Safety of Lithium-ion Cells and Batteries with Varying States-of-Charge

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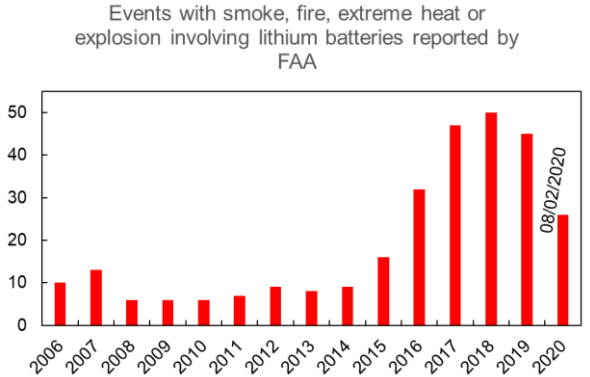
Background

•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.

•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 and this has been a major concern for certain sectors such as the shipping and transportation industry

•International Civil Aviation Organization (ICAO) 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%.



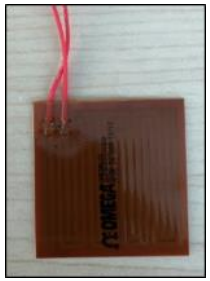
Laptop and spare with Lithium-ion battery in carry-on baggage

Batteries in a bag of audio-video equipment caused a fire in an overhead compartment

Courtesy: https://www.faa.gov/hazmat/resources/lithium_batteries/media/Battery_incident_chart.pdf
https://www.fire.tc.faa.gov/2007conference/files/Cabin_and_Hidden_Area_Protection/WedPM/WilkeningLithiumBatteries/WilkeningLithiumBatteryPres.pdf

Heating Test

- 40W Kapton heater was 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
- Cells were subjected to thermal runaway test at 6 different states-of-charge
  -100%, 50%, 40%, 30%, 15%, and 0%

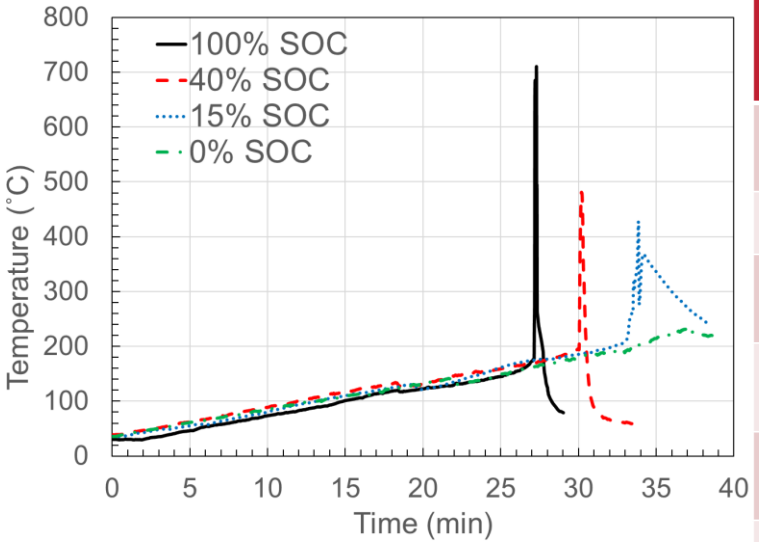


2” x 2” Kapton Tape Heater

1” x 2” Kapton Tape Heater

Manufacturer	Cell Design	Cathode Chemistry	Rated Capacity (mAh)	Measured 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 526495	NMC	3300	3180	18
E	26650	LFP	2500	2520	6
F	Pouch 8790160	LFP	10000	10400	8
G (Single cell Smart phone battery)	Single pouch cell with BMS	Unknown	2915	2770	57
H (2P2S Camcorder battery)	18650	Unknown	4900	4950	111

Manufacturer A (18650, 3.2 Ah, NCA)



State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0- none, 1-minor, 2-moderate, 3-heavy)	Observations
100	118	174	710	TR + Smoke (2) + Fire (3)	Electrolyte leakage. Ejection of content upon TR and sustained fire for 2-3 mins.
50	129	171	649	TR + Smoke (2) + Fire (2)	Electrolyte leakage. Sustained fire for 60 seconds.
40	129	191	482	TR + Smoke (3) + Fire (2)	Electrolyte leakage. Sustained fire for 30 seconds
30	132	193	468	TR + Smoke (3) + Fire (1)	Electrolyte leakage. A lot of smoke at TR, no sustained fire but cell was red hot
15	129	213	427	Mild TR + Smoke (3) + Fire (0)	Electrolyte leakage. A lot of smoke at TR, no obvious fire but cell was red hot
0	143	N/A	238	No TR + Smoke (1) + Fire (0)	Electrolyte leakage. No smoke or fire.
SOC↓	***Venting T ↑***	***TR onset T ↑***	***Max T ↓***	***Hazards ↓***	-

100% SOC

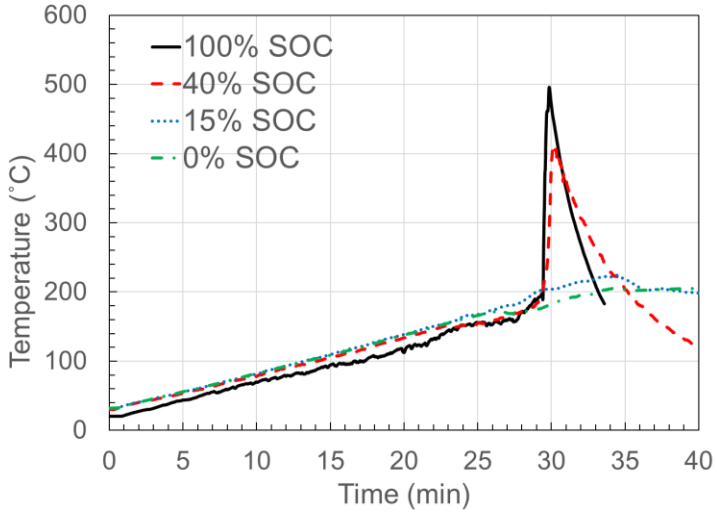
40% SOC

15% SOC

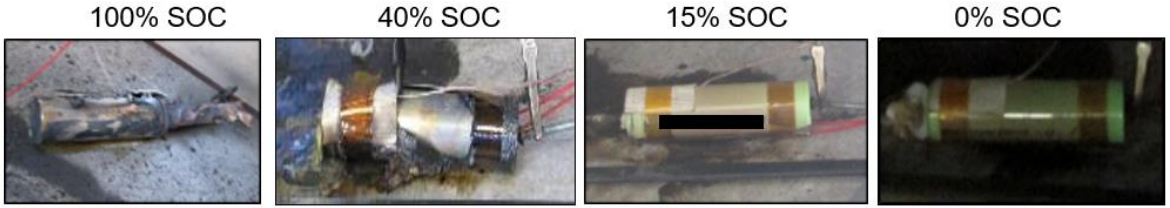
0% SOC

Manufacturer B (18650, 1.8 Ah, NCA)

