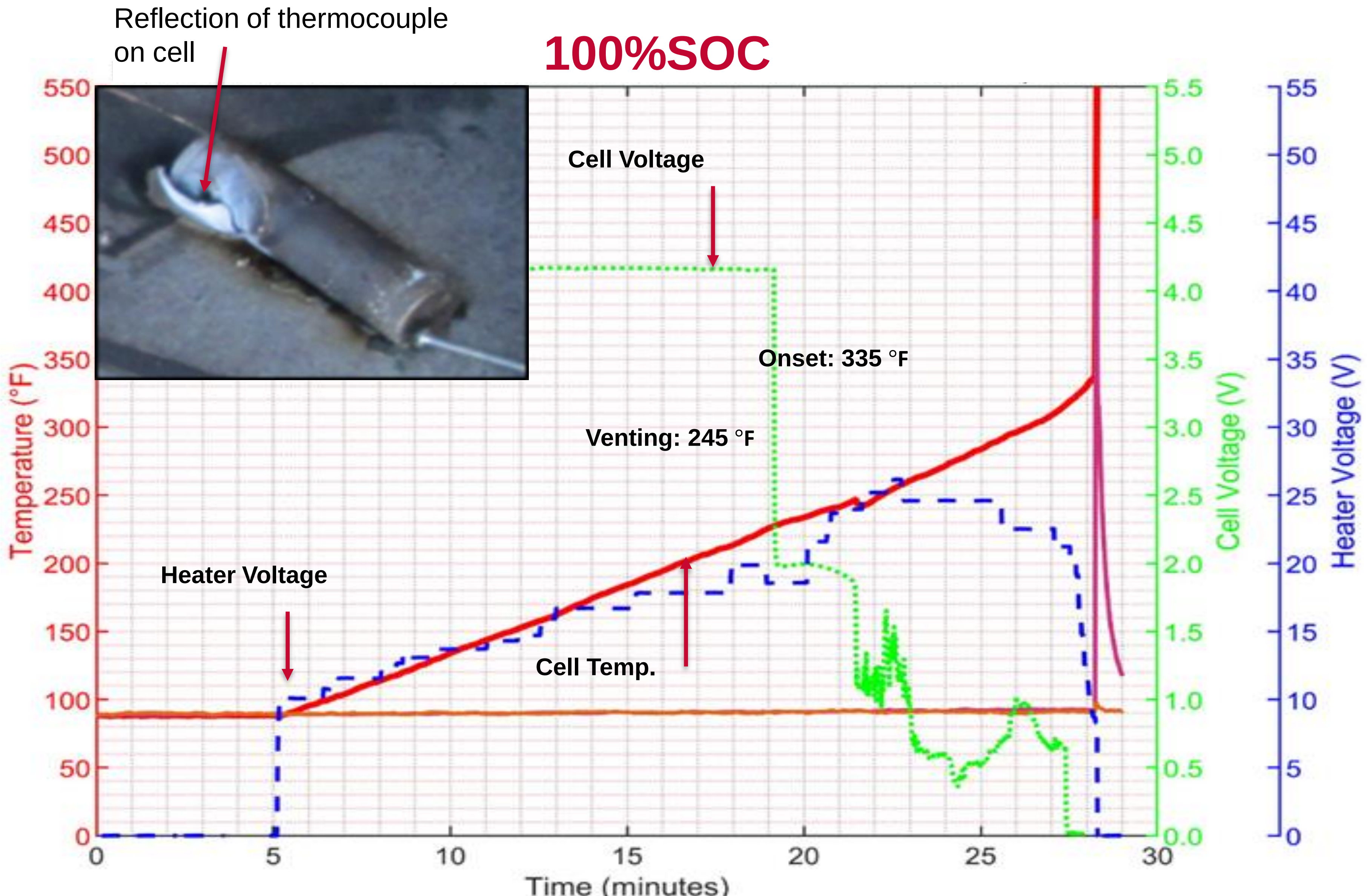






Cell with heater-Manuf H

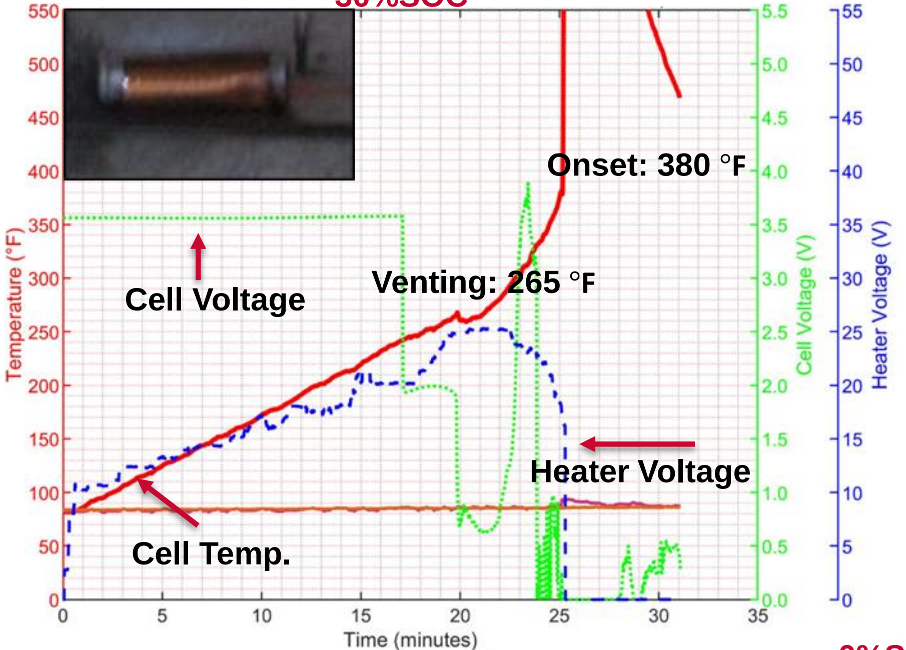
Heating Method - Manufacturer A (18650, 3.2 Ah, NCA)



