PCTEST® ENGINEERING LABORATORY, INC.
A PERSONAL COMMUNICATIONS TESTING COMPANY

Evaluation of battery safety at lower and higher temperature charging and cycle

- to search a verification test method & condition -

Nov . 28 , 2018

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PCTEST Engineering Laboratory

Introduction of PCTEST

- Founded in 1989 (~30yrs) in MD USA by former FCC engineer.

  Location: 3 Bld. in Columbia MD, 2 Bld. in San Jose, CA, 1 Bld. in MI

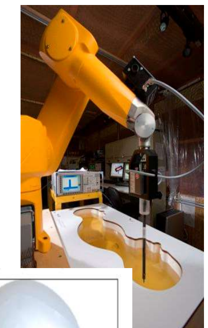
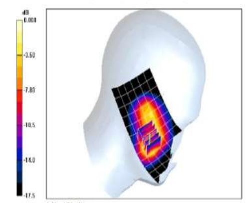
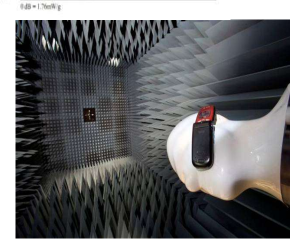
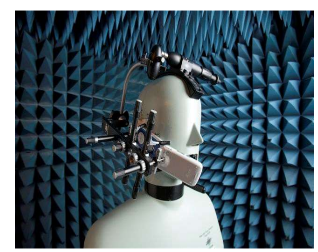
  Approved the First 5G mmW Device for FCC Certification
- Verizon / at&t / Sprint Authorized Test Lab: for wireless Device.
- Test capabilities for 5G, VoLTE, LTE, EMC/EMI, SAR, CTIA, OTA and HAC
  - A2LA ISO/IEC 17025 accreditation since 2000.
  - US NIST / NVLAP ISO/IEC 17025 accredited since 1995.
  - ANSI ISO/IEC Guide 65 TCB, FCB, CAB.
- CATL ISO/IEC 17025 accreditation for CDG/OTA/HAC/Battery
- CDMA Certification Forum (CCF) Authorized Testing Facility.

Battery Performance, Safety/Reliability& Mechanism R&D and Risk Assessment

- R&D support and verification. Product Approval and Certification
- CTIA Authorized Test Lab: Battery Safety/Life Certification, Hardware
- Smart phone, NBPC, EV, ESS, Aerospace, Medical, Robotics and Power tools

• EMC/EMI: Electromagnetic compatibility/Interference, * SAR: Specific Absorption Rate
• OTA: Antenna Performance: Over-the-Air, * HAC: Hearing Aid Compatibility
• ANSI: American National Standard Institute, * CTIA: Cellular Telecommunications and Internet Association

ACCREDITED CERTIFICATE #2041.01 · ANSI Accredited Certification Program · NVLAP Lab Code #100431-0 · CTIA Authorized Test Lab LAB CODE 20020221-00 · CDMA Certification FORUM

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Scope of LiB Testing, Certification and R&D Support

PCTEST has various kinds of test equipment, skills, and experiences for the Test, Certification and R&D for LiB Performance, Safety, Reliability, and Risk Assessment

1. CTIA Certification Program: IEEE 1625/1725, Battery Life, Hardware Reliability

: Smart phone, Notebook PC, GPS, Smart Watch, and Wearable Technologies

- Design & Manufacturing Verification: Cell, Battery Pack, Adaptor/Accessories & Host System
- Cell Manufacturing Site Audit, - Approval Process Consulting

2. UN 38.3 Manual test for the Battery Transportation Regulation

3. Battery Performance, Safety & Reliability, Surveillance with Risk Assessment

- Cell, Battery Pack, Adaptor and Host System : System base Risk Assessment
- Applications: Portable Devices, Medical, EV, ESS, Aerospace, Medical, Robotics and Power tools
- Standard base Test, Customized Test or Consulting the test item and method

4. Failure and Deformation Mechanism Analysis of Lithium ion Battery

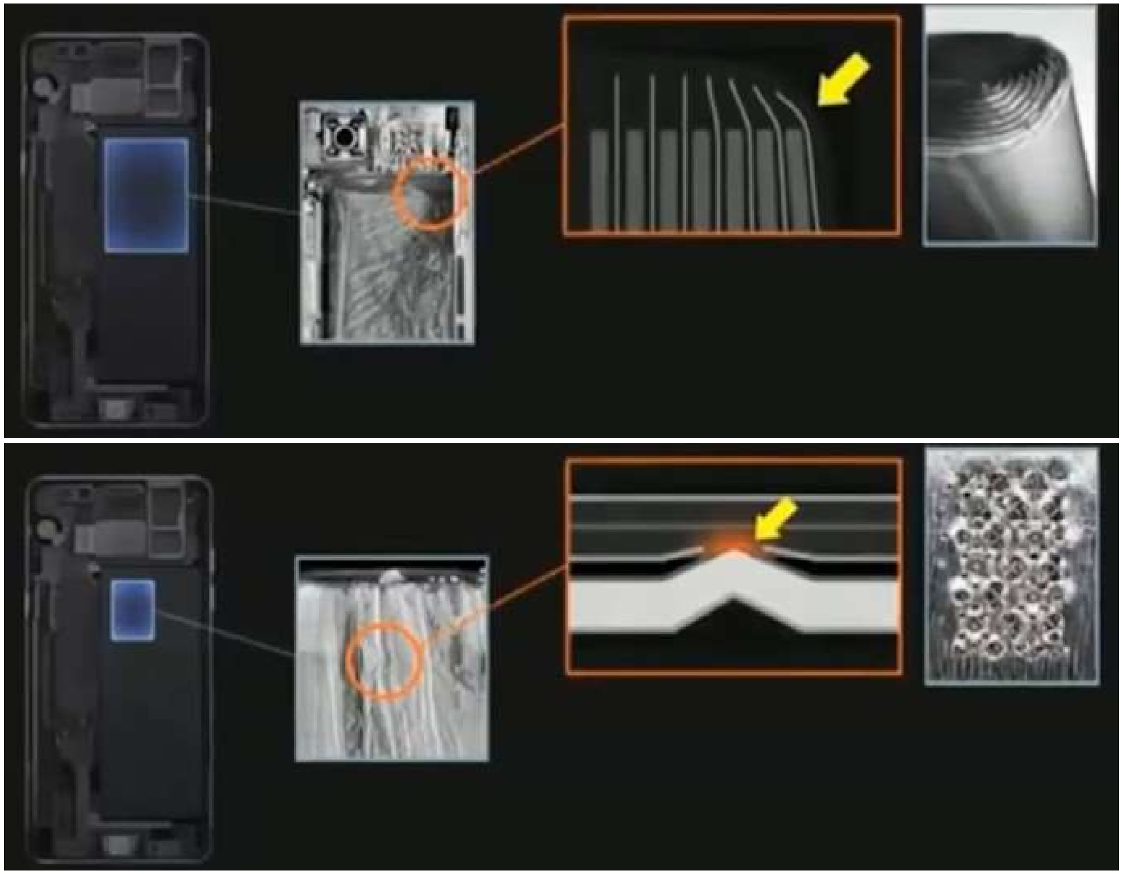
- Micro-Macroscopic Safety Mechanism Analysis: Cell Teardown and Inspection/Material Analysis
- Design Review & Safety Risk Assessment: System base Analysis
- Consulting: Cell/Pack Selection & Design, Surveillance test, Failure Analysis/Corrective Action.

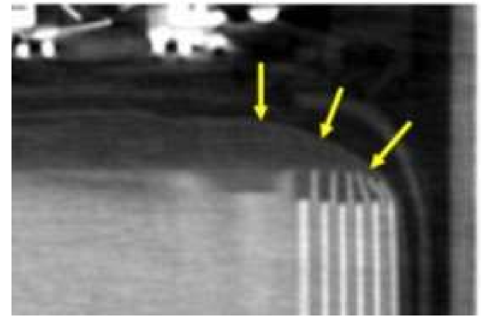
5. Develop New Test/Analysis Method for LiB Safety, Reliability and Risk Assessment

6. Benchmarking, Field Issue(Failure) Analysis/Corrective Action and Recall support

History: Galaxy Note7 Battery Issues Analysis & Preventive action

Reported root cause analyses by Samsung and their two patterners





*** Reference: Samsung Report- Business Insider - Jan. 23 2017**

Preventive Action at the CTIA Certification under IEEE 1725 Standard :

Add test item to cell certification; External short Circuit test after 25 cycles at Min. & Max charging Temp.

Corrective Action: Maker:8-point Battery safety check Test / Cell maker: Add X-ray check after formation.

History: Tesla fire in Norway caused by a short circuit

What would be the unknown root-causes of these incidents?

The root cause analysis, preventive and corrective actions were not clear reported.

Tesla Model S in Norway, Jan. 2016

Tesla confirmed to ***Autoblog:*** "there was an isolated incident where a Model S caught fire due to a short circuit in an electrical distribution box in the vehicle while Supercharging. The Supercharger turned off once it detected the short circuit.