- Low quality cells, lower capacity measured (1.8 Ah) compared to rated (3.2 Ah)
- Same label as that of manufacturer A

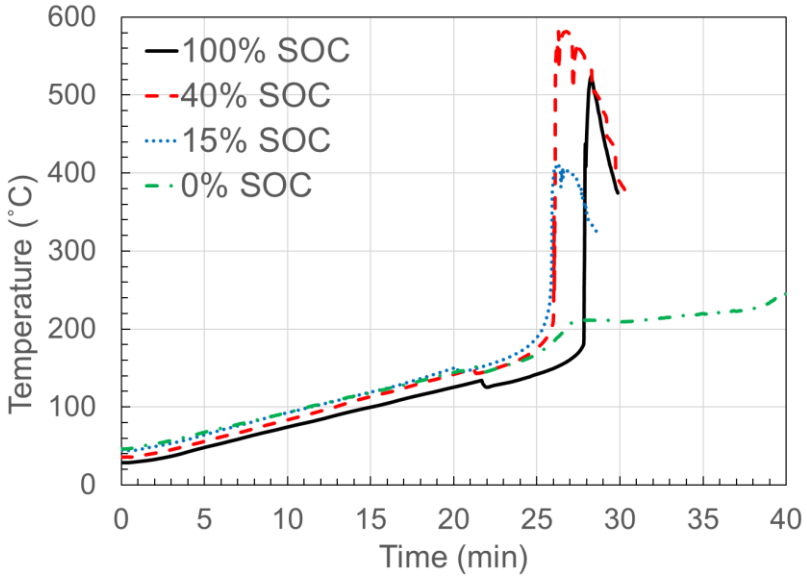


State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0-none, 1-minor, 2-moderate, 3-heavy)	Observations
100	96	191	493	TR + Smoke (3) + Fire (1)	No electrolyte leakage. Ejected part of content upon TR with a lot of smoke, but no sustained fire
50	121	141	310	TR + Smoke (3) + Fire (0)	Electrolyte leakage. Upon TR, a lot of smoke, but no fire
40	149	177	413	TR + Smoke (3) + Fire (0)	Electrolyte leakage. Upon TR, a lot of smoke, but no fire
30	143	182	349	TR + Smoke (3) + Fire (0)	No obvious electrolyte leakage. Upon TR, there is smoke, but no fire
15	N/A	N/A	221	No TR + Smoke (2) + Fire (0)	Electrolyte leakage. No TR, but some smoke observed
0	177	N/A	205	No TR + Smoke (1) + Fire (0)	Electrolyte leakage. No TR, but very light smoke observed
SOC↓	***Venting T ↑***	***No correlation***	***Max T ↓***	***Hazards ↓***	-

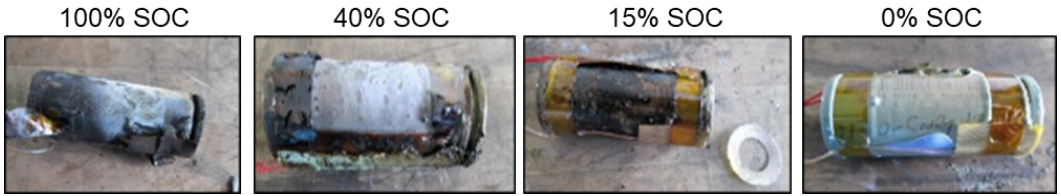


Manufacturer C (26650, 5.0 Ah, NMC)

- Thermal runaway at 15% SOC and higher
- Electrolyte leakage and smoke for all tests

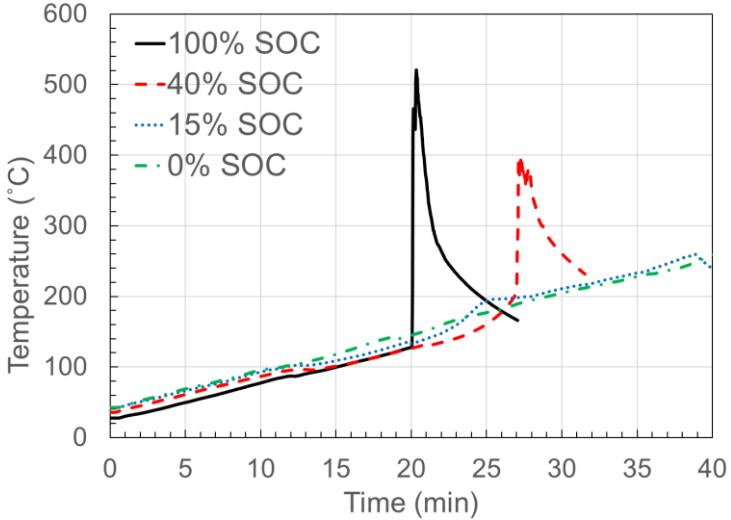


State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0-none, 1-minor, 2-moderate, 3-heavy)	Observations
100	135	177	522	TR + Smoke (3) + Fire (3)	Electrolyte leakage. Upon TR, cell ejected its content with sustained fire for 1-2 mins
50	143	188	628	TR + Smoke (3) + Fire (2)	Electrolyte leakage. Upon TR, a lot of smoke with sustained fire for 30-60 sec. White solidified materials on the header observed, after
40	149	188	581	TR + Smoke (3) + Fire (0)	Electrolyte leakage. Upon TR, a lot of smoke with no fire. White solidified materials on the header observed, after
30	143	199	557	TR + Smoke (3) + Fire (0)	Electrolyte leakage. Upon TR, a lot of smoke, with no fire
15	146	193	409	TR + Smoke (3) + Fire (0)	Electrolyte leakage. Upon TR, a lot of smoke, with no fire
0	154		246	No TR + Smoke (1) + Fire (0)	Electrolyte leakage with minimum smoke from the heater
SOC↓	***Venting T ↑***	***TR onset T ↑***	***Max T ↓***	***Hazards ↓***	-



Manufacturer D (3.3 Ah, NMC)

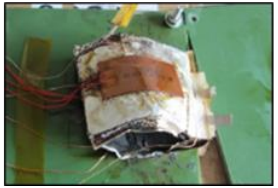
- Lower venting temperatures compared to cylindrical cells
- Thermal runaway in 40% SOC and higher
- Cell swelling and electrolyte leakage



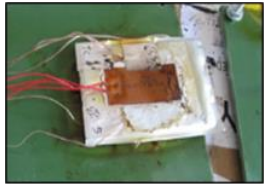
State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0-none, 1-minor, 2-moderate, 3-heavy)	Observations
100	77	113	521	TR + Smoke (3) + Fire (2)	No obvious electrolyte leakage. Upon TR, spark on the header area for 10-30 sec with a lot of smoke. Cell opens up eventually
50	81	169	467	TR + Smoke (3) + Fire (0)	No obvious electrolyte leakage. Upon TR, a lot of smoke from all sides. Cell opens up eventually
40	88	171	395	TR + Smoke (3) + Fire (0)	No obvious electrolyte leakage. Upon TR, a lot of smoke from all sides. Cell opens up eventually
30	93	N/A	248	No TR + Smoke (1) + Fire (0)	Electrolyte leakage from header. Light smoke.
15	96	N/A	260	No TR + Smoke (1) + Fire (0)	Electrolyte leakage from header. Light smoke. Cell swelled only
0	96	N/A	259	No TR + Smoke (1) + Fire (0)	Electrolyte leakage from header. Light smoke. Cell swelled only
SOC↓	***No correlation***	***TR onset T↑***	***Max T↓***	***Hazards↓***	-

