DANGEROUS GOODS PANEL (DGP)

TWENTY-FIFTH MEETING

Montréal, 19 to 30 October 2015

Agenda Item 5: Development of a comprehensive strategy to mitigate risks associated with the transport of lithium batteries including development of performance-based packaging standards and efforts to facilitate compliance

STATE OF CHARGE FOR LITHIUM ION CELLS AND BATTERIES

(Presented by PRBA – The Rechargeable Battery Association)

SUMMARY

This information paper responds to DGP/25-WP/22 and state of charge requirements for lithium ion cells and batteries.

1. INTRODUCTION

1.1 At the DGP-WG/15 meeting, PRBA submitted Information Paper (DGP-WG/15-IP/1) that included a technical paper on the role state of charge (SOC) plays in the manufacturing, transport and storage of lithium ion cells and batteries. The technical paper is attached for reference. Based on the information provided in our technical paper, we have very significant concerns with ICAO's consideration of a 30% SOC limit on lithium ion cells and batteries.

1.2 Also attached are excerpts from PRBA testing data on SOC presented to the ICAO DGP-WG/14 in Brazil that shows the outcome of abuse tests on 18,650 lithium ion cells at different SOC levels. The data show that at 50% SOC, all tests but one resulted in a minimum outcome. (The one test resulted in a moderate outcome (case rupture)). At 40% SOC, all of the tests resulted in a minimum outcome. The test data confirm that cells at a SOC even above 30% can provide an additional level of safety in transport. All of the test data are available on ICAO's website: http://www.icao.int/safety/DangerousGoods/Working%20Group%20of%20the%20Whole%2014/DGPWG.14.IP.008.5.en.pdf.

1.3 It is well recognized that shipping lithium ion cells and batteries at a reduced state of charge provides an additional level of safety in transport, which is the reason manufacturers generally ship their cells and batteries at less than 60% SOC. It also is well recognized that lithium ion cells require protection from both high and low SOC and voltages. Prolonged low SOC and low voltage conditions can pose a hazard and result in dissolution of metals (principally copper) within a cell. This dissolved copper can be re-plated within the cell upon subsequent charging, cause undesirable effects and compromise cell performance (*e.g.*, low capacity, poor cycle life, high self-discharge). Adopting a base line SOC limit of 30% could lead to these undesirable effects and compromise cell performance.

1.4 In light of the work that will commence on a lithium battery performance-based standard in 2016, PRBA believes it is premature to adopt a SOC limit on lithium ion cells and batteries, even as an interim measure. Adopting a SOC limit now and then removing it two years later after the performance-based standard is adopted will cause significant confusion for shippers, freight forwarders, operators and enforcement agencies.

1.5 It also is difficult to understand how the DGP can adopt a complex SOC requirement when the current regulations are not being consistently enforced and shippers regularly mislabel their batteries and falsify UN lithium battery test data. Another example of such non-compliance is well-documented in the United Kingdom’s Information Paper (DGP/25-IP/1).

1.6 In light of these concerns, we recommend that a SOC limit not be adopted at this time and the issue be revisited in 2016 and 2017 as the performance-based standard is being developed.

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APPENDIX

TECHNICAL CONCERNS REGARDING THE STATE OF CHARGE OF LITHIUM ION CELLS DURING TRANSPORTATION AND STORAGE

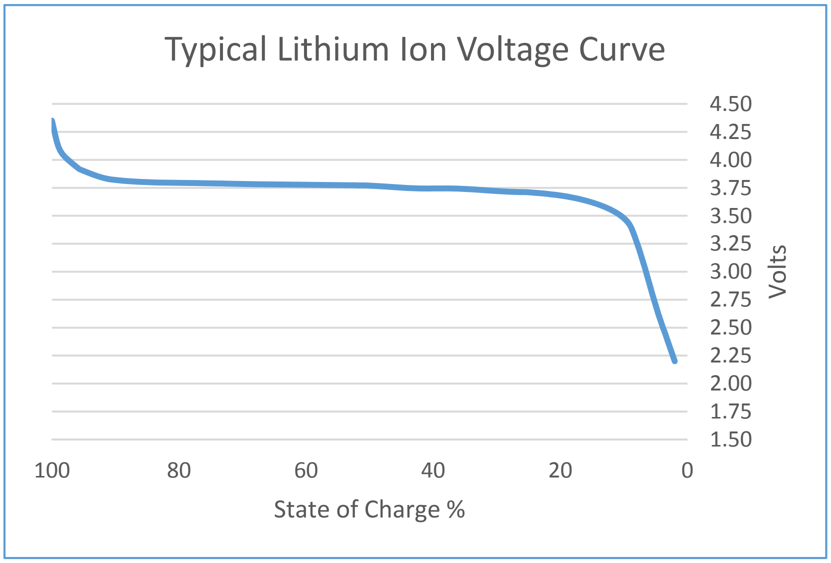
(DGP-WG/15-IP/1, Appendix)

Rechargeable lithium ion (Li-ion) cells and batteries are ubiquitous throughout consumer electronics and are used in many industrial applications such as hybrid and electric vehicles. The term ‘lithium ion’ includes many different chemistries with a variety of properties. These include lithium cobalt oxide ($LiCoO_2$, or LCO), lithium manganese oxide ($LiMn_2O_4$, or LMO), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$, or NMC), lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$, or NCA) and lithium iron phosphate ($LiFePO_4$, or LFP) as well as many variations on these basic chemistries.