Cooling fan responsible for Karma fire, Aug. 2012

Tesla Model X crashed into a barrier on U.S. Highway 101 in Mountain View on March 23.

Purpose and Agenda

Purpose

- Charging and discharging battery at lower and higher temperature (outside of recommended operating Temp. zone) are routinely occurring.

- There are many research papers/presentations are studying the LiB degradation and safety mechanism on charging & cycling the battery at lower and higher temperature, but there is no standard/certification have a test item to verify this issues by testing.

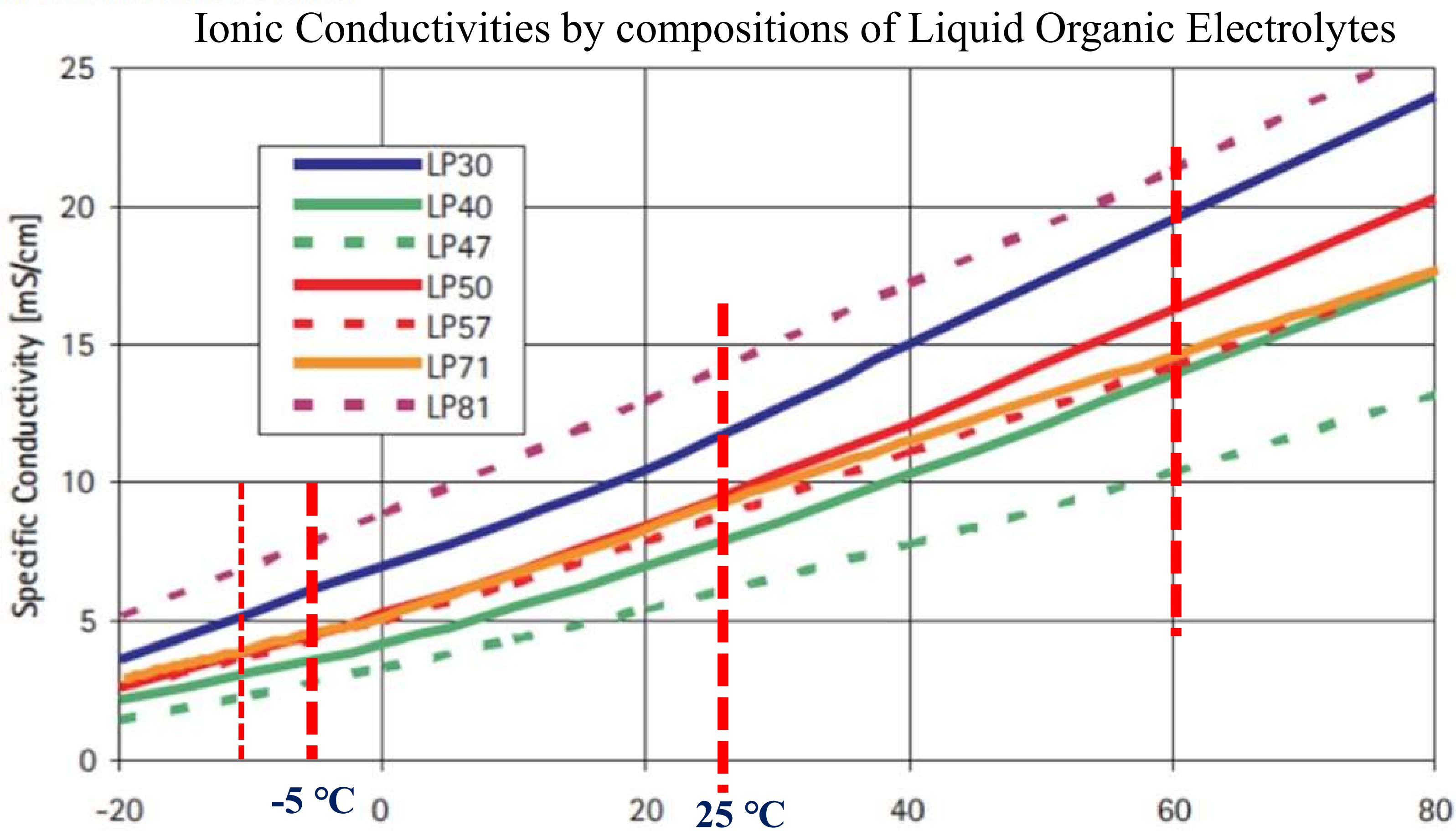
- Review and summary papers and presentations about this issue LiB.

- Review the items on the LiB safety standard/certification scheme and will propose a simple/adequate test method/conditions to validate battery safety at lower and higher temperature usage.

Agenda

1. Review research papers/presentations: LiB Degradation and Safety Mechanism at lower and higher temperature. Analysis method and result
2. Verification Test / Result summary : Cycles at Lower, Room, Higher Temperature and compare the results by ARC, External Sort Circuit, Thermal test.
3. Summary and Conclusion

1-1. Electrolyte Conductivities on Temperature



Merck		LiPF6	LiPF6	LiPF6	Density (20°C)
SelectiLyte		mol/L (M)	mol/kg (m)	wt.%	g/cm3
LP30	1 M LiPF6 / EC-DMC (1:1 Gew.)	1	0,886	11,8	1,28
LP40	1 M LiPF6 / EC-DEC (1:1 Gew.)	1	0,936	12,4	1,22
LP47	1 M LiPF6 / EC-DEC (3:7 Gew.)	1	0,967	13,1	1,19
LP50	1 M LiPF6 / EC-EMC (1:1 Gew.)	1	0,911	12,2	1,25
LP57	1 M LiPF6 / EC-EMC (3:7 Gew.)	1	0,963	12,7	1,19
LP71	1 M LiPF6 / EC-DEC-DMC (1:1:1 Gew.)	1	0,943	12,4	1,21
LP81	1 M LiPF6 / EC-DMC-EA (1:1:1 Gew.)	1	0,982	13	1,17

Merck: SelectiLyte®, Materials for Li-ion batteries and double-layer capacitors, 2009-2011.

1-2 High Temperature cycle effect to Battery Safety

- Catastrophic failures due to excessive temperature variations at high temperatures can cause a thermal runaway reaction that ignites a fire and consequently cause an explosion.

1) Markevich *et al.* : degradation of carbon negative electrode at elevated temperature (up to 80 °C)/J. Power Sources 215 (2012) 248.
2) Gabrisch *et al.* : degradation of thermally aged LiCoO2 and LiMn2O4 cathode /J. Electrochem. Soc. 145 (1998) 194.
3) Handel *et al.*: thermal aging of electrolytes and investigated the degradation product from electrolyte and the influence ~. /Materials 6 (2013) 1310.
4) Schalkwijk *et al.*: temperature effect on the degradation at electrode/electrolyte interface/Anal. Chem. 83 (2011) 478.
5) Ramadass *et al.*: capacity fade of Sony 18650 ($LiCoO_2$/Graphite) electrode materials at RT, 45 °C, 50 °C & 55 °C/J. Power Sources 178 (2008) 409

-Electrodes Morphological/Structural changed & Electrode thickness increase during HT cycling.
-Elevated temperatures accelerate the degradation of the cathode and formation of the SEI on anode.
Chemical reactions of degradation was identified by XRD (X-ray diffraction) / Li MAS NMR
-Degradation of Cathode / SEI and SEI film growth at Anode: Main contributor to increase the cell internal resistance and capacity loss.

1)Thomas *et al.:* used scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), inductively coupled plasma (ICP), and measurements of to compare the aged and fresh materials of cathodes and anodes / J. Power Sources 196 (2011) 8147.
2) Journal of Power Sources 262 (2014), 129 ~135 / Temperature dependent ageing mechanisms in Lithium-ion batteries - A Post-Mortem study.

Ref.: Journal of Power Sources 262 (2014), 129 ~135_Temperature dependent ageing mechanisms in Lithium-ion batteries - A Post-Mortem study.
Experimental: commercial 18650 cells (LixNi1/3Mn1/3Co1/3O2/ LiyMn2O4 blend // graphite/carbon)
Cycled Temperature range between - 20 C and 70 C until an SOH limit of 80% was reached.
Result: 1) Low Temp.: Plating of metallic Lithium on the anodes and subsequent reaction with the electrolyte, leading to loss of cyclable Lithium.
2) High Temp. : Accelerate degradation reactions on Cathode and grow SEI film on the anode leads capacity fade and internal resistance increase. Dissolved Mn deposited on anodes made a thicker SEI on the anode which may contain Li which cannot be intercalated into the cathode.

1-3 High Temperature cycle effect: Journal of Power Sources 262 (2014), 129 ~135 / Temperature dependent ageing mechanisms in LiB- A Post-Mortem study

1) Formation of a binder layer at the surface of the Cathode and led to a poor Li-re-intercalation.

2) Several changes in the composition of the SEI, cycled at 50 ~ 70 °C

* Observed: -Disappearance of carbonate species/ - Increase of inorganic species at the surface of negative electrode.

