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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

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Item 4 (c) of the provisional agenda
Electric storage systems: transport provisions

Proposal to add state of charge (SOC) provision to large lithium-ion cells and batteries during transportation

Transmitted by the expert from China*

Introduction and background

1. At the twenty-sixth, twenty-seventh and twenty-ninth sessions of the Sub-Committee, The Rechargeable Battery Association (PRBA) presented a number of proposals and documents (ST/SG/AC.10/C.3/2004/96, ST/SG/AC.10/C.3/2005/13, ST/SG/AC.10/C.3/2005/43 and ST/SG/AC.10/C.3/2005/44) regarding state of charge (SOC) limit to lithium-ion cells and batteries during transportation. These documents demonstrated that lithium-ion cells and batteries are safer when they are at lower state of charge (SOC).

2. Lithium-ion cells and batteries have many advantages, such as high voltage platform, good cycle life, high energy density, significant cost reduction and so on. They have been industrialized in more and more fields such as consumer electronic equipment, transportation vehicles (electric vehicles) and energy storage. While the scale of lithium-ion cells and batteries industry is expanding rapidly and the transportation volume of lithium-ion cells and batteries is also increasing day by day, the safety of lithium-ion cells and batteries during transportation is also attracting wide attention around the world.

3. The safety risk grade of lithium-ion cells and batteries during transportation is mainly related to their thermal stability. The main factors affecting thermal stability of lithium-ion cells and batteries are chemical system and state of charge (SOC). A lot of research results show that for same lithium-ion cells and batteries, the thermal stability of lithium-ion cells and batteries becomes worse as the state of charge (SOC) increases. That means, with the increase of the state of charge (SOC) of lithium-ion cells and batteries, the safety risks in transportation also increases. When some NCM lithium-ion cells and batteries are in high state of charge (60 % SOC), triggering their thermal runaway could cause fire. These substances usually consist of organic molecules, which are building blocks, intermediates, or active ingredients for pharmaceutical or agricultural chemicals. Although not designed to be

* In accordance with the programme of work of the Sub-Committee for 2019–2020 approved by the Committee at its ninth session (see ST/SG/AC.10/C.3/108, paragraph 141 and ST/SG/AC.10/46, paragraph 14).

explosives of Class 1, many of these substances carry functional groups listed in tables A6.1 and/or A6.3 in Annex 6 (screening procedures) of the Manual of Tests and Criteria, indicating potential explosive or self-reactive properties.

4. The International Civil Aviation Organization (ICAO) TI has clearly stipulated that the state of charge (SOC) of UN 3480 lithium-ion cells and batteries during transportation should not exceed 30 %. Apart from air transport, there is no uniform regulation on the state of charge (SOC) of lithium-ion cells and batteries in other transport methods. As a result, companies use different state of charge (SOC) when lithium-ion cells and batteries are transported by land or waterway, leading to uncontrollable safety risk. Excessive state of charge (SOC) will increase the safety risk of transporting lithium-ion cells and batteries, but insufficient state of charge (SOC) of lithium-ion cells and batteries during transportation or storage can cause risk of excessive discharge of lithium-ion cells and batteries from their normal self-discharge, thus affecting the normal usage of lithium-ion cells and batteries. Therefore, it is necessary to specify reasonable state of charge (SOC) of lithium-ion batteries, especially lithium-ion cells and batteries with large capacity in "Recommendation on the transport of dangerous goods model regulation".

Analysis and verification

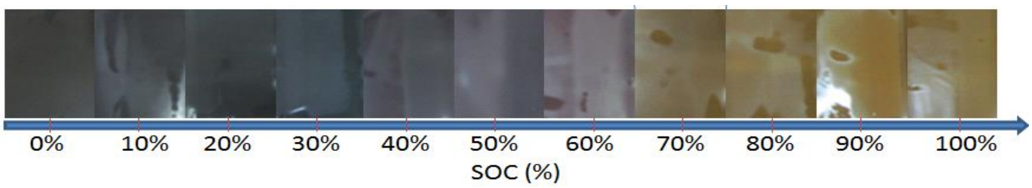
5. According to the cathode materials used, the present mainstream lithium ion batteries include lithium iron phosphate (LFP), nickel cobalt manganese oxide (NCM), nickel cobalt aluminum oxide (NCA) and lithium cobalt oxide (LCO). LFP batteries will only smoke in most thermal runaway scenarios regardless of the state of charge (SOC), since LFP batteries has the good thermal stability. While NCM/NCA batteries as well as LCO battery behave quite differently under thermal runaway when they are in different state of charge (SOC). Below analysis and verification are based on the NCM batteries which battery type is most popular in the future. An overview of the current classification criteria is shown in Figure 1. For reasons of simplification, special cases such as pyrotechnics, articles and ammonium nitrate emulsions, suspensions or gels (ANEs) are summarized as "intentional explosives" and not discussed in this document since they are not relevant for the context.