The rechargeable Li-ion batteries in consumer electronics and other products are comprised of one or more Li-ion cells. These cells are the basic building blocks of the battery and can be manufactured in a variety of shapes and sizes. Cylindrical cells, prismatic cells and pouch cells are the three main form factors. The first two are in cans of varying dimensions, while the pouch cells are contained in a foil pouch and are much more easily customized for handheld devices. All form factors utilize similar chemistries, so they can be simply referred to as Li-ion cells for the purposes of this paper.

Li-ion cells require protection from both high and low voltages as well as extreme temperatures. High voltage, resulting from overcharging, can result in thermal runaway conditions and pose a safety hazard. Multiple levels of protection are built into batteries, chargers and devices to prevent this type of failure. Additionally, prolonged low voltage conditions can pose a hazard and result in when dissolution of metals (principally copper) will occur. Copper dissolves into the electrolyte solution at open circuit voltages below ~0.7 volts. This dissolved copper is re-plated within the cell upon subsequent charging and can cause undesirable effects and almost certainly will compromise cell performance (*e.g.*, low capacity, poor cycle life, high self-discharge). Well-designed lithium ion batteries include safety circuits that protect the cells. However, inherent self-discharge within the cells can lead to a low voltage condition if the cells are left uncharged for long periods of time.

The nature of Li-ion is such that the relationship between state of charge (SOC) and voltage is fairly flat throughout much of the cell's range. A typical discharge curve is shown below.[1]



The rapid fall of voltage at the end of discharge provides a relatively accurate means of determining when energy will run out. However, this also means that the state of charge drops much more rapidly and can lead to an over-discharged condition if the cell or battery is left to sit for prolonged periods at this low state of charge. Ambient temperature can have a profound effect on this curve and must be considered during transportation and storage when the cells may be exposed to extreme high or low temperatures.

High voltage can also cause degradation of the cell, especially at elevated temperature. When a Li-ion battery is plugged into a charger, charging continue along a prescribed path until a SOC of 100% is sensed by the circuitry. The charging is terminated and the battery is allowed to very slowly discharge. It is quite detrimental to the cells to be kept at 98-100% SOC for prolonged periods of time. This is why they are allowed to discharge to around 95% SOC or less before charging is re-initiated.

Li-ion cells have an inherent self-discharge rate independent of any circuit load that the battery assembly may require. This discharge rate is quite low at room temperatures around 20-25˚C or less. Values of around 2% per month are typical, but this is quite variable depending on specific chemistry and manufacturing quality. Temperatures above 30˚C can easily double this self-discharge rate. This has profound implications on transportation and storage of cells and batteries. In addition, self-discharge rates can be significantly higher for Li-ion battery packs and/or batteries installed in equipment (due to added leakage current through attached circuitry).

The manufacture of Li-ion batteries often requires the transportation of the cells at three separate stages. The first is from the cell manufacturing factory to the factory that will assemble the cells into batteries with the safety circuitry. The second stage is from the battery assembly factory to the host device manufacturer, such as a cell phone or notebook PC. The third is when the host device itself is shipped to a customer or retailer. Each stage in this supply chain comes with different requirements of the cell or

[1] Based on a C/20 discharge of lithium cobalt oxide – graphite cells

battery to ensure that a fully functioning product is delivered to a customer. Let us examine the implications of the SOC of the cells at each of the aforementioned steps.

The manufacture of Li-ion cells requires a formation and test period in order to sort out potentially defective cells and to put the cells in their initial electrochemical state. This involves an initial charge period, storage time at different temperatures and subsequent discharge and charge cycles. The precise details of these steps are chemistry dependent and manufacturer specific. In the end, cells are shipped between 40% and 60% SOC, depending on the manufacturer's processes.

When cells arrive at a battery pack manufacturing factory, they are placed in an incoming inspection area that should be temperature and humidity controlled. This is to avoid excessive self-discharge from the high temperatures that may be seen in parts of the world such as south China, Malaysia and Viet Nam where many batteries are assembled. Unfortunately, not all battery manufacturers adhere to these best practices. During the battery pack assembly process, there is testing that takes place and the batteries may be charged to a specified SOC before shipping out to the device manufacturer. This level of SOC is again typically 40-60% to ensure that low voltage conditions are not reached.

Finally, the original equipment manufacturer (OEM) receives battery pack assemblies and they are placed in an incoming inspection area. Again, the batteries are tested and installed into the device. The SOC of the battery when the device is shipped out is 40-60% to ensure the customer receives the device in working order and not over-discharged.