100% SOC

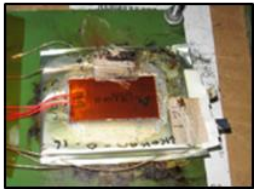
40% SOC



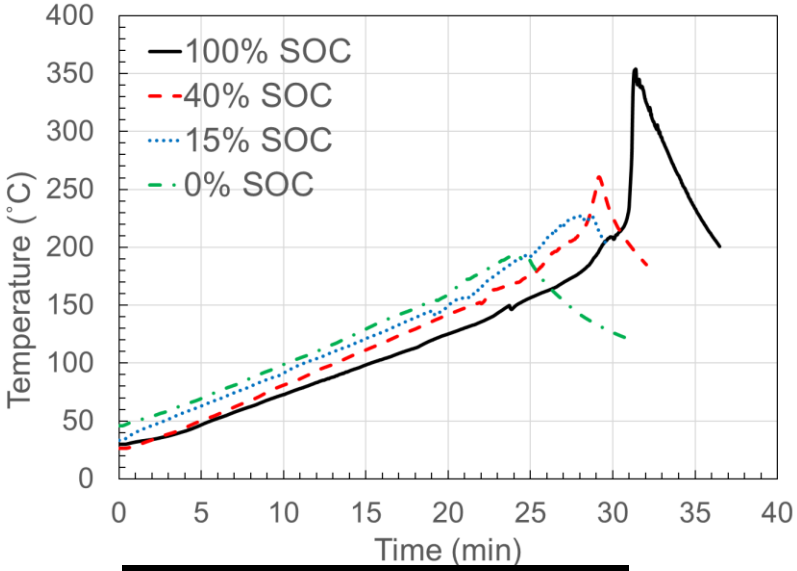
15% SOC



0% SOC



Manufacturer E (26650, 2.5 Ah, LFP)



State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0-none, 1-minor, 2-moderate, 3-heavy)	Observations
100	149	210	354	TR + Smoke (3) + Fire (0)	Obvious electrolyte leakage and boiling. After venting, the header area has a pin-hole where gas and separator material leaks. At TR, a lot of smoke with no signs of fire
50	154	224	277	TR + Smoke (3) + Fire (0)	Same as above
40	154	221	260	Minor TR + Smoke (3) + Fire (0)	Same as above
30	152		191	No TR + Smoke (2) + Fire (0)	Same as above with less smoke
15	146		227	No TR + Smoke (2) + Fire (0)	Same as above with less smoke
0	160		194	No TR + Smoke (1) + Fire (0)	Same as above with lesser smoke
SOC↓	***No correlation***	***TR onset T↑***	***Max T↓***	***Hazards↓***	-

100% SOC

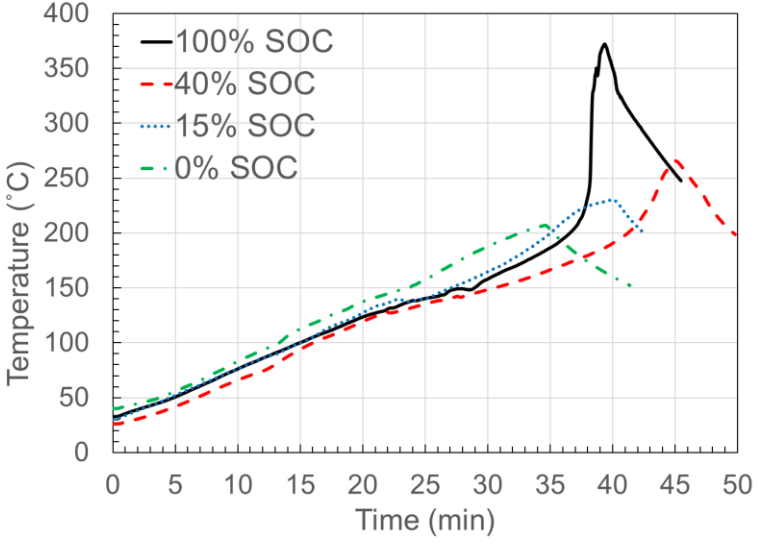
40% SOC

15% SOC

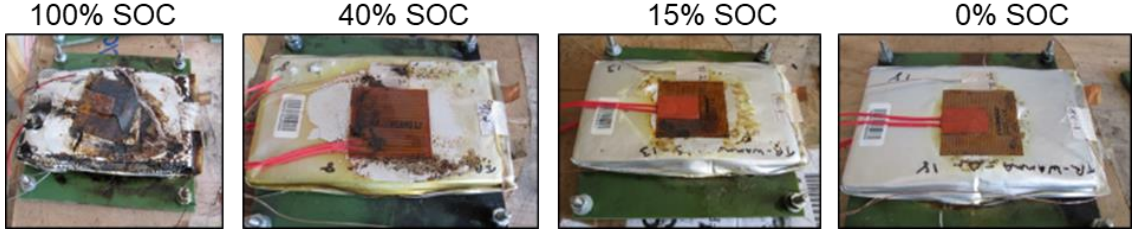
0% SOC

Manufacturer F (10 Ah, LFP)

- Thermal runaway in 40% SOC and higher, no fire
- Cell opening, smoke, and electrolyte leakage

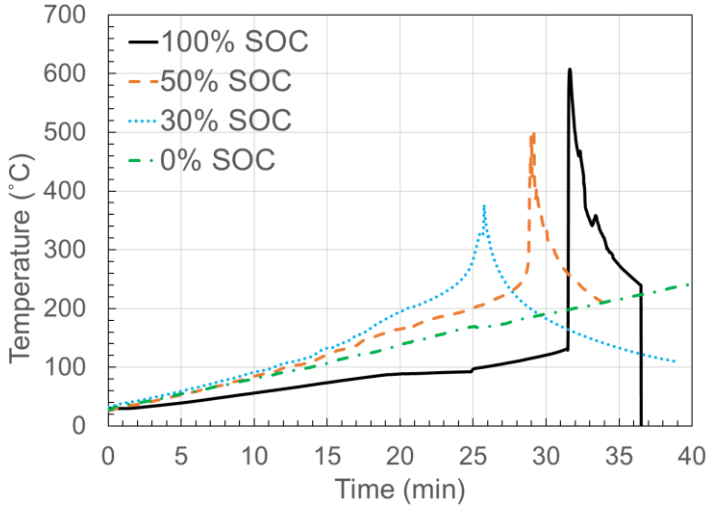


State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0- none, 1-minor, 2-moderate, 3-heavy)	Observations
100	88	132	372	TR + Smoke (3) + Fire (0)	Electrolyte leakage from the corner. Upon TR, a lot of smoke with no fire. The cell opens up from the sides
50	99	154	288	Minor TR + Smoke (3) + Fire (0)	Same as above with lesser charring and cell integrity is maintained
40	88	157	264	Minor TR + Smoke (3) + Fire (0)	Same as above
30	93	N/A	244	No TR + Smoke (3) + Fire (0)	Electrolyte leakage from the corner. No TR, but a lot of smoke
15	88	N/A	230	No TR + Smoke (2) + Fire (0)	Electrolyte leakage from the corner. No TR, but smoke observed
0	88	N/A	207	No TR + Smoke (1) + Fire (0)	Electrolyte leakage from the corner. No TR, but some smoke observed
SOC↓	***Constant***	***TR onset T ↑***	***Max T ↓***	***Hazards ↓***	-