Materials analysis

6. On material level, the thermal stability of lithium ion battery is mainly characterized by the lithium ion intercalation state and heat generation.

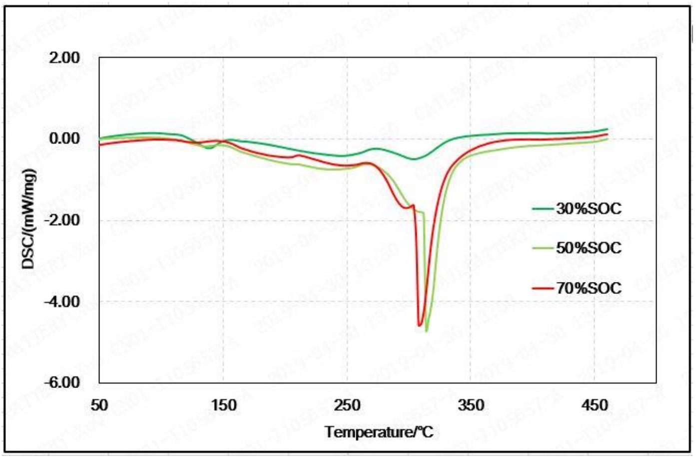
(a) The lithium ion intercalation state in anode material is dependent on the state of charge (SOC) for the same battery. As shown in Figure 1, more lithium ion intercalates into the anode material as the state of charge (SOC) increases, leading to poor thermal stability.

Figure I: Effect of state of charge (SOC) on lithium ion intercalation state



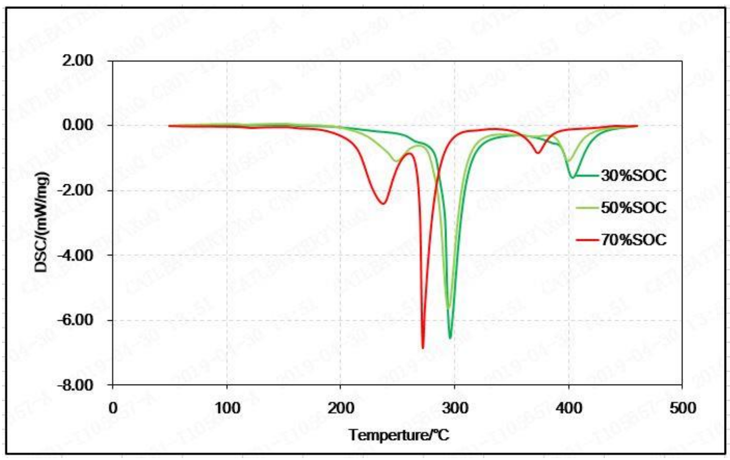
(b) The heat generation is dependent on the state of charge (SOC) for the same battery. Differential scanning calorimetry is used to investigate the NCM cathode and graphite anode materials at different state of charge (SOC), and the results showed that: lithium ion cells and batteries at 30 % SOC have good thermal stability, the anode material generates much less heat than that at 50 % to 70 % SOC, and the temperature for cathode exothermic reaction is much higher than that at 50 % to 70 % SOC.

Figure II: The heat generation of anode materials with different state of charge (SOC)



7. As shown in Figure 2, for the battery at 50 % to 70 % SOC, severe exothermic reaction happens with a lot of heat generated when heating the anode material at 300 ℃. While no obvious exothermic reaction happens at 300 ℃ for the anode at 30 % SOC.

Figure III: The temperature of exothermic reaction of cathode materials with different state of charge (SOC)



8. As shown in Figure 3, for the lithium ion battery anode material at 70 % SOC, severe exothermic reaction happens with a lot of heat generated when heating the anode material at 240 ℃. For the anode at 30 % SOC, the exothermic reaction happens at nearly 300 ℃, which is higher, and the generated heat is less compared with that for the anode at 70 % SOC.

Thermal runaway test of NCM battery

9. The NCM cell with different state of charge (SOC) are triggered to thermal runaway by heating, and the thermal behaviors under each condition are observed to evaluate the safety.

As listed in Table 1, 51 Ah NCM cell with different state of charge (SOC) are triggered to thermal runaway by heating, and the results are quite different.

(a) State of charge (SOC) 10 % to 30 %: mild reaction, while smoke only, no sparks and no fire;

(b) State of charge (SOC) 40 %: a lot of white smoke mixed with black smoke, no sparks and no fire;

(c) State of charge (SOC) 50 %: a lot of white smoke mixed with sparks, no fire;

(d) State of charge (SOC) 60 % to 100 %: fire;

(e) Test detail is shown in Annex I.

Thermal runaway test of LFP battery

10. The LFP battery with 100 % SOC is triggered to thermal runaway by heating, and only some white smoke could be observed (see Annex II).