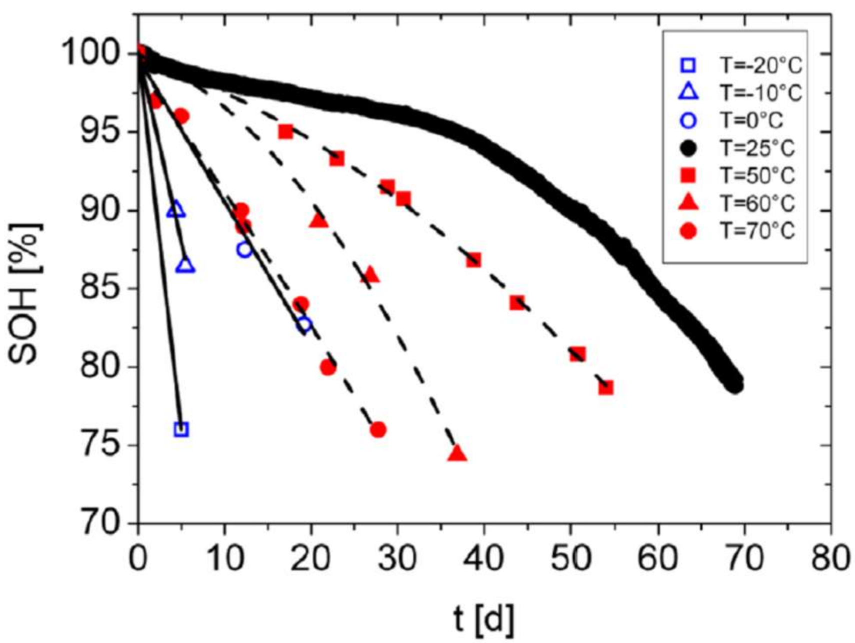


Fig.-1. Measured SOH curves as a function of time for cycling at a rate of 1 C and different temperatures. In the case of T= 25 C all data is shown, for all other tests, only capacity measurements at 25 C are plotted. The solid and dashed lines are drawn to guide the eye for the tests below and above T = 25 C, respectively.

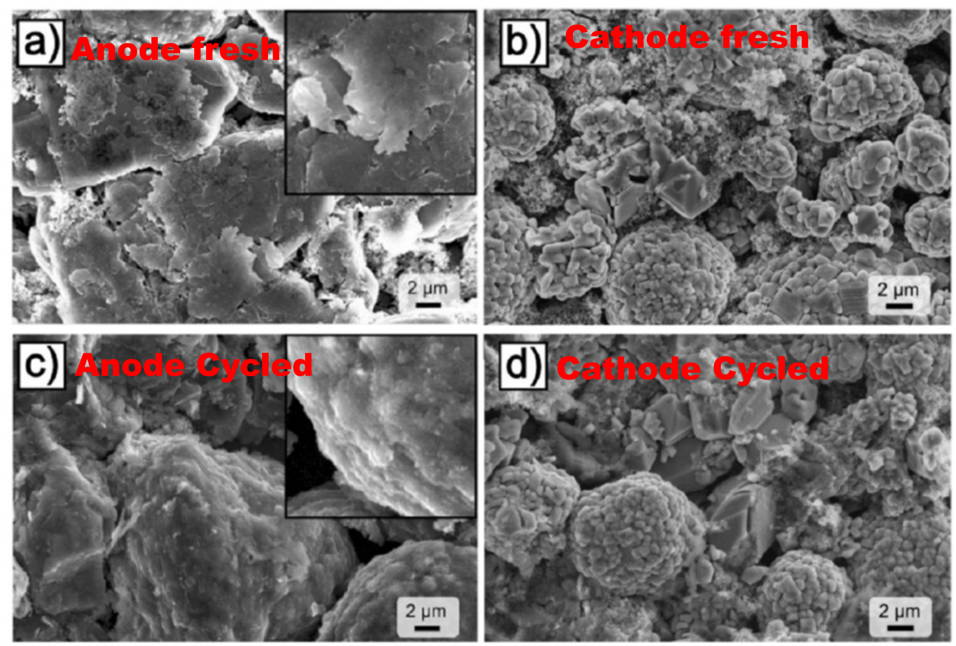


Fig.-2. SEM images (magnification: 10^4) of an un-aged (SOH=100%) a) anode and b) blend cathode and an aged (SOH= 80%, cycled at T=70 C) c) anode and d) blend cathode. /Insets in a) and c) show magnifications of graphite particles. The aged anode shows increased SEI thickness (compare (a) and (c)), while the aged cathode looks similar to its un-aged situation (compare (b) and (d)).

Ref.: Journal of Power Sources 262 (2014) 129 ~135 /Temperature dependent ageing mechanisms in Lithium-ion batteries e A Post-Mortem study

1-4 High Temperature cycle effect: Journal of Power Sources 262 (2014), 129 ~135 / Temperature dependent ageing mechanisms in LiB- A Post-Mortem study

3) Modification of SEI composition layer is proposed as a cause for the capacity loss and impedance increase at high temperature, in addition to the binder on the electrode surface of the positive electrode.

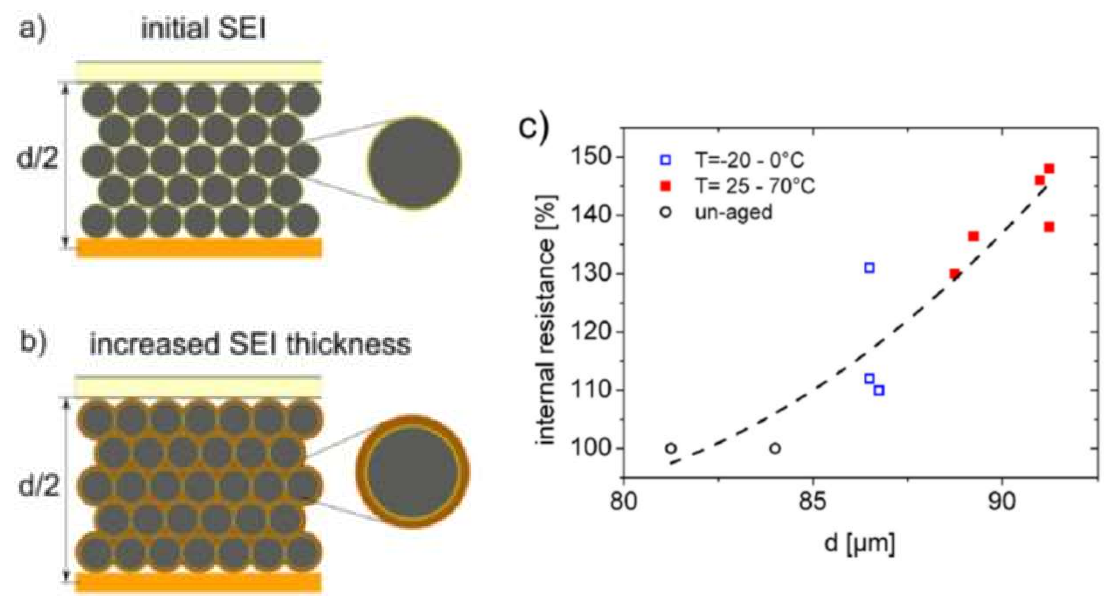


Fig.-3. Model for the explanation of anode thickness d. The grey objects represent the carbon/graphite spheres of the anode, the SEI formed during formation of the battery is colored green and the SEI films growing during ageing are illustrated in brown color. The anode thickness in (b) is increased in comparison to (a). c) Correlation of anode thickness d and internal resistance of 18650 cells.
The dashed line is drawn to guide the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

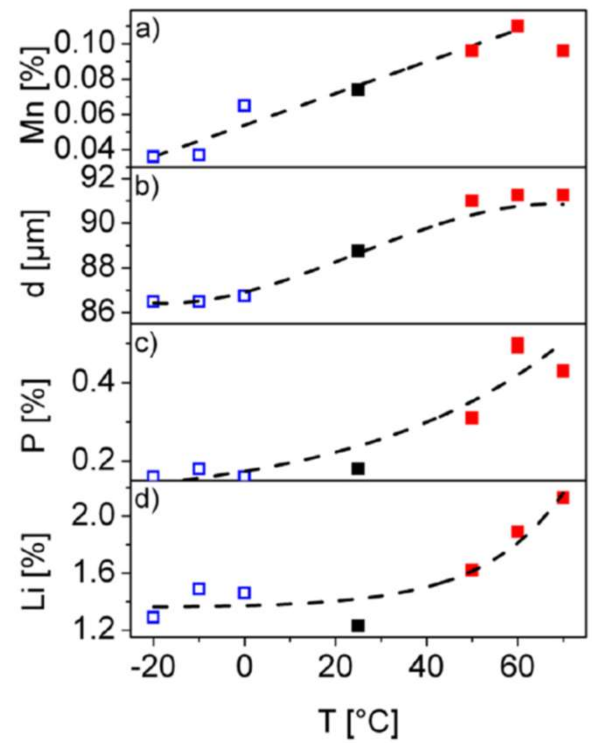


Fig. -4. Results of the Post-Mortem analysis of anodes from 18650 cells cycled at different temperatures. a) Mn content, b) anode thickness, c) P content and d) Li content. The dashed lines are drawn to guide the eye.