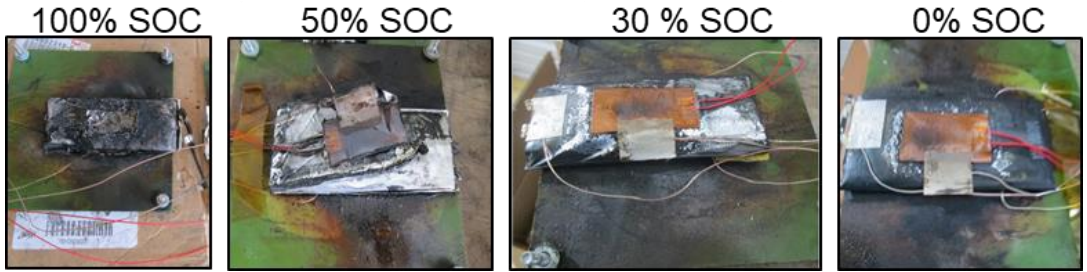


Manufacturer G (2.8 Ah)

- Single cell battery
- Thermal runaway in 30% SOC and higher
- Smoke and electrolyte leakage from tab area

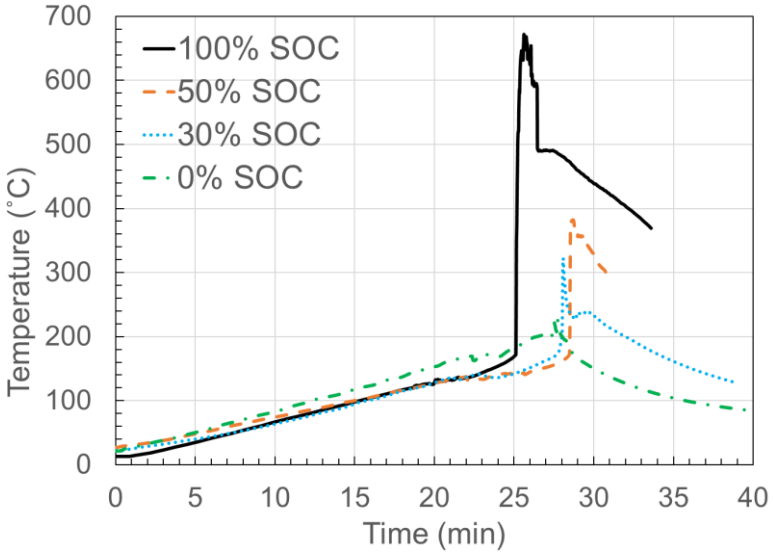


State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0-none, 1-minor, 2-moderate, 3-heavy)	Observations
100	84	129	608	TR + Smoke (3) + Fire (1)	Venting and electrolyte leakage from the header area. At TR, heavy smoke from header area. Also, spark of fire at TR, but no sustain fire
50	107	168	498	TR + Smoke (3) + Fire (0)	Venting and electrolyte leakage from header area. At TR, a lot of smoke, but no fire
40	99	163	399	TR + Smoke (3) + Fire (0)	Same as above
30	N/A	182	377	TR + Smoke (1) + Fire (0)	Venting and electrolyte leakage from header. Minimal smoke
15	88	N/A	272	No TR + Smoke (2) + Fire (0)	No video
0	113	N/A	242	No TR + Smoke (1) + Fire (0)	No video
SOC↓	***No correlation***	***TR onset T ↑***	***Max T ↓***	***Hazards ↓***	-

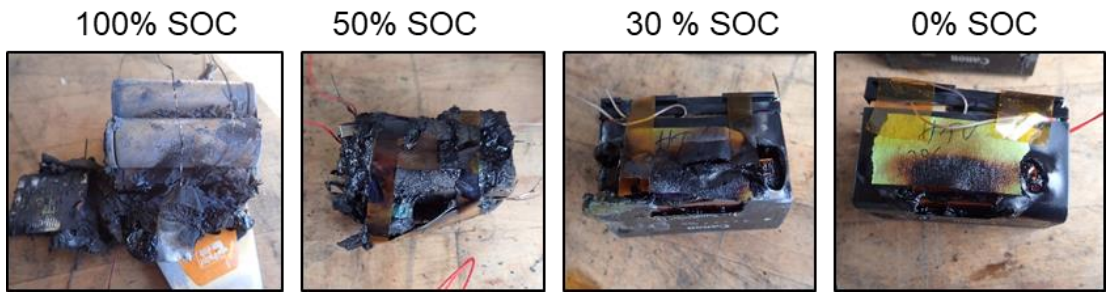


Manufacturer H (4.9 Ah)

- 2P2S battery
- Trigger cell thermal runaway in 30% SOC and higher, propagation for 50% and higher

