

DANGEROUS GOODS PANEL (DGP) MEETING OF THE WORKING GROUP OF THE WHOLE

Rio de Janeiro, Brazil, 20 to 24 October 2014

Agenda Item 5: Review of provisions for the safe transport of lithium batteries 5.6: Miscellaneous lithium battery issues

SHIPPING LITHIUM ION CELLS, IMPLICATIONS ON STATE OF CHARGE

(Presented by PRBA – The Rechargeable Battery Association)



Shipping Lithium ion Cells, Implications on State of Charge

October 20 – 24, 2014 ICAO Dangerous Goods Panel Working Group of the Whole

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Lithium ion Cells and State of Charge (SOC)

- Properly designed and manufactured lithium ion cells have low self-discharge rate provided cells are shipped and stored according to manufacturer's specifications
- Cells shipped and stored at high SOC and elevated temperatures may result in enhanced degradation of cell components
- Cells shipped and stored at low SOC can result in over-discharged cell and degradation of cell (*e.g.*, corrosion of copper current collectors, rapid impedance growth; could result in cell thermal runaway upon recharging)



Lithium ion Cells and State of Charge (SOC)

- Lithium ion cell manufacturers ship at approximately 40 50% SOC for optimal maximizing of cell performance
- Shipped at approximately 40 50% SOC, high quality lithium ion cells experience minimal degradation
- Shipping by air v. sea transport and use of refrigerated containers ("reefers")





Measuring SOC and Open Circuit Voltage (OCV)

- No direct way of measuring SOC of lithium ion cell or battery
- Measuring approximate SOC by OCV is possible but can result in inaccuracies due to variations in chemistries and other factors (*e.g.*, temperature)





SOC and OCV and Lithium ion Chemistries

- SOC and OCV vary depending on lithium ion cell chemistry
 - **-** 100% SOC
 - ~ 4.2 V (Li ion cobalt oxide)
 - ~ 3.6 V (Li ion iron phosphate)
 - 50% SOC
 - ~ 3.6 to 3.9 V (Li ion cobalt oxide)
 - ~ 3.2 V (Li ion iron phosphate)



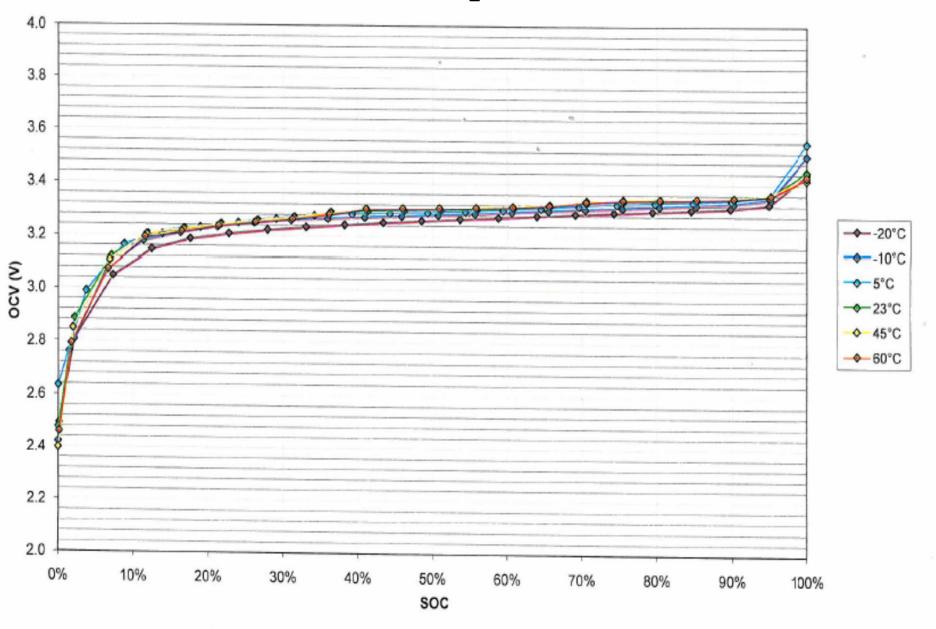


Measuring SOC and Open Circuit Voltage (OCV)

- OCV of lithium ion cell changes significantly at both ends of SOC range
- OCV increases rapidly at high SOC, drops significantly at low SOC

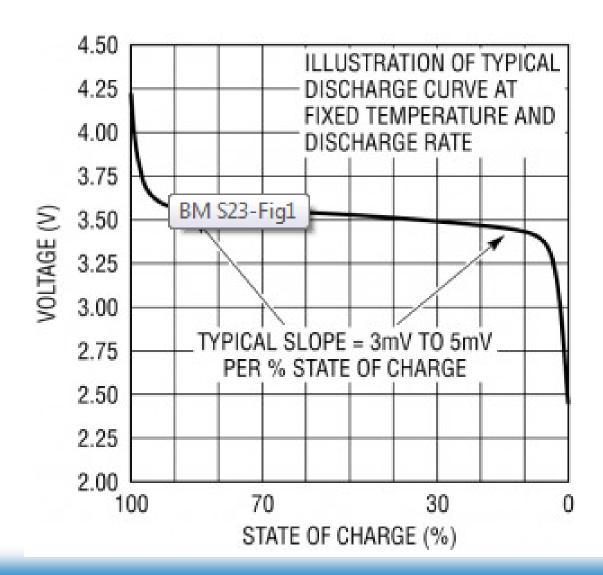


OCV and SOC for Lithium ion Iron Phosphate Cell





"Typical" OCV and SOC for Lithium ion Cell







Over-discharge of Lithium ion Cells and Batteries

- Over-discharge occurs when voltage of cell or battery falls below manufacturer's recommended "safe" level; can result in degradation of cell or battery
- Safety features in cells and batteries generally protect against over-discharge conditions (*e.g.*, battery protection circuit puts battery into sleep mode, renders battery unserviceable and recharge not possible)