In summary, the flatness of the Li-ion discharge curve makes it difficult to determine SOC from the voltage alone. Specifying a range of SOC when shipping from the cell manufacturer to the battery assembler to the OEM to the customer is necessary to ensure that the customer receives a good working product. The amount of time that a cell or battery or device may sit in a warehouse cannot be accurately determined, and the temperature that the battery is exposed to during transportation or storage is also unpredictable. Therefore, the SOC must be set to handle 'worst case' scenarios. A SOC of 40%, the low end of most specifications, will allow 4-6 months of shelf life before the cell or battery is in critical need of re-charging. With product sitting in warehouses or on shelves for unpredictable lengths of time, specifying an SOC between 40% and 60% is needed to ensure that the customer receives a good functioning product and that the manufacturers do not have to add additional process time to discharge a cell or battery even further.

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STATE OF CHARGE TEST DATA

(DGP-WG/14-IP/14)

(Full report available at http://www.icao.int/safety/DangerousGoods/Working%20Group%20of%20the%20Whole%2014/DGPWG.14.IP.008.5.en.pdf)

Purpose of Testing

- Examine the effect of cell state-of-charge (SOC) on the outcome of a low impedance internal cell fault
- SOC is the charge level of a battery cell divided by its charge capacity
  - The 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:
    - Fire
    - Energetic disassembly
  - For a given cell, the nature of the internal cell fault will determine the initial rate of energy release and potentially the severity of outcome

Raw Data in Order of Testing

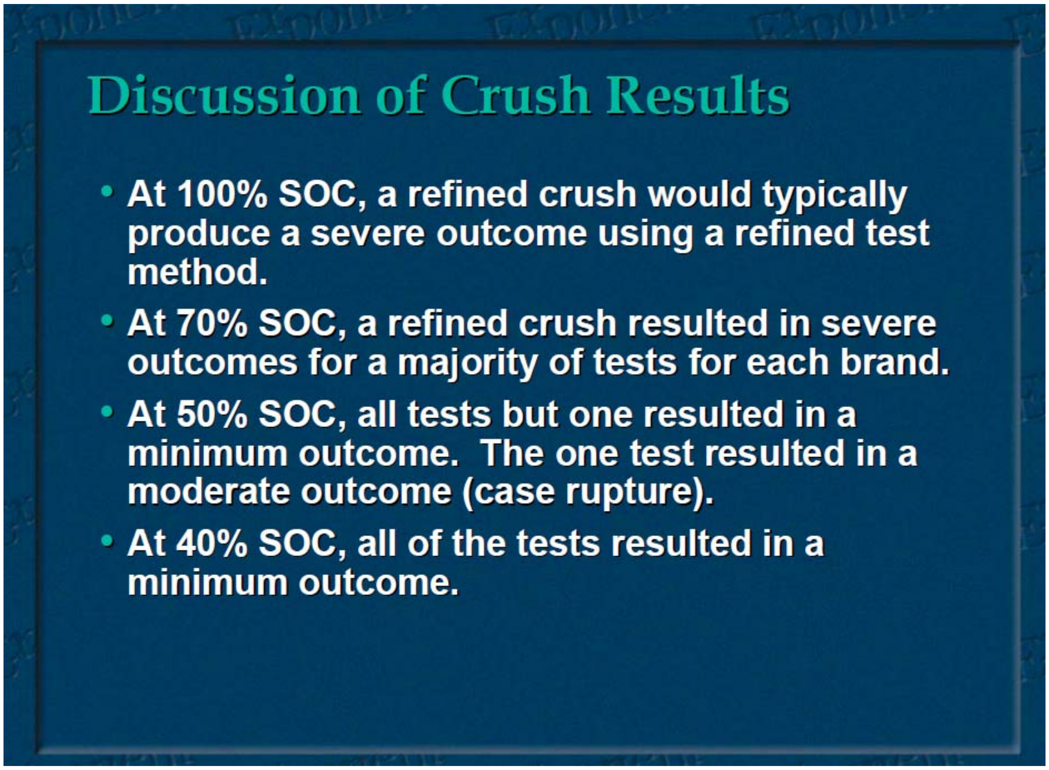
Fire				**XXX (3)** **XXXXX (5)** **XXXX (4)**		*xxxxxx (6)* *xxxx (4)*
Energetic Disassembly				**XXXX (4)** *xx (2)* **X (1)**		*x (1)*
Case Rupture		**X (1)**		**XXX(3)**		
Internal Short	**XXXXXXXXX (9)** **XXXXXCC (7)** *xxxx (4)* **XXCXXCXXCX (10)**	**XXXXXCXXX (9)** **XXCXXXCX (8)** *xxx (3)* **CXXXXXXX (8)**		**X (1)** **CCCC (4)** *x (1)* **C (1)**		*xxc (3)*
High impedance internal short Temperature Rise < 70 C	*xc (2)*	*cxxxxx (6)*		*cxxcxx (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


Discussion of Crush Results
• At 100% SOC, a refined crush would typically produce a severe outcome using a refined test method.
• At 70% SOC, a refined crush resulted in severe outcomes for a majority of tests for each brand.
• At 50% SOC, all tests but one resulted in a minimum outcome. The one test resulted in a moderate outcome (case rupture).
• At 40% SOC, all of the tests resulted in a minimum outcome.

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