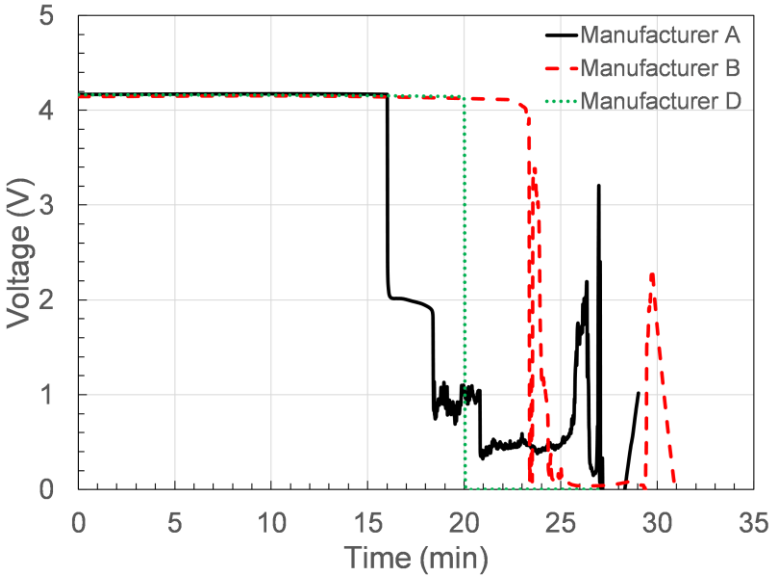


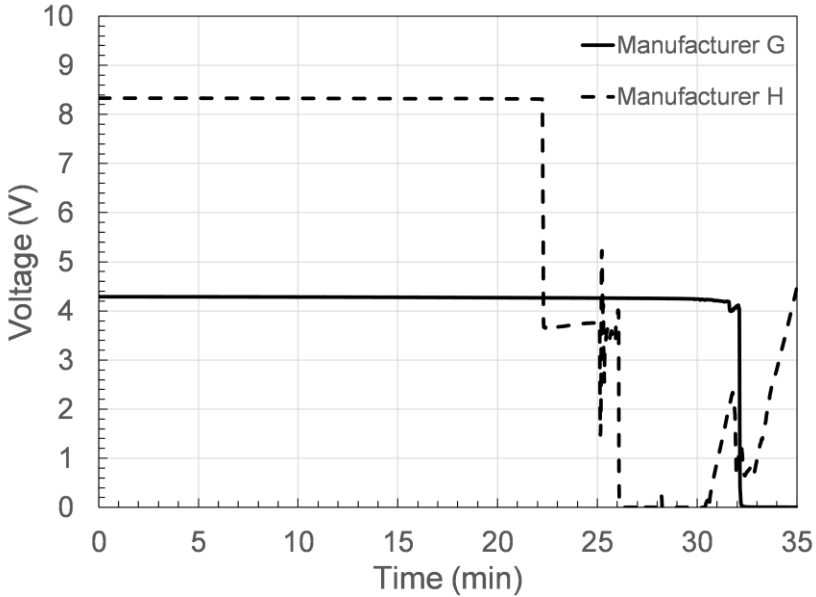
State of Charge (%)	Venting Temperature (°C)	Thermal Runaway Onset Temperature (°C)	Maximum Temperature (°C)	Hazards (0-none, 1-minor, 2-moderate, 3-heavy)	Observations
100	135	172	672	TR + Smoke (2) + Fire (3)	No venting or electrolyte leakage. At TR, battery moved from its original location due to intense fire, which sustained for 5 mins with smoke. All cells went into TR.
80	132	182	593	TR + Smoke (2) + Fire (3)	No venting or electrolyte leakage. At TR, intense fire, which sustained for 5 mins with smoke. All cells went into TR.
50	136	171	382	TR + Smoke (3) + Fire (0)	No venting or electrolyte leakage. At TR, al of smoke, but no fire. All cells went into TR
30	135	178	322	Mild TR + Smoke (2) + Fire (0)	Electrolyte leakage observed. At TR, smoke smoke, but no fire. Not all cells went into TR*
0	168		227	No TR + Smoke (1) + Fire (0)	Venting and electrolyte leakage observed. Only light smoke. No TR
SOC↓	***Venting T ↑***	***No correlation***	***Max T ↓***	***Hazards ↓***	-



Voltage change during heating

- Manufacturer A and manufacturer G cells contain PTC and CID devices





Summary of Heating Method

•Voltage behavior

•Cell voltage drops *directly* to 0V for pouch format cells and cylindrical cells with no PTC/CID (Manufacturer B)

- Cell voltage drops *incrementally* (first to 2V and then 0V) for cylindrical cells with PTC/CID

•Venting temperature

- Most of the cells followed similar trends, where temperature at which venting occurs increases (↑) as SOC goes down (↓)
- Except for Manufacturer D, E, and F (LFP & Pouch) – venting temperature is around the same value

•Thermal runaway onset temperature

- Onset temperature increases (↑) as SOC goes down (↓) except for manufacturer B (low-cost cells)

•Electrolyte leakage observed for all Manufacturers at all SOCs, except for Manufacturer B (no correlation) , and D (only low SOCs)

Cell Type	% SOC						Trends
	100	50	40	30	15	0	SOC ↓
A – 18650 **NCA**	TR, Fire, Smoke	TR, Fire, Smoke	TR, Fire, Smoke	TR, Fire, Smoke	Mild TR, Smoke	-	Venting T (↑) Onset T (↑) Max T (↓)
B- 18650 **NCA**	TR, Fire, Smoke	TR, Smoke	TR, Smoke	TR, Smoke	-	-	Venting (same) Onset T (no correlation) Max T (↓)
C – 26650 **NMC**	TR, Fire, Smoke	TR, Fire, Smoke	TR, Smoke	TR, Smoke	TR, Smoke		Venting T (↑) Onset T (↑) Max T (↓)
D – Pouch **NMC**	TR, Fire, Smoke	TR, Smoke	TR, Smoke	-	-	-	Venting T(same) Onset T (↑) Max T (↓)
E – 26650 **LFP**	TR, Smoke	TR, Smoke	TR, Smoke	-	-	-	Venting T(same) Onset T (↑) Max T (↓)
F – Pouch **LFP**	TR, Smoke	-	-	-	-	-	Venting T(same) Onset T (↑) Max T (↓)

External Short

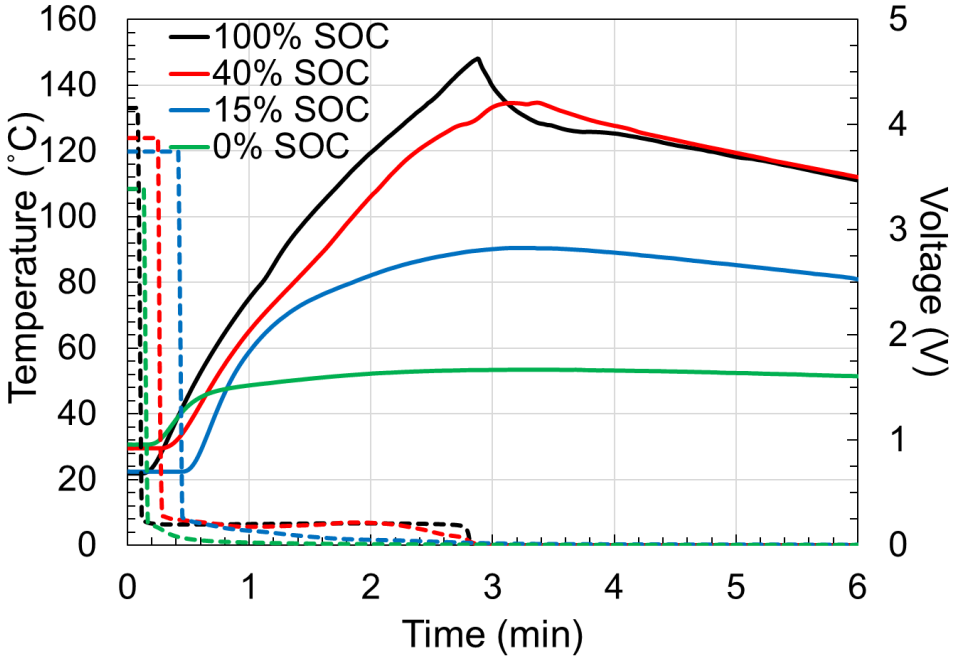
- External short was carried out on cells that do not contain the internal PTC device. This includes low quality cells, pouch format, and LFP cells.
- The load was held for 3 hours, or until thermal runaway.
- Load used for the short was 8-10 mohms.
- Pouch cells were restrained, and tabs reinforced with Ni tabs.
- Cells were subjected to external short at 6 different states-of-charge (SOC) -100%, 50%, 40%, 30%, 15%, and 0%. Three cells were tested under each condition.
- Cells and batteries from 6 different manufacturers were tested:
  - Manufacturer: B, D, E, F, G, and H