Exponent Testing for PRBA on Lithium ion Cells

- Examine effect of cell state of SOC on outcome of a low impedance internal cell fault
- Higher the SOC, the more energy available for release by an internal cell fault for comparable capacity cells
- Higher energy release increases the probability of severe outcomes (*e.g.*, fire, disassembly)





Crush Profile

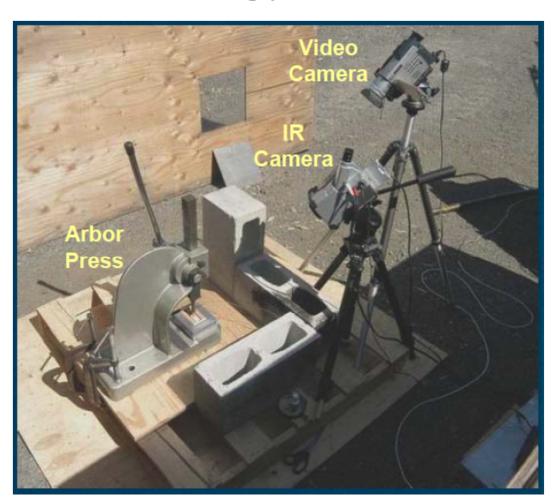
- Goal: Induce "internal short" condition in cell through controlled crush to thermal runaway on multiple cells: 40%, 50%, 70% and 100% SOC
- Crush must not be so aggressive to crack cell case
 - A case crack would act as secondary cell vent and reduce severity of outcome





Test Methodology

- Induce internal cell fault in controlled and repeatable manner
- Cells crushed with arbor press







Categorization of Crush Results

- Observed crush outcomes classified into four categories:
 - 1. Fire: "Severe" outcome
 - 2. Energetic Disassembly: a "Severe" outcome
 - 3. Case Rupture: "Moderate" outcome
 - 4. Internal short: "Minimum" outcome



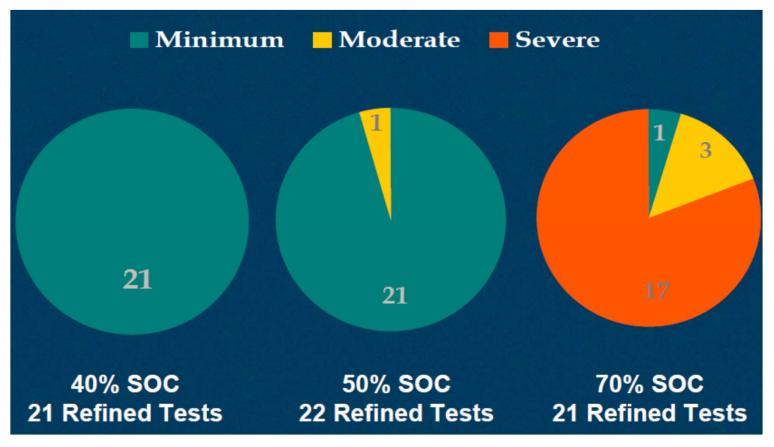


Results of Crush Test

- At 100% SOC, a refined crush typically produced severe outcomes
- At 70% SOC, a refined crush resulted in severe outcomes for a majority of tests
- At 50% SOC, all tests but one resulted in a minimum outcome (one test resulted in a moderate outcome (case rupture))
- At 40% SOC, all of the tests resulted in minimum outcome



Results of Crush Tests





Fire			XXX (3) XXXXX (5) XXXX (4)	xxxxxx (6) xxxx (4)
Energetic Disassembly			XXXX (4) xx (2) X (1)	x (1)
Case Rupture		X (1)	XXX(3)	
Internal Short	XXXXXXXXX (9) XXXXXXCC (7) XXXX (4) XXCXXCXXCX (10)	XXXXXXXXX (9) XXCXXXXX (8) XXX (3) CXXXXXXX (8)	X (1) CCCC (4) x (1) C (1)	xxc (3)
High impedance internal short Temperature Rise < 70 C	xc (2)	cxxxxx (6)	сххсхх (6)	cxxc (4)
soc	40%	50%	70%	100%

'X' denotes individual crush test w/o case crack

'C' denotes individual crush test with case crack

Bold face denotes refined crush method

Italic/lower case denote preliminary crush method



Lithium ion Cells Subject to Crush Tests







Conclusions

- Industry has outstanding safety record on shipping lithium ion cells by all modes of transport
- Manufacturers of lithium ion cells ship at approximately 40 50% SOC, which provides an additional level of safety in transport (as reflected in test data)
- Placing low SOC limits $(e.g., \le 30\%)$ on lithium ion cells could lead to cell degradation and over-discharge conditions and compromise cell quality
- Very difficult to enforce SOC limits in the field