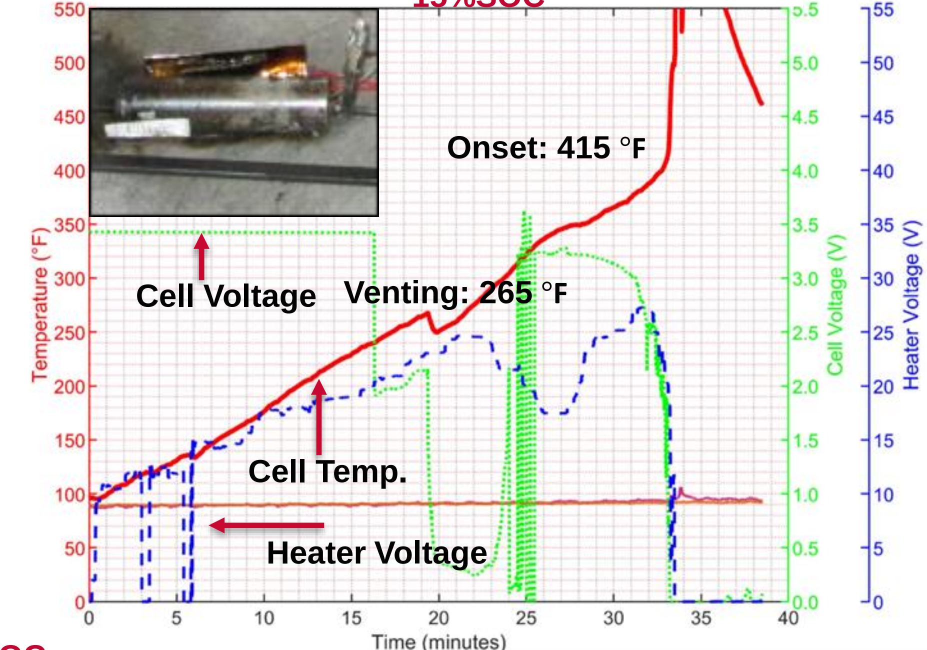
Preliminary data set used to show details of variables recorded during test

Heating Method - Manufacturer A (18650, 3.2 Ah, NCA)

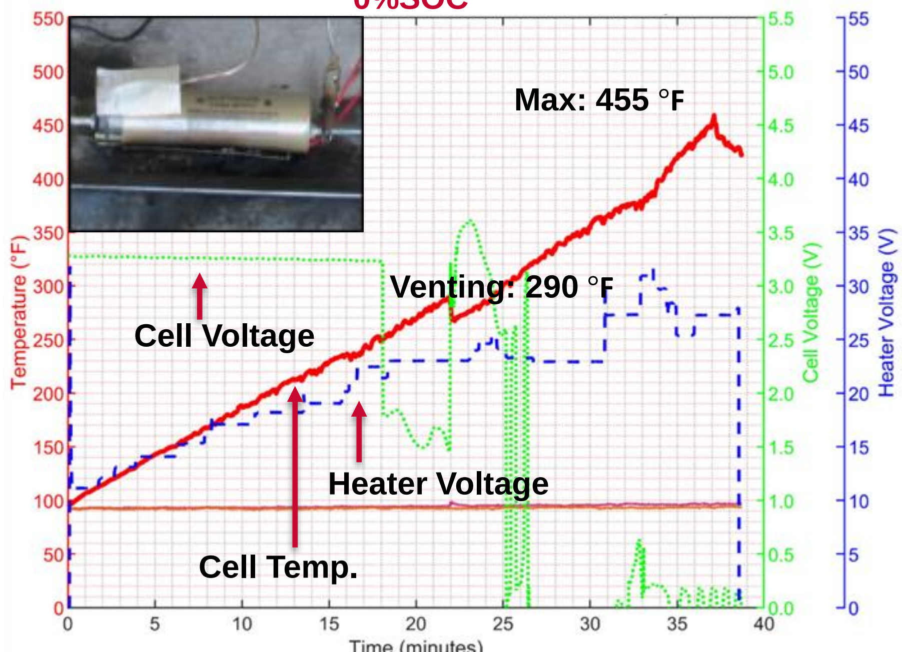
30%SOC



15%SOC



0%SOC



Preliminary data set used to show details of variables recorded during test

Summary of Results for Manufacturer A (18650, 3.2 Ah, NCA)

State of Charge (%)	Venting Temperature (°F)	Venting Time (min)	Thermal Runaway Onset Temperature (°F)	Onset Time (min)	Maximum Temperature (°F)	Observations
100	245	16.5	335	23	1095	Fire and smoke
50	270	21	365	29	1200	Fire and smoke
40	240	15.5	275	19	1325	Fire and smoke
30	265	19	380	25	875	Fire and smoke
15	265	19	415	33	800	Smoke
0	290	22	N/A	N/A	455	No fire or smoke