Manufacturer	Cell Design	Cathode Chemistry	Rated Capacity (mAh)	Actual Capacity (mAh)	Internal Resistance (mΩ)
B	18650	NCA	3200	1810	35
D	Pouch 526495	NMC	3300	3180	18
E	26650	LFP	2500	2520	6
F	Pouch 8790160	LFP	10000	10400	8
G (Single cell Smart phone battery)	Single pouch cell with BMS	Unknown	2915	2770	57
H (2P2S Camcorder battery)	18650	Unknown	4900	4950	111

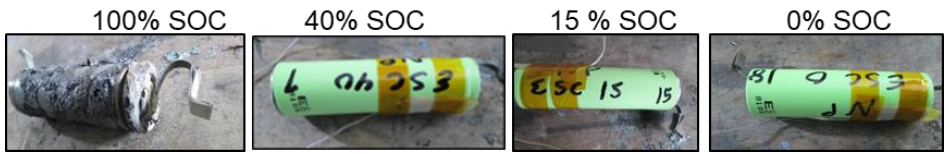
Test setup

Manufacturer B (18650, 1.8 Ah, NCA)

- Electrolyte leakage observed only in higher SOCs.

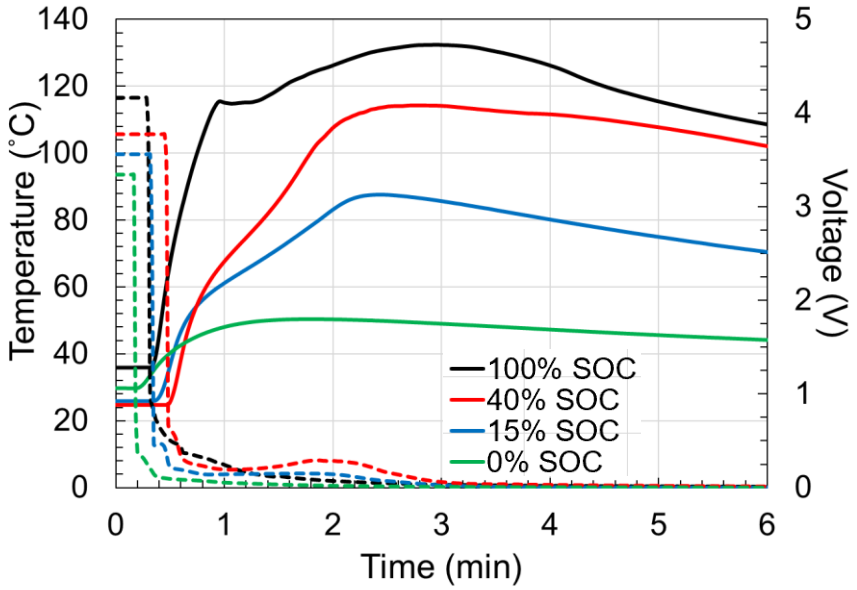


State of Charge (%)	Maximum Temperature (°C)	Maximum Current (A)	Observations
100	149	27	Upon short, the cell tabs get red hot for 2-3 mins. This happens until the cell vents from the header and electrolyte leaks. Some smoke is observed. One of the cell (out of 3) did go into TR, but no data for this (just video/picture)
50	134	26	Upon short, the tabs get red hot for 2 mins. This happens until the cell vents from the header and electrolyte leaks. Barely any smoke
40	135	28	Same as above, but no smoke
30	96	18	Upon short, the tabs get red hot for only 30 seconds with no venting or electrolyte leakage
15	90	30	Upon short, the tabs get red hot for only 30 seconds with no venting or electrolyte leakage
0	53	23	Upon short, the tabs get red hot for only 6 seconds with no venting or electrolyte leakage
SOC↓	***Max T↓***	***No correlation***	-

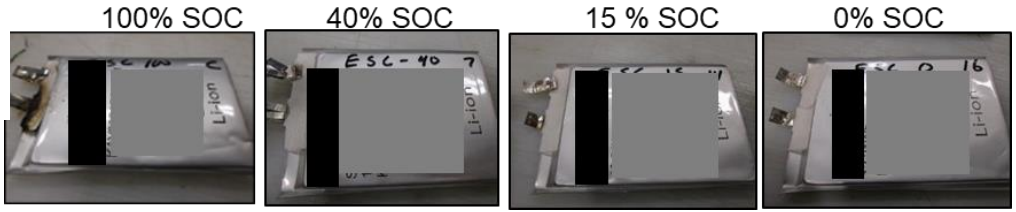


Manufacturer D (3.3 Ah, NMC)

- Cell swelling and electrolyte leakage at higher SOC, negative tab burning.

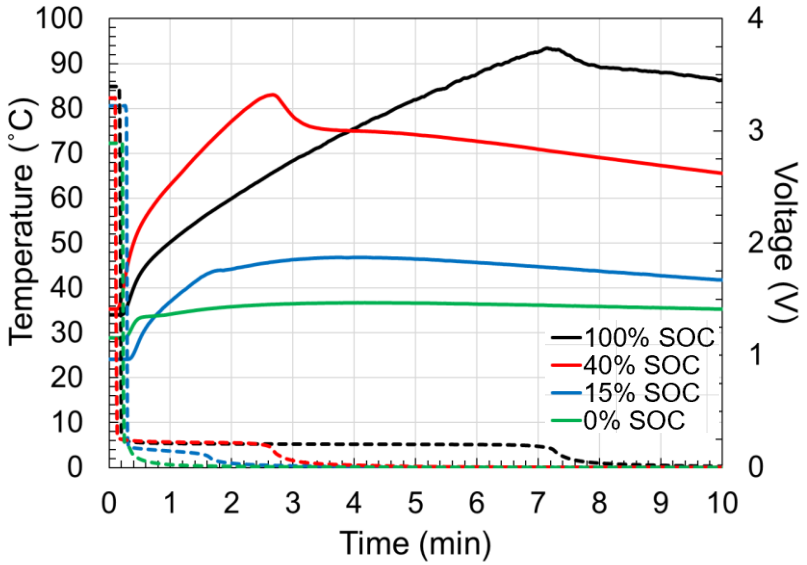


State of Charge (%)	Maximum Temperature (°C)	Maximum Current (A)	Observations
100	132	114	Cell swelling with negative tabs burning and disconnecting
50	111	97	Cell swelling, electrolyte leakage, and smoke from the negative tab. Negative tab charred more
40	114	79	Light cell swelling and electrolyte leakage from negative tab area. Negative tab charred more
30	109	89	Light cell swelling, electrolyte leakage, and smoke from the negative tab. Negative tab charred more
15	87	56	No cell swelling, or electrolyte leakage. Very minimal charring on the negative tab (Observation from post-pictrures_no videos)
0	50	41	No cell swelling, or electrolyte leakage. Very minimal charring on the negative tab (Observation from post-pictrures_no videos)
SOC↓	***Max T↓***	***Max A↓***	-