Ref.: Journal of Power Sources 262 (2014) 129 ~135 /Temperature dependent ageing mechanisms in Lithium-ion batteries e A Post-Mortem study

2. Lower Temp. cycle affect to cell degradation & Safety

Aged cycled cell safety mechanism analysis

1) Metal lithium deposition on an anode.

a) Z. Li, J. Huang, B. Yann Liaw, V. Metzler, and J. Zhang, *J. Power Sources*, **254**, 168 (2014).
b) M.-H. Ryou, Y. M. Lee, Y. Lee, M.Winter, and P. Bieker, *Adv. Funct. Mater*, **25**, 834 (2015).

2) Li metal deposition was intensified at decrease of temp. cells cycling down to T = 0 ◦C.

c) M. Winter, *Z. Phys. Chem.*, **223**, 1395 (2009).
d) C.-K. Huang, J. S. Sakamoto, J.Wolfenstine, and S. Surampudi, *J. Electrochem. Soc.*,**147**, 2893 (2000).
e) J. Vetter, P. Novak/M. R.Wagner/C. Veit, K/C. Moller/J. O. Besenhard/ M.Winter/M. Wohlfahrt/ Mehrens/ C. Vogler, and A.Hammouche, *J. Power Sources*, **147**, 269 (2005).

3) Mechanism of Thermal Runaway of the cycled Lithium-Ion Cells

f) *Journal of The Electrochemical Society*, **165** (7) A1303-A1308 (2018)
g) *Journal of Power Sources V 334, Dec. 2016,* 1-11
h) Electrochimica Acta 230 (2017) 454-460 // i) J. Phys. Chem. C 119 (2015) 16443-16451

1) Cell Sample Information: commercially available 18650 (2.2 Ah, made 2016
: Li(Ni0.5Co0.2Mn0.3)O2/Graphite), i.e. cells (NCM/Graphite).

2) **Charging procedure:** Constant current/constant voltage (CC/CV), on Specification
: CC: 1C (2.2 A) up to voltage 4.2 V, CV: charging current decreased lower than C/20.
Discharging procedure: Constant current (CC) :CC: 1C (2.2 A) Voltage: 2.75 V (Maker's Specification)

3) **Cycle Number**: until the SOH reach 70%, the cell capacity goes under 70% of initial

2-1. Aged cycled cell safety mechanism analysis

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Experimental Summary

1) Number of cycles (NC) of charge/discharge 0, 15, 30 and 45 respectively.

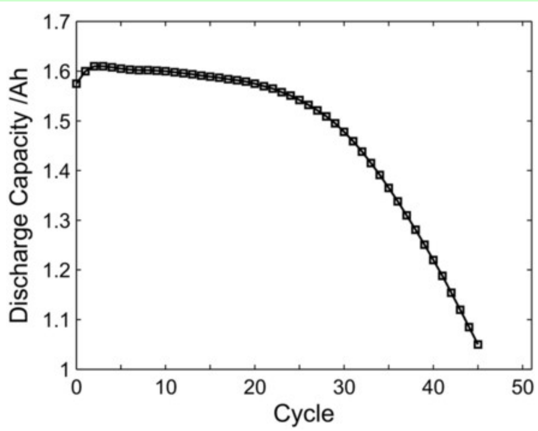
2) After 45 cycles at T = 0 ◦C, their discharge capacity fell down to 70% (SOH: 70%) of their initial discharge capacity, i.e. of the discharge capacity of the first cycle.

3) The initial discharge capacity of the cells is much lower of their nominal capacity as cycling took place at low temperatures and hence at higher resistance of the cells.

4) Evaluate Cell safety mechanism by Li MAS NMR, SEM, and ARC test.

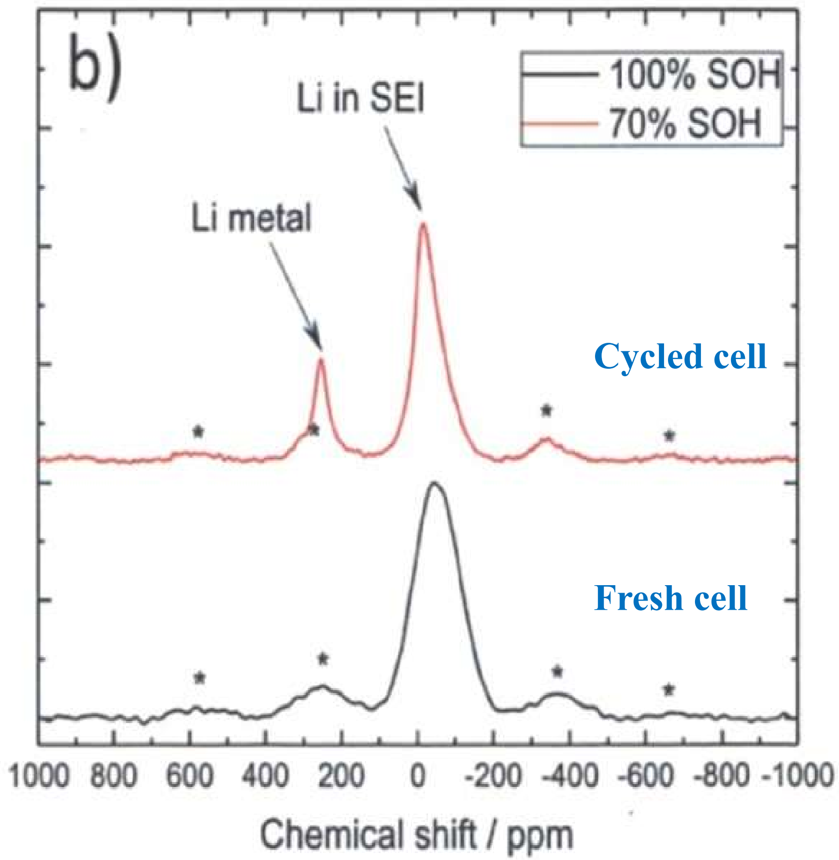
Test Result

Journal of The Electrochemical Society, **165** (7) A1303-A1308 (2018)



2-2 Post-mortem analysis of fresh and aged anode

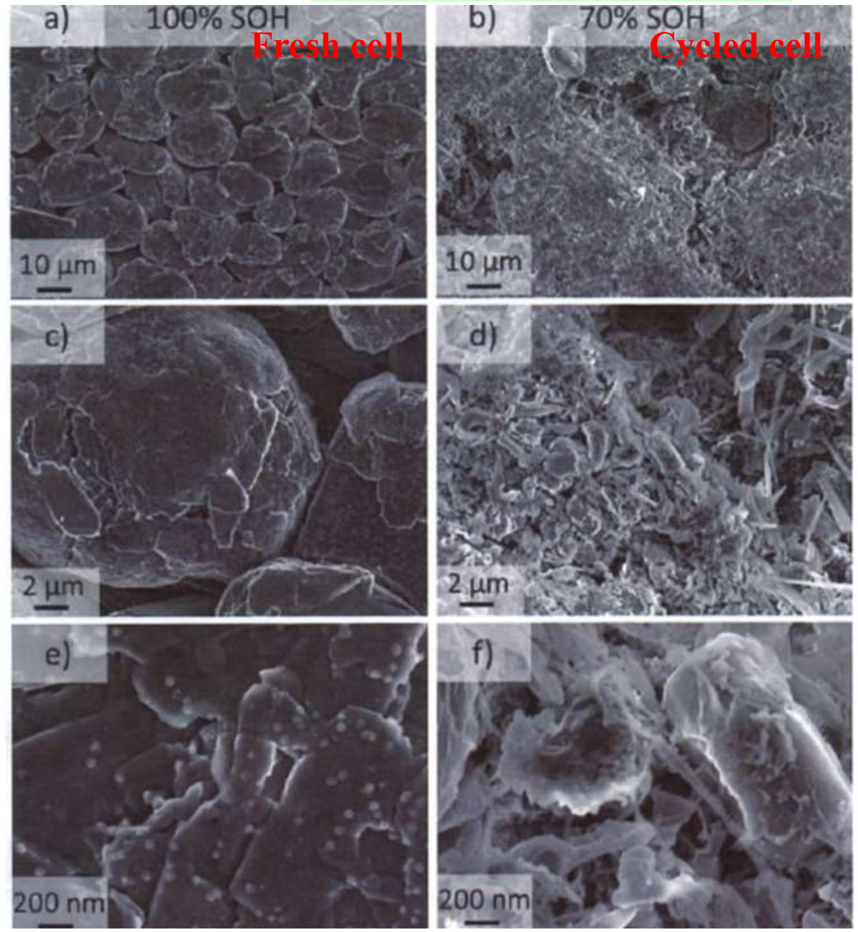
Solid state ^{7}Li MSA NMR



0 ppm: represent Li species incorporated in the SEI.
~255 ppm: contributed Li metal deposition on graphite.