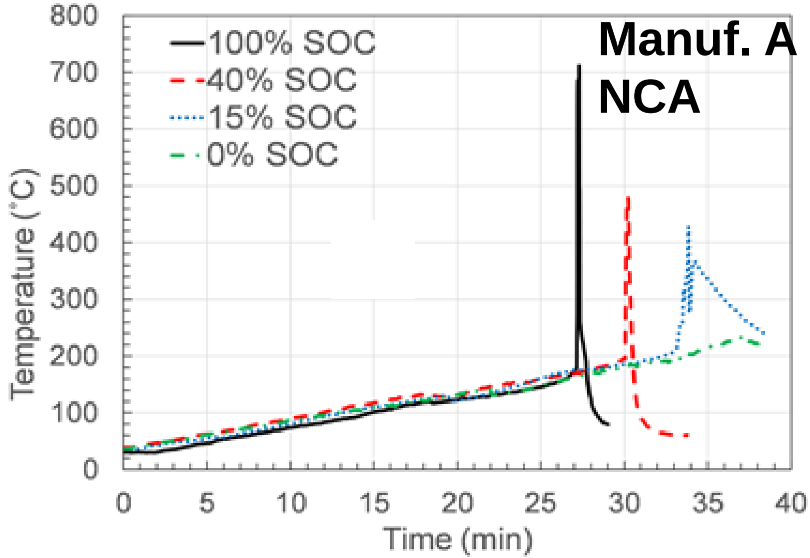
Fire and smoke

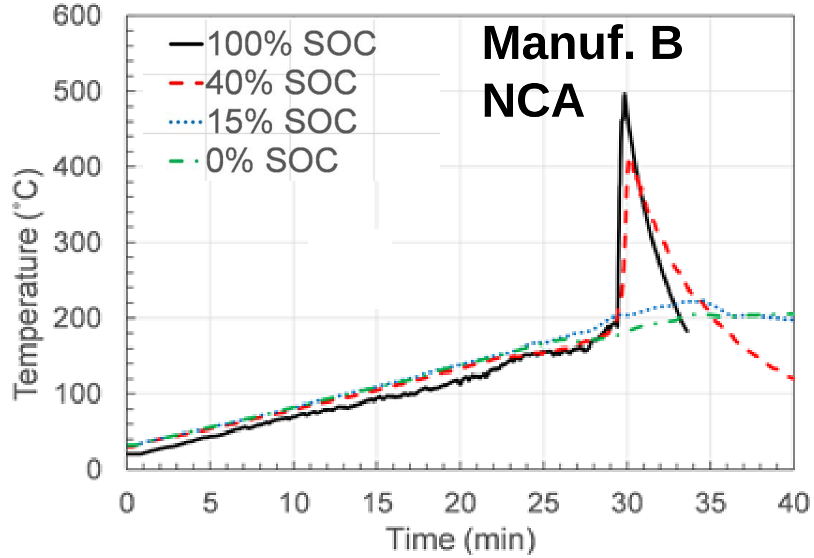
100%SOC

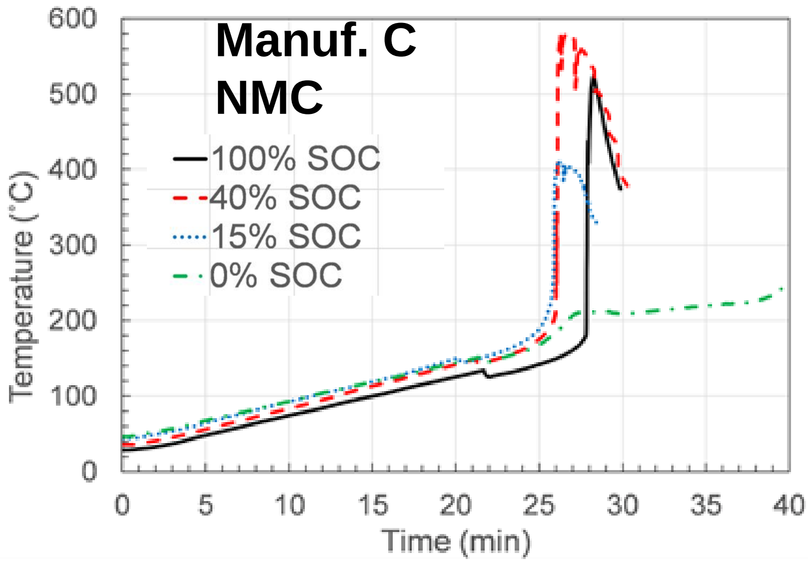
Smoke only

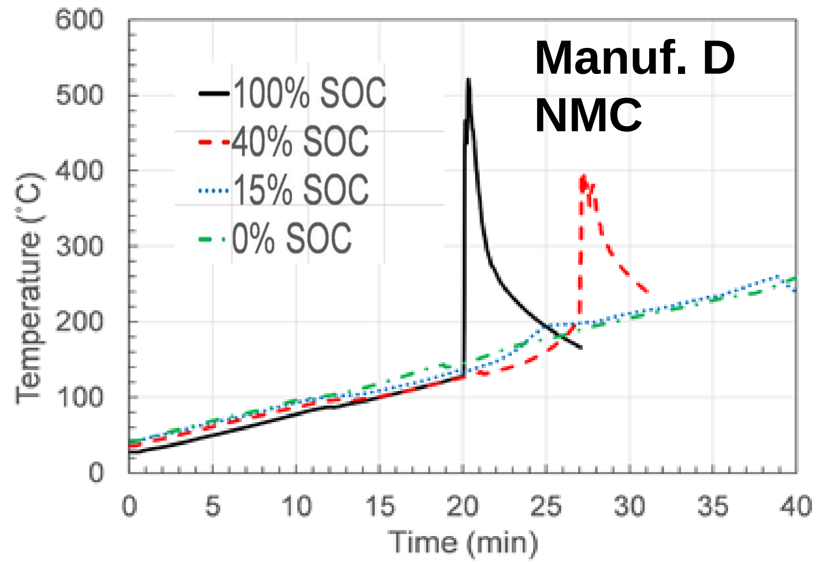
15%SOC

Results for Cells from Various Manufacturers- Heating Method

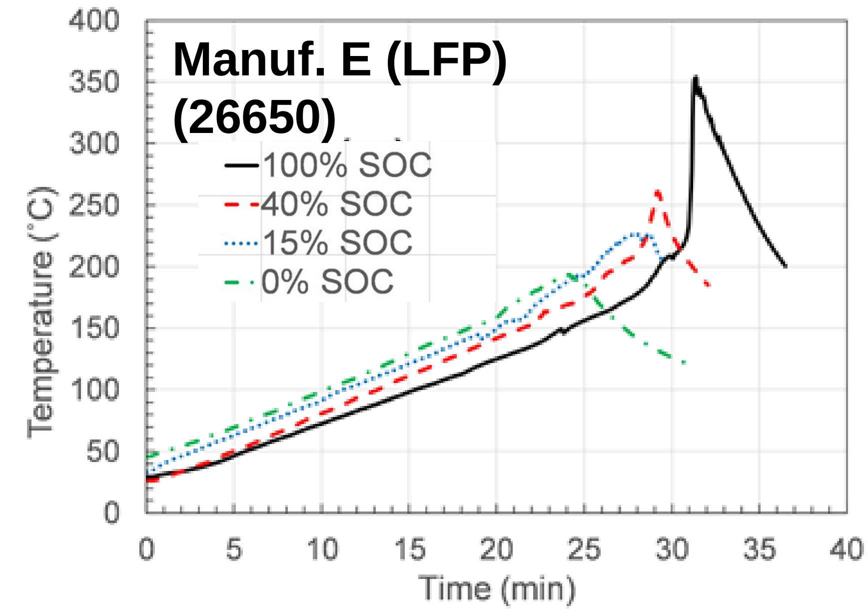


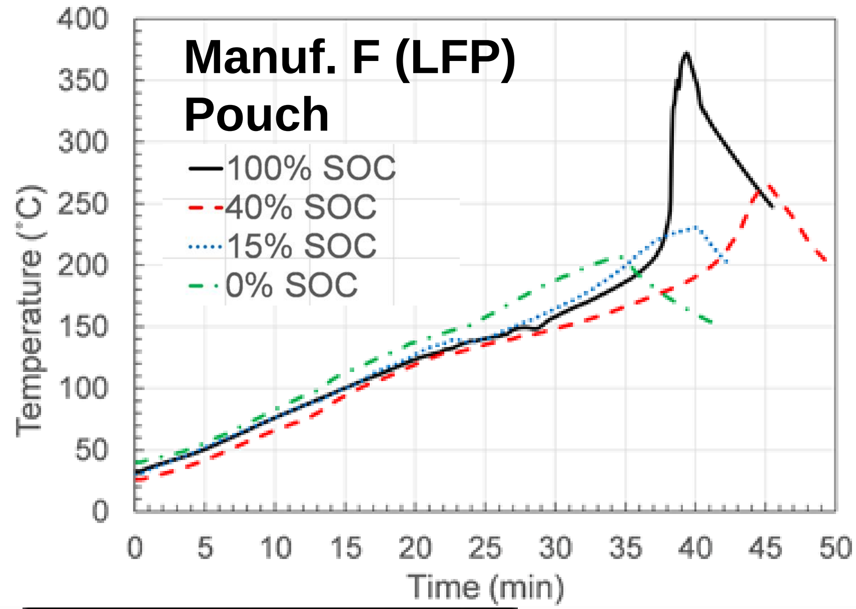






Results for Cells from Various Manufacturers- Heating Method






Manuf. A (NCA)
Post-test 100 % SOC

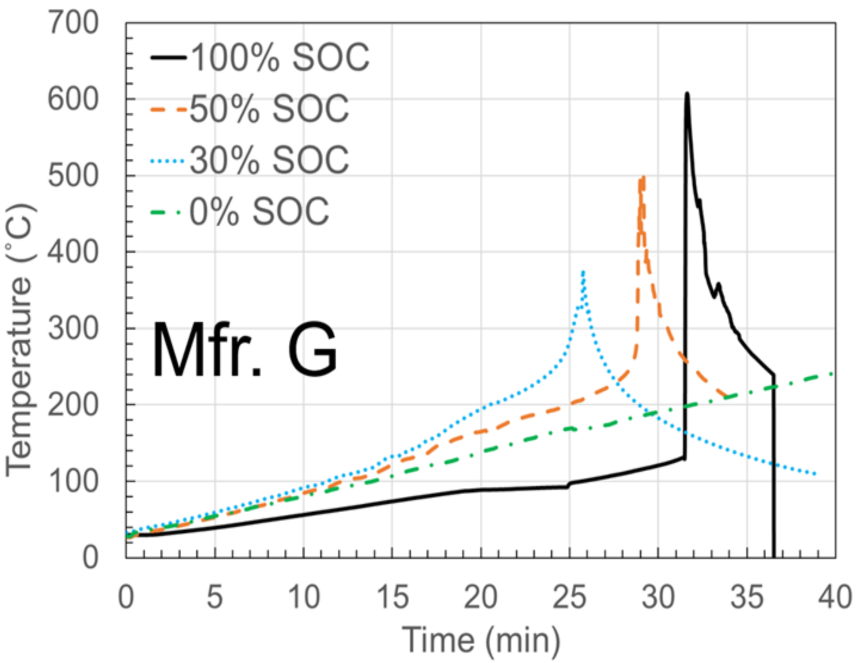

Manuf. C (NMC)
Post-test 100 % SOC

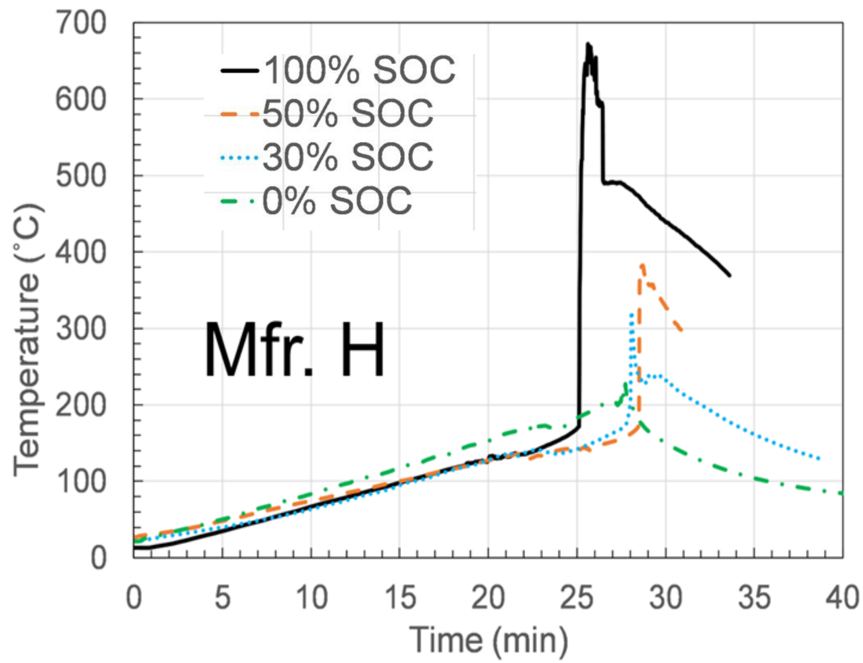

Manuf. E (LFP)
Post-test 100 % SOC


Manuf. F
Post-test
100 % SOC


Manuf. E (LFP)
Post-test 100 % SOC

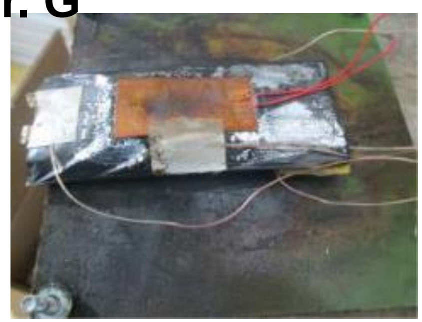
Battery Tests – Heating Method





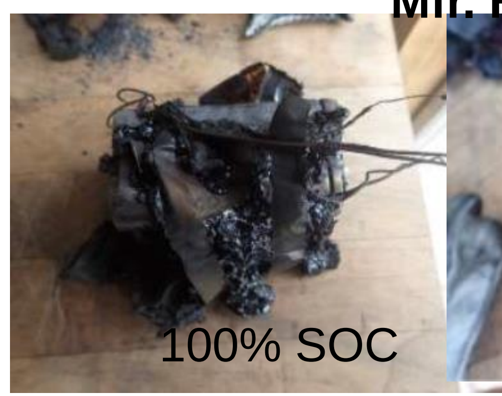
Mfr. G

100% SOC



30% SOC

Mfr. H



100% SOC

30% SOC