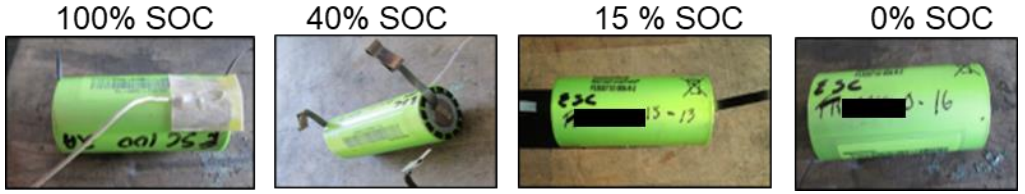


Manufacturer E (2.5 Ah, LFP)

- Minimal hazards observed

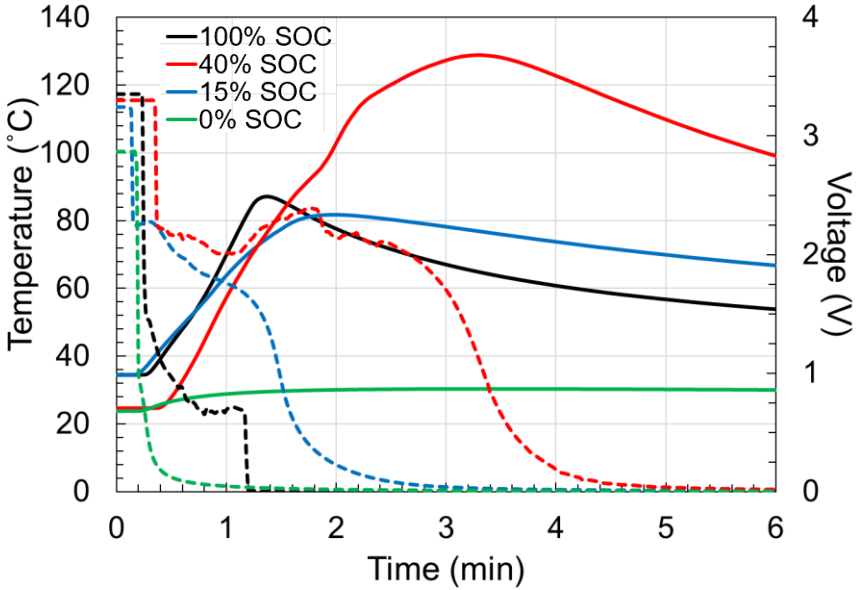


State of Charge (%)	Maximum Temperature (°C)	Maximum Current (A)	Observations
100	93	23	Upon short, the tabs got red hot for 3-4mins, but benign outcome
50	90	40	Upon short, the tabs got red hot for 2-3 mins, but benign outcome
40	83	27	No change (check video stamp)
30	82	34	Upon short, the tabs got red hot for 1-2 mins, but benign outcome
15	46	23	No change
0	36	20	Upon short, the tabs were semi-red for 5 mins
SOC↓	***Max T↓***	***No correlation***	-

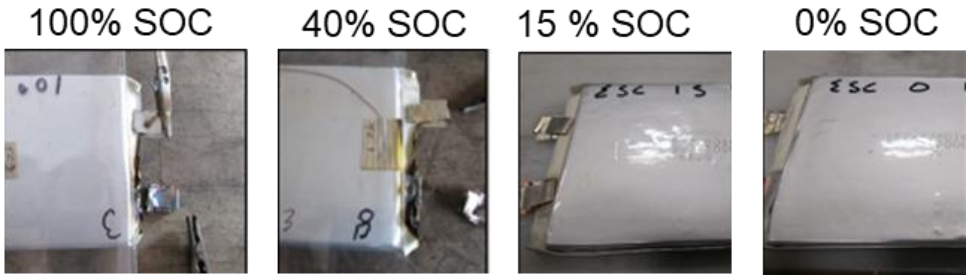


Manufacturer F (10 Ah, LFP)

- Minimal hazard, positive tab burned off.

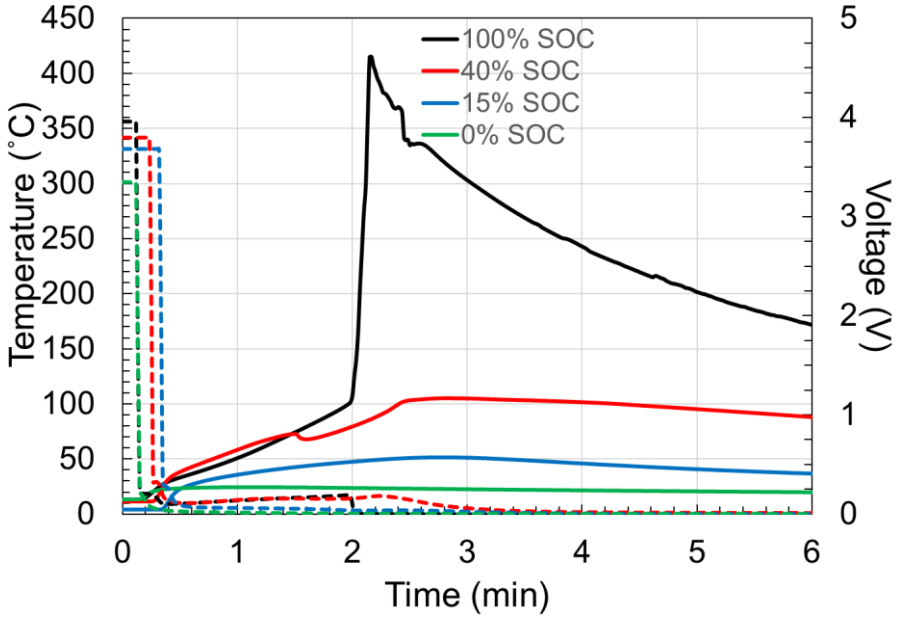


State of Charge (%)	Maximum Temperature (°C)	Maximum Current (A)	Observations
100	87	196	Upon short, both alligator clips to electrically connect to the cell tabs gets red hot and smoke coming from the header area (positive tab). After 3-4 mins, both tabs charred. No cell swelling or venting/electrolyte leakage
50	158	190	Upon short, both alligator clips to electrically connect to the cell tabs gets red hot and smoke coming from the header area (positive tab). Also, a light candle-size flame arose from the positive tab for 30 seconds. Only positive tab charred. No cell swelling or venting/electrolyte leakage
40	129	163	Upon short, only positive alligator clip got red hot for 1-2 mins. Also, a light candle-size flame arose from the positive tab for 30 seconds. Only positive tab charred. Some cell swelling observed, but no venting/electrolyte leakage
30	168	189	Upon short, only positive alligator clip got red hot for 1 mins. Also, a light candle-size flame arose from the positive tab for 30 seconds. Only positive tab charred. Some cell swelling observed, but no venting/electrolyte leakage
15	82	185	Upon short, the negative alligator clip got red hot for 15 seconds, but no change on the cell tabs. Light cell swelling, only.
0	30	128	No change
SOC↓	***No correlation***	***No correlation***	-



Manufacturer G (2.8 Ah)

- BMS was removed for tests.
- Thermal runaway and fire at 100% SOC.