Ref.: J. Phys. Chem. C 119 (2015) 16443-16451
~260 ppm: attributed to mossy Li deposition
~270 ppm: attributed to Dendrite Li deposition

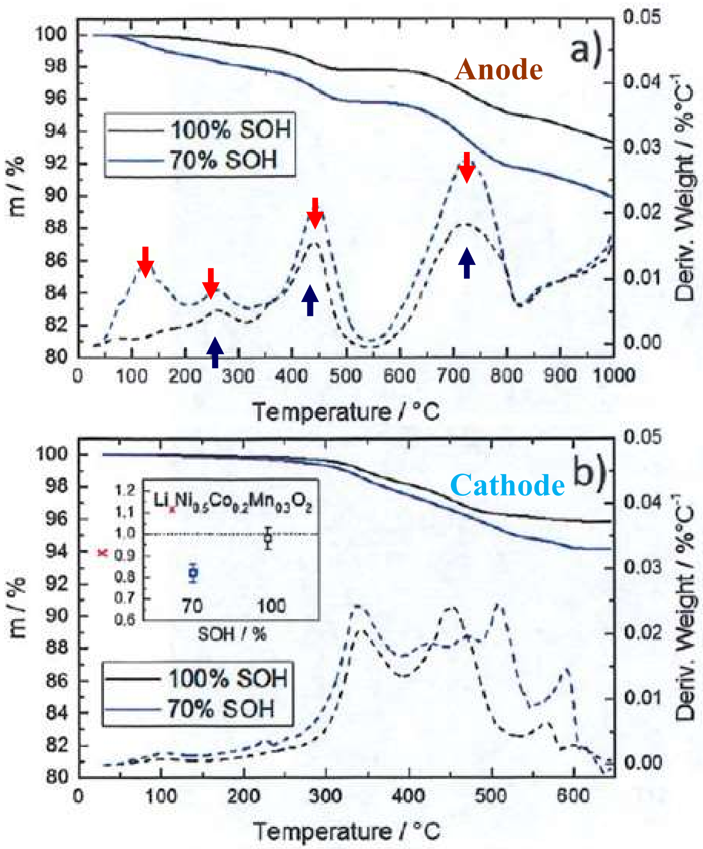
SEM of Anode Surface



<u>SEM of Anode Surface at 255 ppm NMR</u>
Surface of the cycled cell anode was covered with a dense flake-like deposition interfused with needle-like structures HSAL(High surface area lithium)
*lower temp. with higher current density favors a HSAL morphology
* HSAL build up pressure in the cell.

2-3 Thermal stability of electrodes and electrolyte composition of aged cell

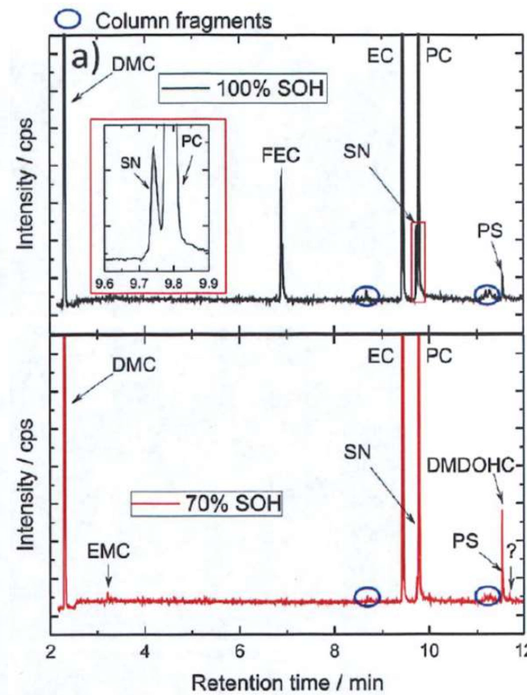
Thermal stability of electrodes



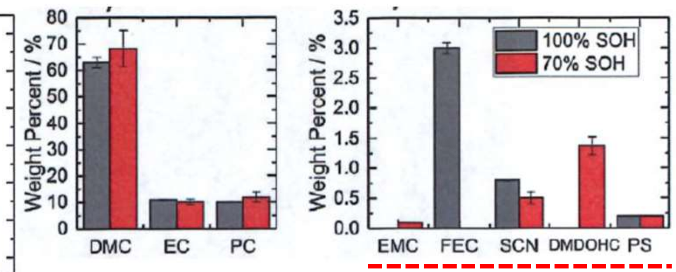
TGA (Thermogravimetric analysis)
ICP-OES(Inductively coupled plasma optical emission spectrometry

Electrolyte composition change of aged cell

GC/MS



FID-MS



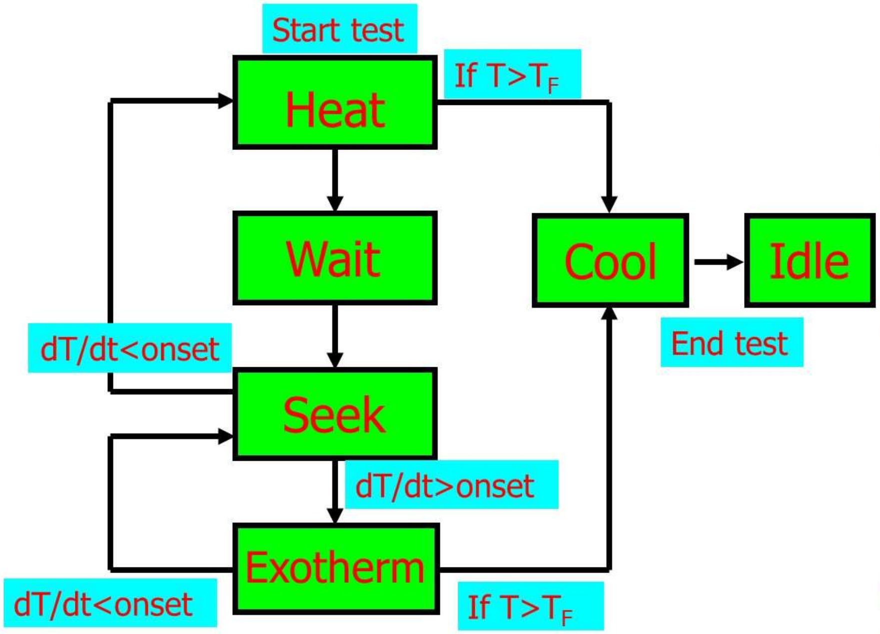
DMC: Dimethy carbonate
EMC: Ethyl methyl carbonate
EC: Ethylene carbonate
PC: Propylene carbonate
FEC: Fluroethylene carbonate
PS: Propane-1,3-sulton
SN: Succino-nitrile
DMDOHC: Dimethy-2,5-dioxahexane carboxylate

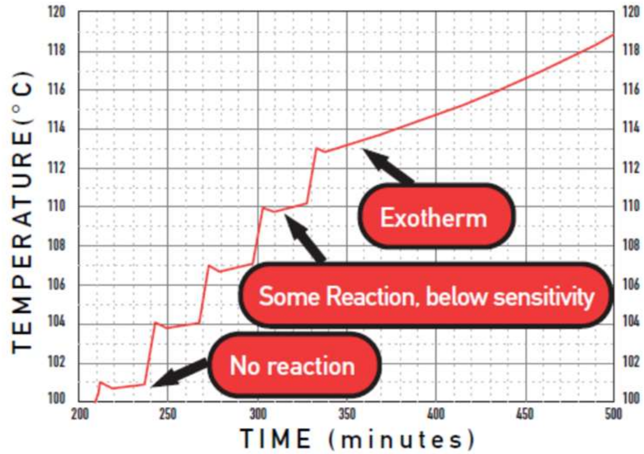
Gas chromatography (GC)/Mass Spectrometry (**MS**)
Flame Ionization Detector (**FID**)
to identify different substances within a test sample.

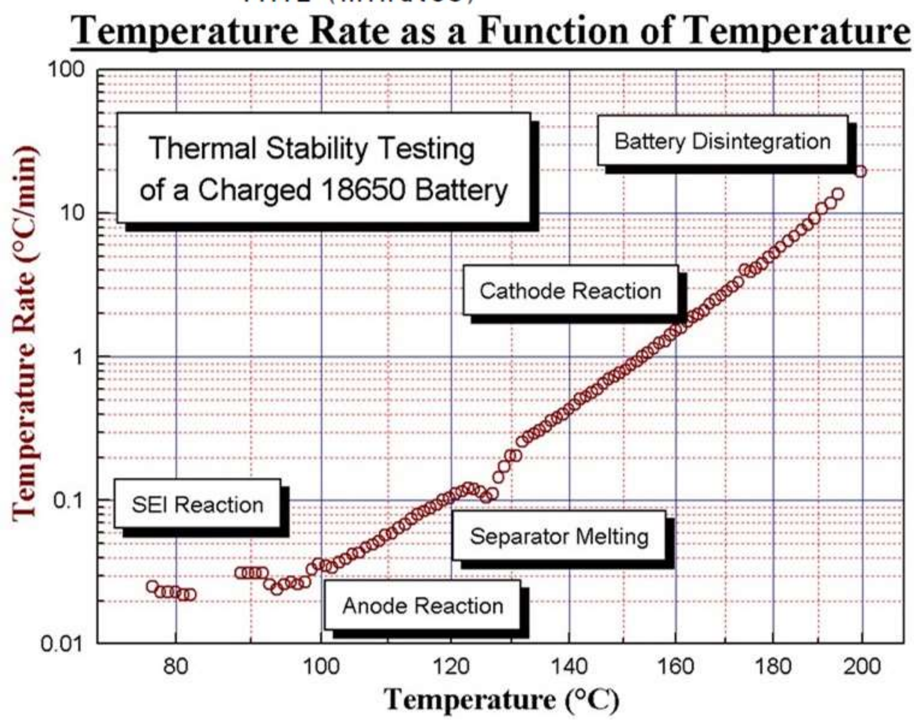
Electrolyte degradation is initiated electrochemically through the cell ageing and generated the DMDOHC in electrolyte and made the SEI layer unstable.