Summary of Results and Observations for the Cell Tests – Heating Method

Cell Type	SOC (%)					
	100	50	40	30	15	0
A – 18650/3.3Ah/NCA	TR + Smoke (2) + Fire (3)	TR + Smoke (2) + Fire (2)	TR + Smoke (3) + Fire (2)	TR + Smoke (3) + Fire (1)	Mild TR + Smoke (3) + Fire (0)	No TR + Smoke (1) + Fire (0)
B- 18650/1.8Ah/NCA	TR + Smoke (3) + Fire (1)	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	No TR + Smoke (2) + Fire (0)	No TR + Smoke (1) + Fire (0)
C – 26650/5.0Ah/NMC	TR + Smoke (3) + Fire (3)	TR + Smoke (3) + Fire (2)	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	No TR + Smoke (1) + Fire (0)
D – Pouch/3.3Ah/NMC	TR + Smoke (3) + Fire (2)	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	No TR + Smoke (1) + Fire (0)	No TR + Smoke (1) + Fire (0)	No TR + Smoke (1) + Fire (0)
E – 26650/2.5Ah/LFP	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	Minor TR + Smoke (3) + Fire (0)	No TR + Smoke (2) + Fire (0)	No TR + Smoke (2) + Fire (0)	No TR + Smoke (1) + Fire (0)