State of Charge (%)	Maximum Temperature (°C)	Maximum Current (A)	Observations
100	415	21	At TR, sustained fire on the header for 1.5 mins.
50	102	41	Light cell swelling
40	105	39	Light, cell swelling
30	83	29	Light cell swelling
15	52	36	Light cell swelling
0	24	23	No change
SOC↓	***Max T↓***	***No correlation***	-

100% SOC

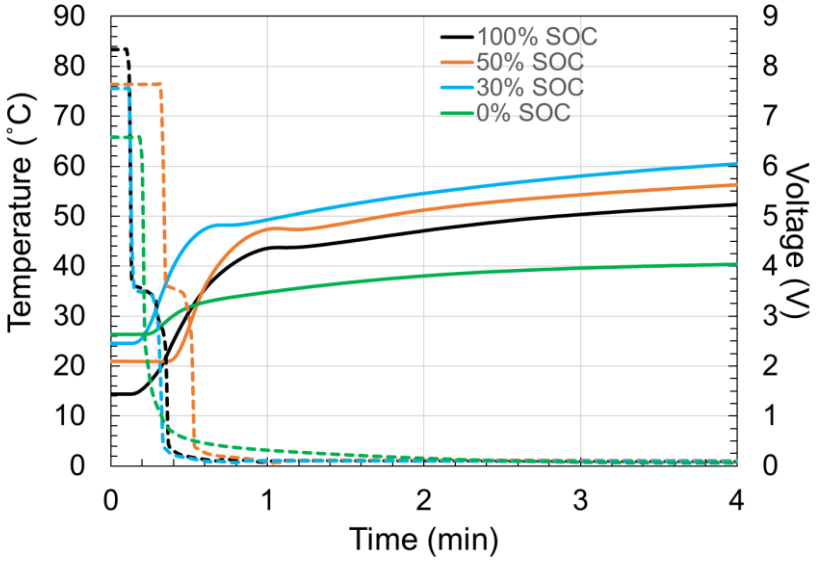
40% SOC

15 % SOC

0% SOC

Manufacturer H (4.9 Ah)

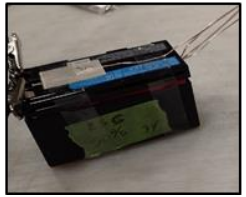
- BMS was removed for tests.
- Minimal hazards observed during tests.



State of Charge (%)	Maximum Temperature (°C)	Maximum Current (A)	Observations
100	79	44	No change
50	79	42	No change
30	85	43	No change
0	41	30	No change
SOC↓	***~Constant (except for 0%SOC)***	***~Constant (except for 0%SOC)***	-

100% SOC

50% SOC



30 % SOC

0% SOC

Summary of External Short Tests

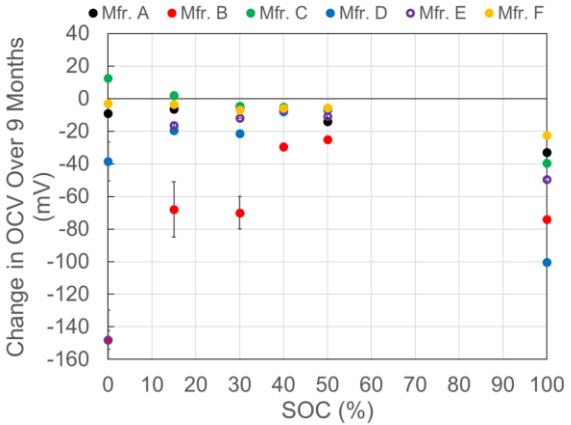
- Thermal runaway observed in 100% SOC for manufacturers B and G.
- Melting tab prevented hazards in some cases (fail-safe conditions).
- BMS provided protection against external short for batteries and were removed for tests.
- Protection against external shorts was provided through BMS in batteries and PTC in cells for manufacturer H.

Storage Test

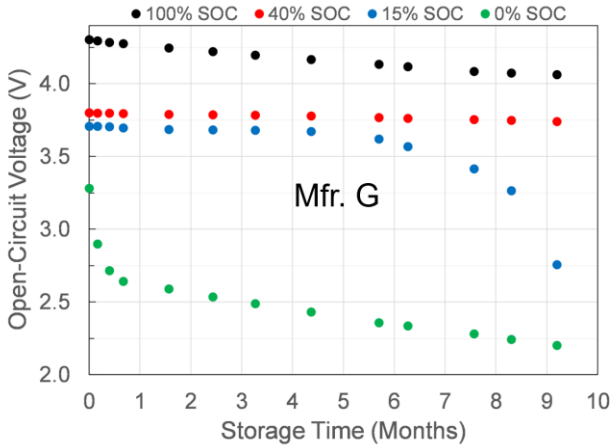
- All manufacturers were subjected to charge retention test to characterize self-discharge.
- Cells were stored in ambient temperature (controlled) at 6 different SOC.
  - 100%, 50%, 40%, 30%, 15%, and 0%
  - 2 cells are under test for each condition.
- OCV was recorded once every week for the first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

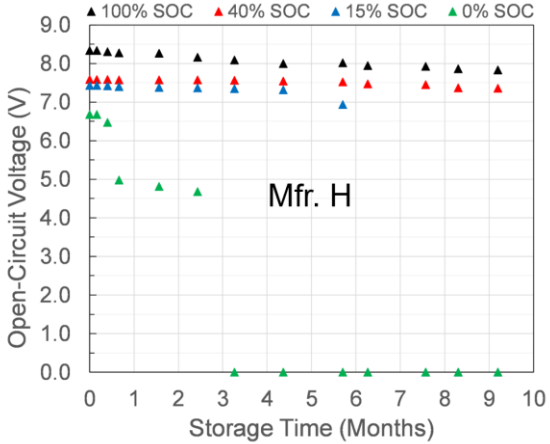
Storage Test

- Excellent charge retention.
- Voltage losses higher at SOC extremes for all manufacturers.
- Higher losses and variability in manufacturer B may be due to quality issues.
- For batteries, higher voltage losses due to drain from functional BMS.
- Voltage drop in manufacturer H due to activation of protective undervoltage MOSFET.



Change in cell voltage during storage.





Battery open-circuit voltage during storage.

Summary/Conclusions

- Most of the cells followed similar trends for venting and thermal runaway onset temperature: T increases (↑) as SOC goes down (↓).
- Minimum SOC for thermal runaway is variable across chemistries and cell formats.
- Cells containing LFP positive electrodes exhibit superior thermal stability.
- Cylindrical NMC and NCA-based cells underwent thermal runaway at 15% SOC.
- Protections offered through PTC, tab designs, and BMS were useful in minimizing hazards.
- Cell voltages are stable over long-term storage while battery voltage stability is affected by BMS.
- Safety and performance of low-quality products are unpredictable and do not follow a typical trend.

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