3. Evaluation SHR by ARC(Accelerating Rate Calorimeter)

Heat-Wait-Seek protocol to detect Self-Heating reaction at quasi-adiabatic condition.







Self-Heating Rate (SHR): temperature of initiation of the exothermic reactions (at SHR = 0.02 K min^{-1})

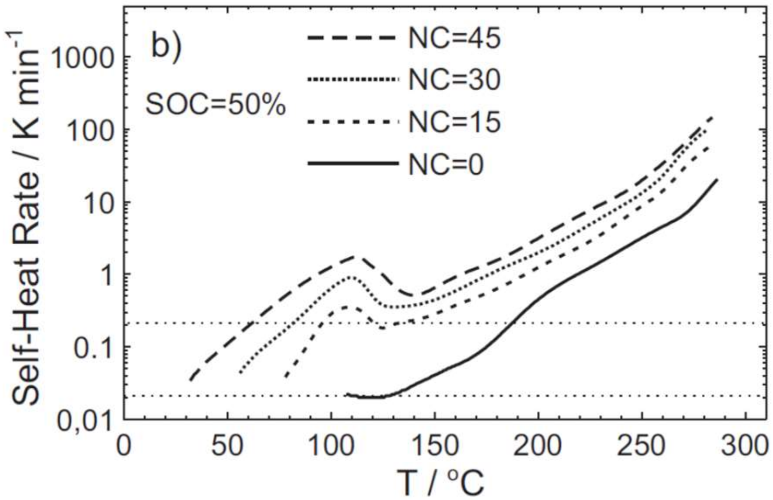
Temperature of thermal runaway at SHR = 0.2 K min^{-1}

THT ARC Introduction: 2009

J. Power Sources 137 (2004) 117-127

THT ARC Introduction: 2009

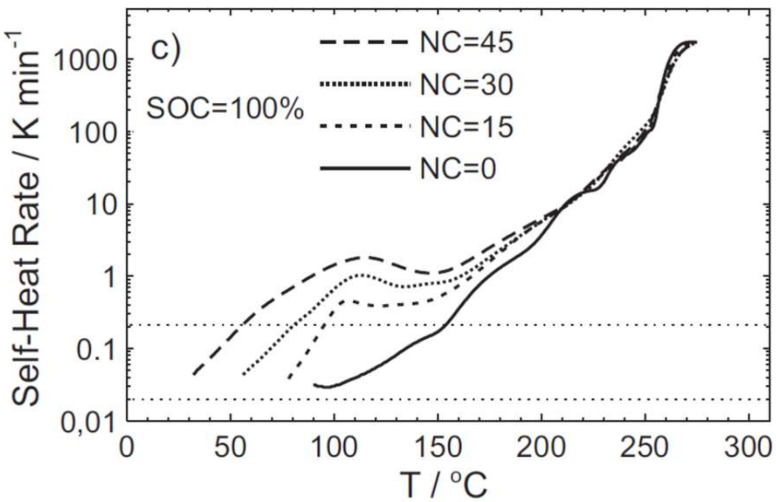
3-1. ARC test Result and Gas generation



* As the cycle number of the cell increasing, the earlier the self-heating temperature start.
* As the SOC of the cell increasing, the earlier the self-heating temperature start.

At the SOC= 100%
1)NC= 0 : self-heating temperature: 89 °C,
2)NC= 15: self-heating temperature: 78 °C,
3)NC= 30 : self-heating temperature: 56 °C,
4)NC= 45: self-heating temperature: 32 °C

Temperature of initiation of the exothermic reactions at SHR = 0.02 K min−1,
Temperature of thermal runaway at SHR = 0.2 K min−1



*** The first exothermic reaction of the aged cells is the exothermic reaction of recombination of atomic hydrogen accumulates in anode graphite, which exists inside of graphite in atomic form.**
***As with a hydrogen amount growth ➔ its activation energy decrease ➔ decrease the initial onset SHR.**

Amount of Gas and H_2 Released

Table II. Gas release from cells as applied to first group of exothermic reactions.[a]

Number of charge/discharge cycles	15			30			45		
SOC (%)	0	50	100	0	50	100	0	50	100
Amount of gas released (ml)	57.3	56.5	57.6	113.5	114.9	113.1	170.9	173.5	171.9
Amount of H_2 released (ml)	56.8	56.0	57.2	112.5	114.1	112.2	169.5	172.1	171.0
Energy of exothermic reaction (Eq. 3) (kJ)	1.11	1.09	1.11	2.19	2.22	2.18	3.30	3.35	3.33

*The relative error in the data in Table is 3%

Journal of The Electrochemical Society, **165** (7) A1303-A1308 (2018)

4. Temp. affect to EV LiB performance and safety

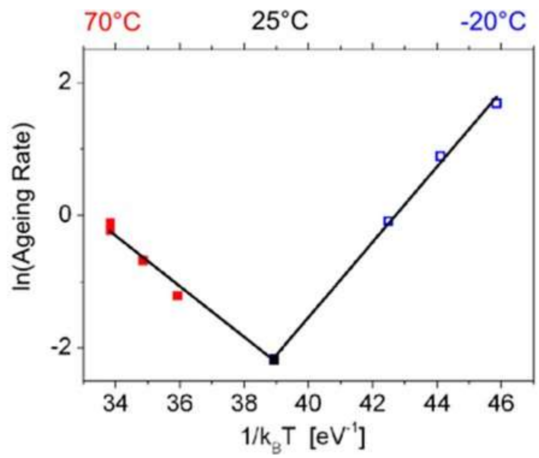
High Temperatures

Side reactions faster
➔ battery degrades faster

: thermally and electrochemically degradation

↓

Mn dissolution
+
SEI thickness increase



Low Temperatures

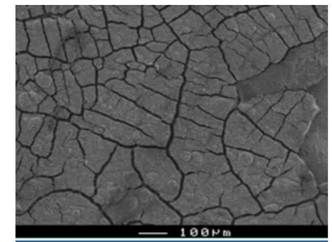
↓

low anode potential

↓

Li Plating

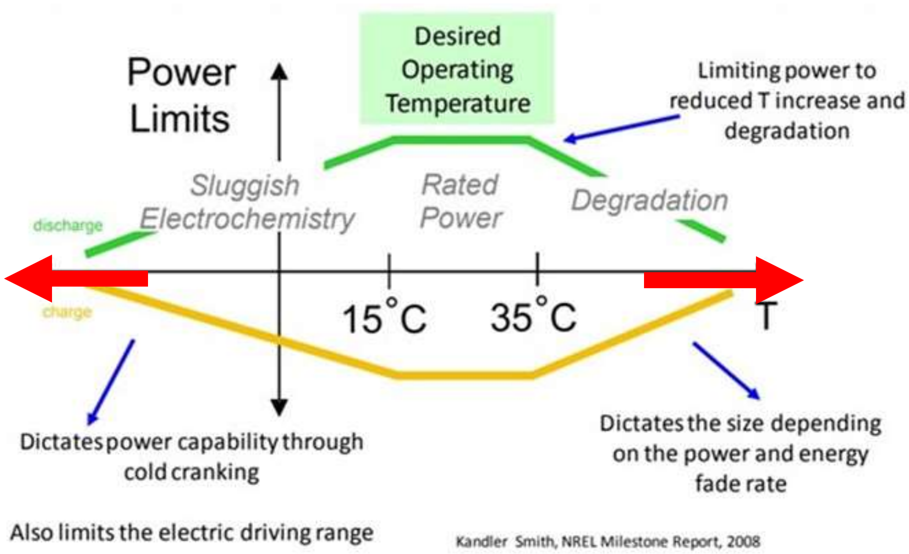
Lower Performance
(Power and Energy)



Binder become brittle
(Active material on electrodes fall apart due to binder failure)

Hot temperature: thermal runaway and safety incidents

EV: Temperature impact on life, performance, safety, and cost of LIBs



Addressing Temperature Issues

- Material Selection
- Cell and Module Design
  : Thermal Management
- Balance of the System

5. Verification Test and result summary

Purpose

- SEM & EDS, TEM, NMR, ARC(Accelerating Rate Calorimeter), XRD, TGA GC-MS, FID-MS and ICP-MS are all useful method to analyze the LiB cell, but those are time-consuming and expensive methods so those are not accepted method for the cell Approval and Certification program.
  : Time consuming, expensive, expert-need to sample preparation and analysis.

- Search and develop a simple but adequate test methods/conditions which can simply identify/verify the safety risk of the cycled cell at lower and higher temp.

Topic

1) Review test item and conditions of the LiB Standards and Certifications.