F – Pouch/10.0Ah/ LFP	TR + Smoke (3) + Fire (0)	Minor TR + Smoke (3) + Fire (0)	Minor TR + Smoke (3) + Fire (0)	No TR + Smoke (3) + Fire (0)	No TR + Smoke (2) + Fire (0)	No TR + Smoke (1) + Fire (0)

Fire	Smoke	
0	0	No
1	1	Minor
2	2	Moderate
3	3	Heavy

Summary of Results and Observations for the Battery Tests – Heating Method

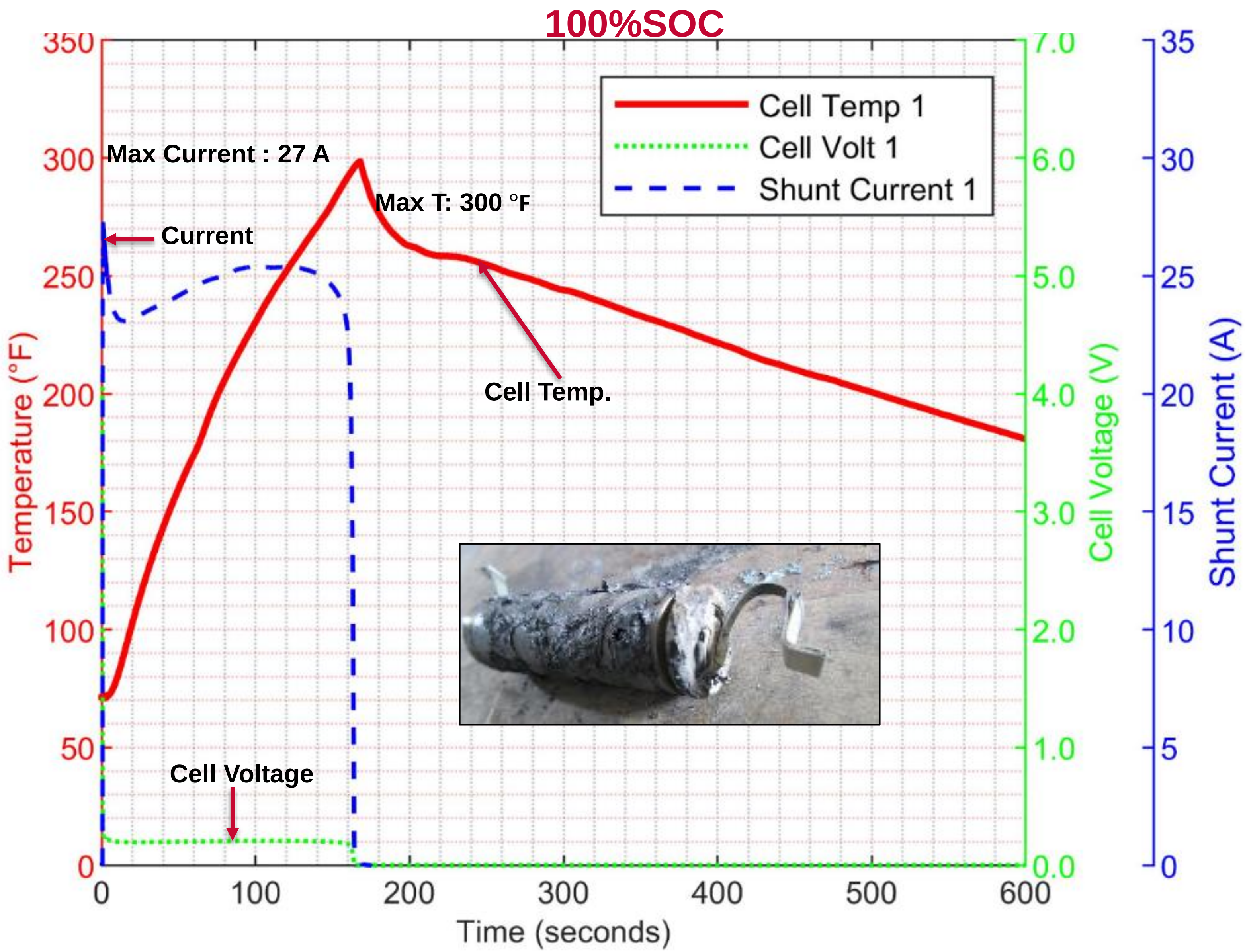
Battery Type	SOC (%)					
	100	50	40	30	15	0
G – Pouch format smart phone battery 2.9 Ah	TR + Smoke (3) + Fire (1)	TR + Smoke (3) + Fire (0)	TR + Smoke (3) + Fire (0)	TR + Smoke (1) + Fire (0)	No TR + Smoke (2) + Fire (0)	No TR + Smoke (1) + Fire (0)
H – 2P2S Camcorder battery with 4 18650 cells 4.9 Ah	TR + Smoke (2) + Fire (3)	TR + Smoke (3) + Fire (0)		Mild TR + Smoke (2) + Fire (0)		No TR + Smoke (1) + Fire (0)

External Short

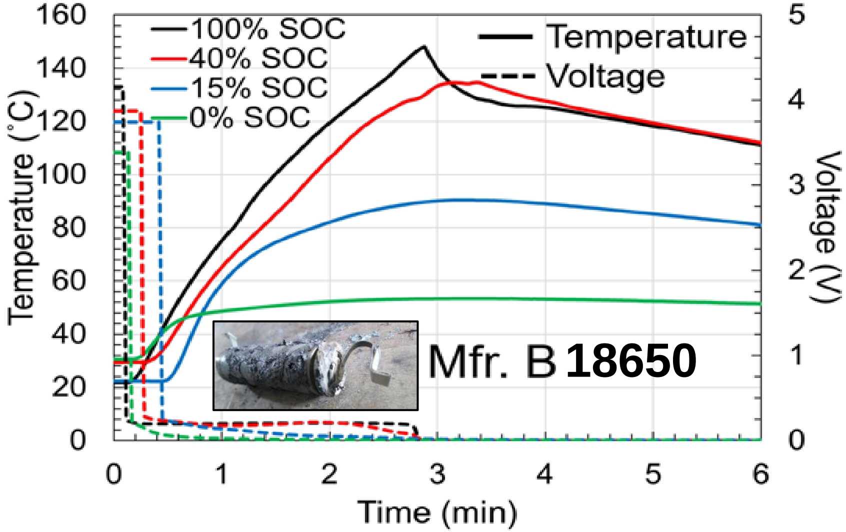
- External short was carried out on cells that do not contain the internal PTC device. The batteries were tested with their protective circuit board bypassed. Table below provides the list of cells and batteries tested.
- The load used for the low impedance short was 8-10 mohms; short was held for 3 hours or until thermal runaway.
- Pouch cells were restrained and the terminal tabs reinforced with Ni tabs.
- Cells and batteries were subjected to external short at 6 different SOCs -100%, 50%, 40%, 30%, 15%, and 0%. Three cells were tested under each condition.

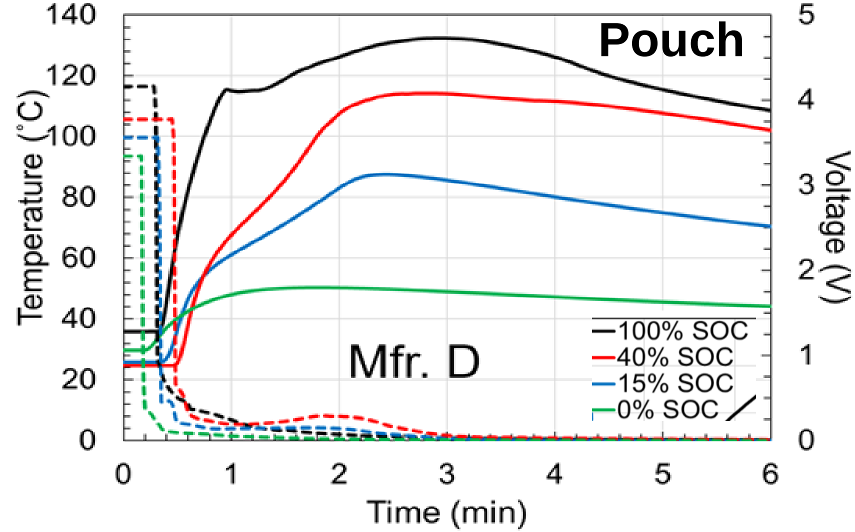
Manufacturer	Cell Design	Cathode Chemistry	Rated Capacity (mAh)	Actual Capacity (mAh)	Internal Resistance (mΩ)
B	18650	NCA	3200	1850	35
D	Pouch	NMC	3300	3220	18
E	26650	LFP	2500	2500	6
F	Pouch	LFP	10000	10300	5
G (Single pouch cell battery)	Pouch	Unknown	2915	2770	57
H (2P2S Camcorder battery)	18650	Unknown	4900	4950	111

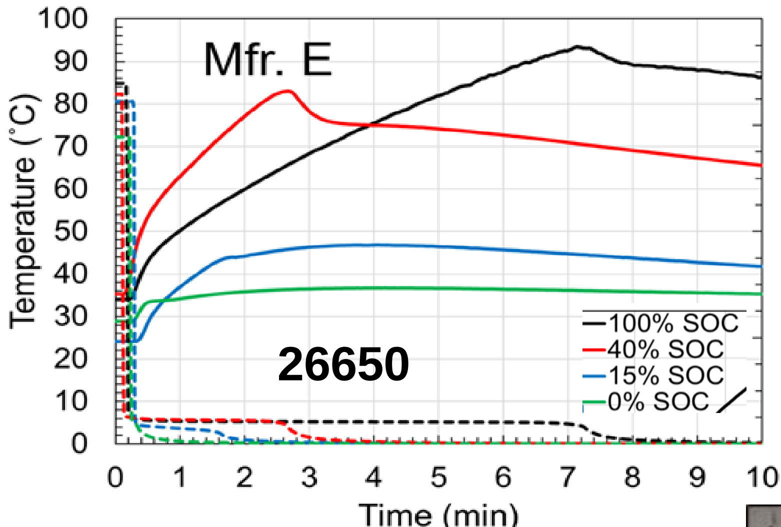
External Short- Manufacturer B (18650, 1.8 Ah, NCA)