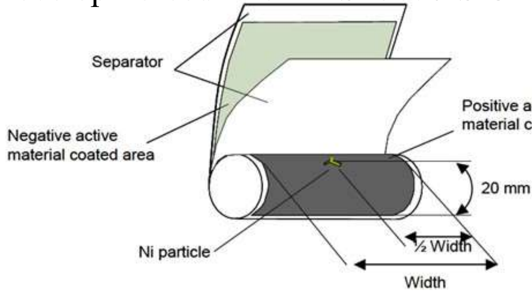
2) Verification test & Review the results
   - 25 cycle test, - ARC, - ESC, and - Thermal Test

3) Conclusion and Summary

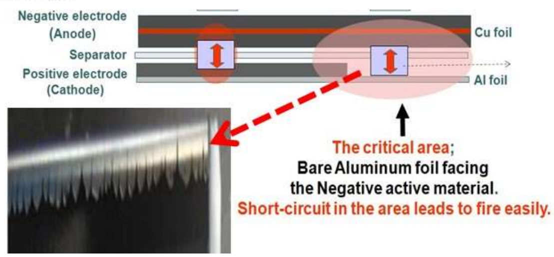
** ESC: External Short Circuit*

5-1. Temp. consideration - IEEE Std 1625/1725

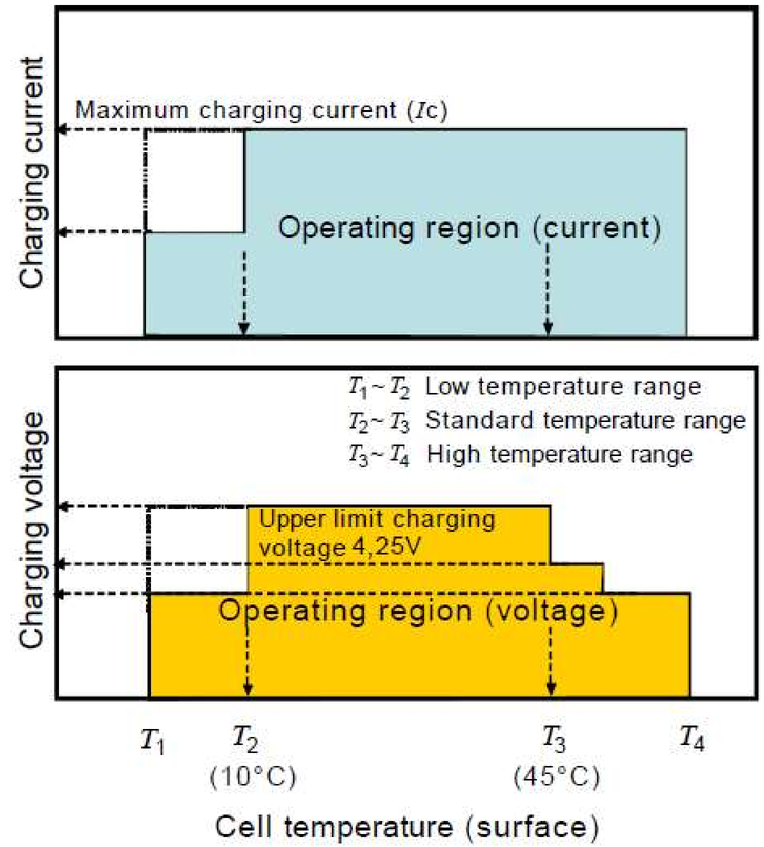
Develop Forced Internal Short: JIS C 8714



Internal Short Avoidance
:IEEE 1625/1725



Schematic operating region of li-ion cell



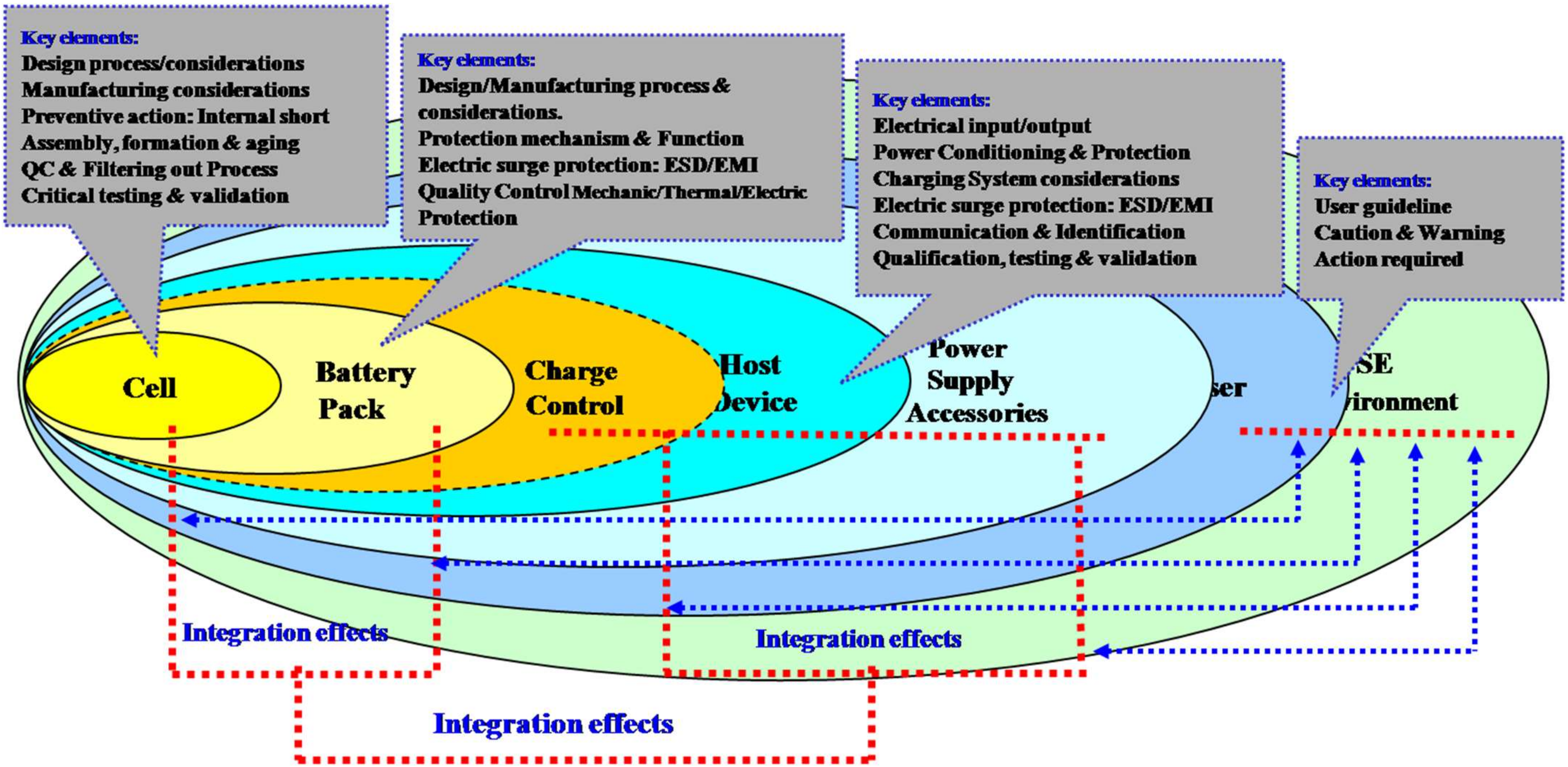
4.1 Introduction

In system design analysis, **it is necessary to consider all system usage scenarios (charge, discharge, and storage) and the associated affected subsystems.** An analysis shall be developed for cell, pack, host, charger, and accompanying accessories that are a part of the system, followed by an analysis that includes the interactions between the subsystems

Smartphones are being exposed to harsher environmental conditions due to increased outdoor use. Users charge and use batteries at more extreme temperatures.

5-2. Concept: IEEE 1625/1725 Standard & Certification

Safety & Reliability of Subsystem + Effects of System Integration



* IEEE Cell Certification requires pre-approval of the Cell Manufacturing Site Audit

*IEEE Cell Certification requires pre-approval of the UL1642, IEC62133 and UN s8.3 certifications.

5-3.Test Item on CTIA Cell Certification for IEEE 1725 Standard

No.	Test Clause and Classification	Purpose	Test condition/ # Sample
1	Isolation Properties	To check the separator/cell design maintain isolation under high temperature stress conditions to maintain the safety of the cell.	80% SOC,150 °C, 10 min. : # 5
2	Cell Thermal Test	To ensure cells demonstrate thermal stability	100% SOC, 130 °C , 60 min. : # 5
3	Short-Circuit test:25 cycled at RT	To check the latent defects due to excess lithium plating	55 °C, 80± 20 m Ohm : # 5
4	Short-Circuit test after 25 cycles at Minimum charging Temp.	To check safety of cell charging at the minimum charging Temp.	55 °C, 80± 20 m Ohm : # 5
5	Short-Circuit test after 25 cycles at Maximum charging Temp.	To check safety of cell charging at the maximum charging Temp.	55 °C, 80± 20 m Ohm : # 5
6	Cell Vent Mechanism	To check Vent activation pressure	Vent activation pressure : # 5
7	-Shrinkage Allowance: Room Temp. -Shrinkage Allowance: High Temp. -Electrode Geometry	To check the Cell Design/Manufacturing Status of the electrode/electrode assembly to keep the cell safety	Measure the gap among Separator, Anode and Cathode : 5 samples
8	-Electrode Tabs -Application of Insulation -Supplementary Insulation -Internal Short Avoidance -Positioning of Insulating Material	To check the Cell Design/Manufacturing Status of the insulation mechanism to prevent cell internal short circuit	Check Cell Design/Manufacturing Status: accuracy & uniformity : 5 samples

CTIA Cell Certification has 1)Sample Test + 2) Product Review(Cell maker test result) + Self Declaration

Pre-requirement: 1) Cell manufacturing site Approval by Audit, + 2) UN38.3/UL1642/IEC62133 certificates.