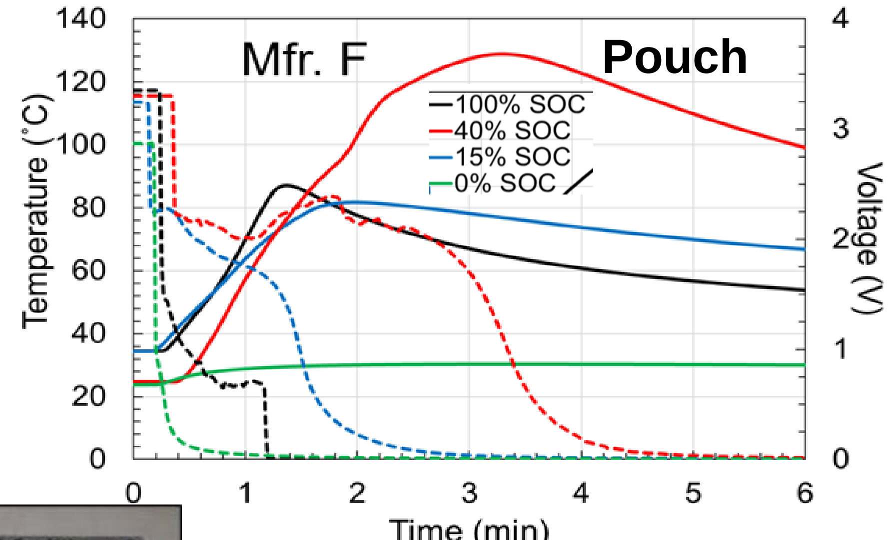


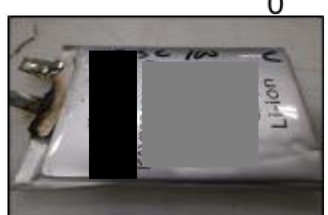
Trends for External Short Test on the Cells at Various SOCs







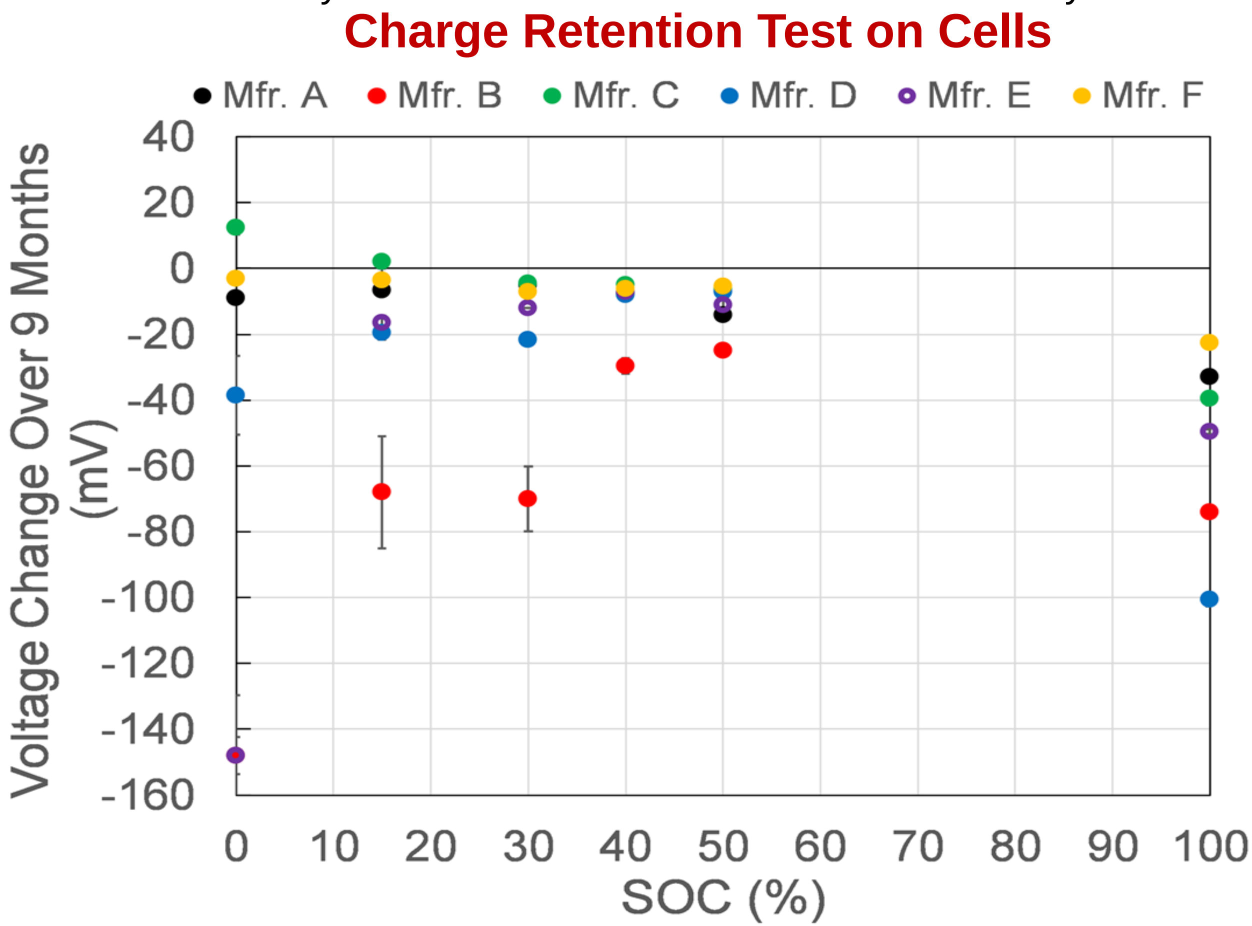




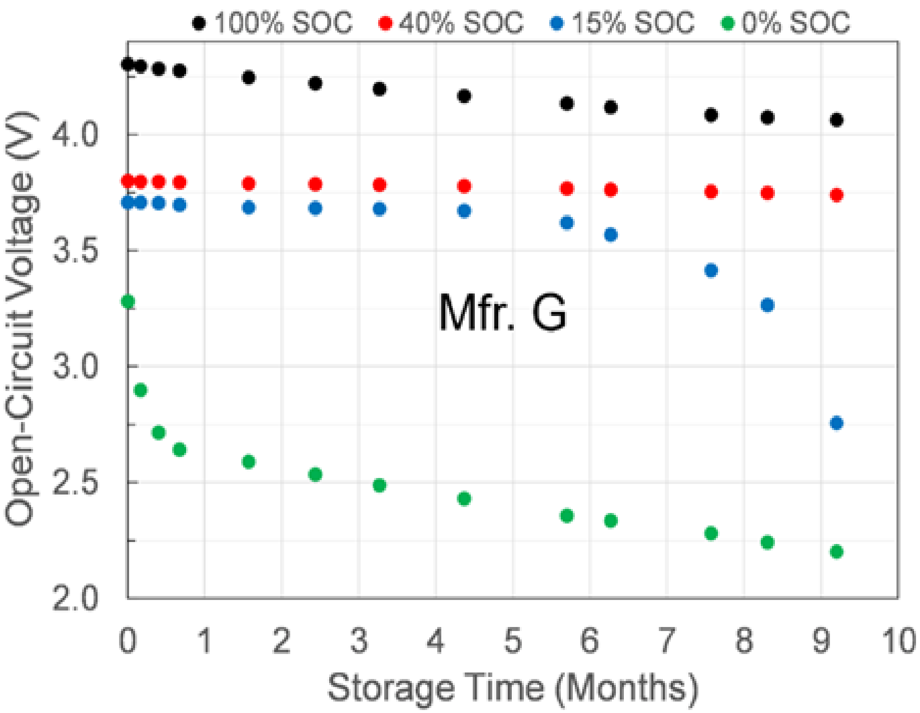
Mfr D
100% SOC
Post-test
(negative tab burns off)

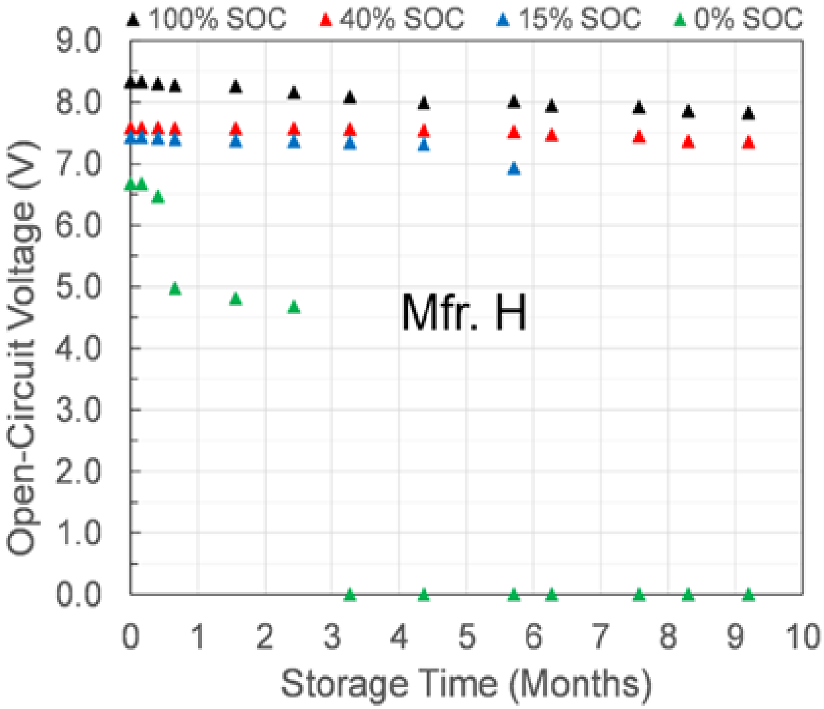
Charge Retention

- Cells and batteries from all manufacturers were subjected to charge retention test to characterize self-discharge.
- Cells were stored in ambient temperature (controlled) at 6 different SOCs
  - 100%, 50%, 40%, 30%, 15%, and 0%
  - 2 samples are under test for each condition.
- OCV was recorded once every week for the first month and then once every month for up to 9 months.



Charge Retention Test on Batteries





Summary and Conclusions

Heating Method:

- Thermal Runaway onset temperature increases (↑) as SOC goes down (↓) except for manufacturer B (low cost cells).
- The maximum temperature observed during thermal runaway increases (↑) with increasing SOC (↑).
- Cells with Ni – based cathodes – NMC and NCA display fire and smoke at high SOC but LFP cells display only smoke even at high SOC; Cells with NMC and NCA cathodes display smoke even at SOC as low as 15%. This may be due to the leakage of electrolyte at low SOCs which can then cause smoke to be generated due to the high temperatures induced by the heater.

External Short:

- Maximum temperatures recorded decrease with decreasing SOC.
- Tabs burn instantaneously for pouch cells at high SOCs and the tab that burns is typically the one that has the lower m.pt.
- Burning of tabs prevents cells from experiencing the short circuit load and hence they don't swell or experience thermal runaway at the high SOCs. Cells show swelling when tabs do not burn off.

Summary and Conclusions

Charge Retention:

- Trends were as expected with cells stored at 100% and 0% SOC showing the highest rate of self discharge.
  - ❖ The higher rates of loss in voltage at the SOC extremes are explained by the higher rates of degradation due to parasitic side-reactions such as decomposition of electrolyte and surface film formation.
- Manufacturer B exhibited high voltage losses across all SOC. This may be attributed to the poor manufacturing quality.
- Batteries from manufacturer G also show large voltage losses at lower SOC, but the voltages remain above 2V.
- For manufacturer H, the OCV recorded for the batteries stored at 15% and 0% SOC dropped to 0V after 6 months and 3 months, respectively. This is due to the activation of the protective undervoltage MOSFET switch, when the battery voltage falls below a certain value.

Acknowledgment

UL Electrochemical Safety Team

Stress Engineering Services

James Martinez (NASA-JSC)

THANK YOU