5-4. Verification Test item and method

Test Item	IEEE	UL1624	IEC62133	UN 38.3	
Isolation Properties	V				
Thermal Test: 130 °C, 1 Hour	**V**	V	V		
External short circuit	V	V	V	V	
External short circuit Cycled cell at Room Temp	**V**				
External short circuit Cycled cell at Minimum Temp.	**V**				
External short circuit Cycled cell at Maximum Temp.	**V**				
Abnormal/ Overcharging		V	V	V	
Forced Discharge		V	V	V	
Altitude Simulation		V	V	V	
Mechanical Test Crush/Impact/Shock/Vibration		V	V	V	
Temperature Cycling		V	V	V	

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5-5. Verification experimental

Sample

- Cell models are designed for smart phone application.
- Cell Design and Cell Specification of these tests have considered the CTIA Cell certification at the Minimum and Maximum temp. cycle test
- Cell capacity and Charging voltage 3,000 ~ 3,600 mAh / 4.4V, 1C rate C/D

Experimental

1) Cycle test at different Temperature: follow the IEEE1725, Cell Certification process

   **Cycle number 25 was compromised considering the period of the Smart phone certification.*

   :IEEE 1625: 100 cycles, UN 38.3 Manual: Small size: # 50 cycles at Room Temp.

   - Room Temperature 25 cycles
   - Minimum Temperature 25 cycles (Minimum Charging Temperature condition)
   - Maximum Temperature 25 cycles (Maximum Charging Temperature condition)

2) ARC Test Comparison: to 200 °C: long test period: calibration/sample test – 5-6 days

   : Compare the onset temp. of SHR

3) External Short circuit Test: 55 +/- 5 °C, 80 +/-20 m Ohm: **IEEE1725, Cell Certification : short period**

   : Compare the result of the Max. Temp. of the cell

4) Thermal Test: 130 °C for 1.0 Hour : IEEE1725, Cell Certification : Short test period

   : Compare Pass or Fail of the test result.

5-6. Test Result - Cycle Test

The cycle test condition was compromised as:

- Cycle temperature was compromised to - 5 °C / Spec.: Charge: - 5 °C, Discharge: - 20 °C
- Cycle Number was compromised to 25 cycles / IEEE 1625: 100 cycles, UN 38.3: 50 cycles

25 Cycle Test Condition				
Model	Cell #1	Cell #2	Cell #3	Cell #4
Capacity	3,000 mAh / 4.4V	3,200 mAh / 4.4V	3,500 mAh / 4.35V	3,600 mAh / 4.35V
- 5 °C	C: 0.5 C, 4.2 V D: 0.5 C, 2.75 V	C: 0.3 C, 4.2 V D: 0.3 C, 2.75 V	C: 0.3 C, 4.2 V D: 0.5 C, 2.8 V	C: 0.3 C, 4.2 V D: 0.3C, 3.0 V
Capacity loss	8.8 ~ 12.9 %	7.6 ~ 10.9 %	6.7 ~ 8.9 %	6.4 ~ 8.4 %
25 °C	C: 1.0 C, 4.4 V D: 1.0 C, 2.75 V	C: 1.0 C, 4.4 V D: 1.0 C, 2.75 V	C: 1.0 C, 4.35 V D: 1.0 C, 2.75 V	C: 1.0 C, 4.35 V D: 1.0 C, 2.75 V
Capacity loss	1.3 ~ 3.0 %	1.0 ~ 1.8 %	0.5 ~ 1.3 %	0.4 ~ 1.0 %
60 °C	C: 0.8 C, 4.3 V D: 1.0 C, 2.75V	C: 0.7 C, 4.25 V D: 1.0 C, 2.75 V	C: 0.7 C, 4.2 V D: 1.0 C, 2.8 V	C: 0.5 C, 4.2 V D: 1.0 C, 3.0 V
Capacity loss	2.6 ~ 4.3 %	2.3 ~ 3.7 %	0.9 ~ 3.2 %	0.8 ~2.8 %

At lower temperature (- 5 °C) , some cell models were not charged enough compared to the specification and the 1st cycle capacities were 38 ~ 67 % of the cell rated capacity.
Some cell models, which is not on the test result list, could not be charged at all. The capacity loss at the lower temperature (- 5 °C) does not have meaning much.
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5-6. Test Result - ARC Test

Test temperature range of the ARC is from room temp. to 400 °C, but it was compromised to 200 °C, because the thermal behaviors of the cell at the lower temperature (room temp. ~ 110 °C) are more important for this test and it can also reduce the test period.

Self-Heating Temperature 2 samples per model				
Model	Cell #1	Cell #2	Cell #3	Cell #4
- 5 °C : Minimum T	**64.7 °C**	**65.5 °C**	**67.8 °C**	**71.2 °C**
25 °C : Room T	**71.9 °C**	**72.1 °C**	**73.3 °C**	**76.8 °C**
60 °C : Maximum T	**70.1 °C**	**70.8 °C**	**71.4 °C**	**73.6 °C**

- Onset temp. of SHR of the cells cycled at - 5 °C (Minimum charging Temp.) and 60 °C (Maximum charging Temp.) were affected by cycled temperature & conditions.

- Onset temp. of SHR at - 5 °C cycled cells are higher (64.5~71.2 °C) than that of the reference papers(32 ~ 56 °C), because the Cell design/Specification had already considered for the certification.

- Cycle test condition at - 5 °C & 60 °C was not the worst conditions and the 25-cycle number was not enough to identify the cell capacity decline at the maximum and minimum temperature.

  * Charging voltage and current was reduced a lot considering for the certification.

* SHR : Self Heating Rate

5-6. Test Result - External Short Circuit & Thermal test after 25 cycles at the Room., Min./Max. Temp.

Peak Temp. on External Short Test at 55 +/-2 ° & 80 +/-2 m Ohm per 5 samples				
Model	Cell #1	Cell #2	Cell #3	Cell #4
- 5 °C	104.2 ~ 118.9	103.6 ~ 114.8	90.7 ~ 101.3	94.0 ~ 101.8
25 °C	99.2 ~ 106.1	98.8 ~ 104.9	88.3 ~ 97.9	92.3 ~ 97.7
60 °C	103.2 ~ 112.5	101.7 ~ 108.2	88.1 ~ 98.3	92.6 ~ 102.2

- Cell peak Temp. of the External SC test were affected by 25-cycled temperature & condition.
: Cell surface temp. of cycled at Min./Max. temp. were a little higher than the cycled at Room temp.,
: Cell surface temperature depends on Heat Generation and Heat Release of the cell design.

Pass/Fail on Thermal Test at 130 °C, 1 Hour per 5 samples				
Model	Cell #1	Cell #2	Cell #3	Cell #4
- 5 °C	*Fail: 2/5*	*Fail : 1/5*	Pass	Pass
25 °C	Pass	Pass	Pass	Pass
60 °C	Pass	Pass	Pass	Pass

- Thermal tests were affected by the 25-cycled temperature & condition.
:The test-failed cells cycled at the - 5 °C (Cell #1 & Cell #2) would be caused by the cell capacity loss of the cells. Additional analysis and verification tests are in progress.

6. Conclusion and Summary

Conclusion & Summary

1) The charging & cycle conditions of the cell at the minimum and maximum temperature effect on the safety of the LiB. The ARC, ESC, and Thermal Test are useful method to analyze the safety risk of a cell model.

   ➔ ARC test consumes too long test time compared to other methods.
   ➔ ESC (80 m Ohm) and Thermal Test (130 °C/1 hour) are an appropriate methods to evaluate the safety risk of a cell models for the approval and certification.

2) The "Thermal Test", compare to "ESC Test" seems more effective validation method to identify the effect of the cycle test condition.
   But additional analysis and verification tests are needed to quantify the effectiveness.

3) The 25 cycle-number was not enough and the cycle test condition at both - 5°C and 60 °C are not the worst conditions to evaluate and validate the cell model's safety risk level. : the condition at the 0 °C and 50 - 55 °C is more sever.

* *ESC: External Short Circuit*
ARC: Accelerating Rate Calorimeter

Thank you for your Attention!!!

It is not easy to predict, prevent and eliminate the field incident at the point of manufacture and certification process, But it is not an impossible thing.

The greatest factor is the way in which every difficulty is foreseen, victory awaits him who has everything in order luck, People said it. ; Amundsen

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