11. The technical report (EVS 1541-616) in the revision of the global technical regulation UN GTR No. 20 mentioned that more than 200 different LFP cells were triggered to thermal runaway by heating or overcharging, and no fire occurred.

Self-discharge character

12. The self-discharge rate of lithium ion cells and batteries with 30 % SOC at 25 ℃ ambient temperature conditions is usually not faster than 2 % per month (similar conclusions can be found in ICAO document DGP-WG/15-IP/1 in 2015). Severe environmental conditions could accelerate the self-discharge rate, however it could not exceed 3 % per month even at 45 ℃ conditions. Therefore, the lithium ion cells and batteries with 30 % SOC could afford transportation and storage for as long as 10 months even at harsh transportation conditions. However, the transportation of lithium ion cells and batteries usually takes less than three months.

13. Through the analysis of various aspects of lithium-ion cells and batteries Chinese manufacturers, application manufacturers, and dealers, we can get the electric energy consumption detail list, see Annex III.

14. According to preliminary statistics for Chinese lithium ion battery manufacture, lithium-ion cells larger than 500 g or lithium-ion batteries larger than 12 kg are basically transported with 30 % SOC in international transportation (including shipping, aircraft and road transportation).

Conclusion

15. Material mechanism analysis and verification results show that the safety of lithium-ion cells and batteries has a strong correlation with their state of charge (SOC). The higher the state of charge (SOC) is, the worse the thermal stability and safety of lithium-ion batteries are.

16. Material mechanism analysis and verification results show that the thermal stability and safety of lithium-ion cells and batteries are fairly good when SOC is 30 %.

Proposal

17. Proposal 1: Add a special provision for UN 3480 in chapter 3.2 of the Model Regulation:

SP xxx.

18. Proposal 2: Add a special provision to Chapter 3.3 of the Model Regulation:

xxx The state of charge (SOC) of unused lithium-ion cells and batteries during transportation shall not exceed 30 % of their rated capacity when they meet the following conditions.

(a) Large lithium-ion cell with total mass of more than 500 g;

(b) Large lithium-ion battery with total mass of more than 12 kg or battery consisting of large lithium-ion cell which is heavier than 500 g.

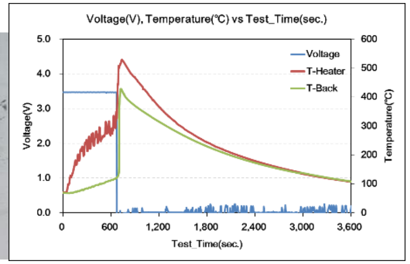
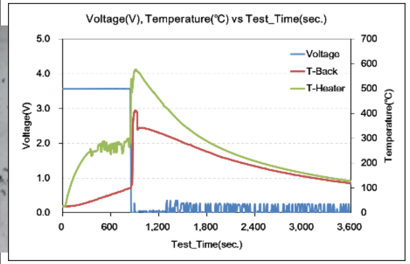
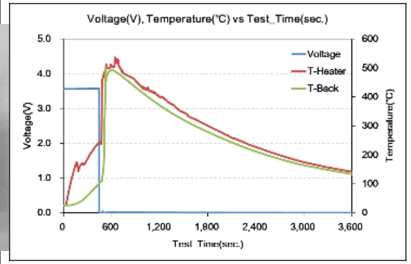
19. Proposal 3: Add the definition of state of charge (SOC) in Chapter 38.3.2.3 of the Manual of Tests and Criteria as follow:

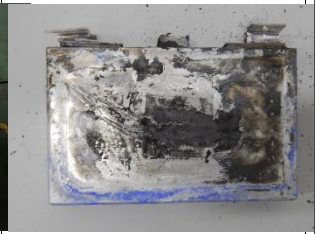
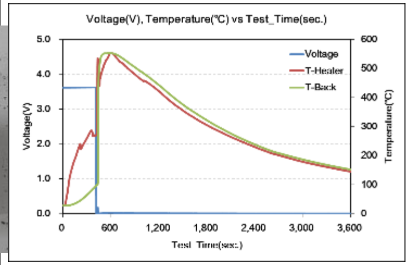
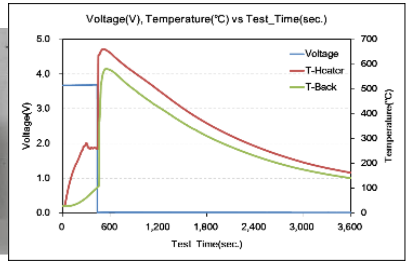
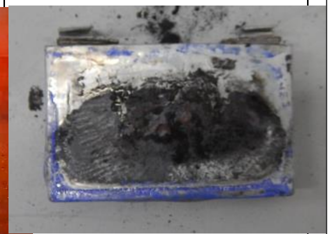
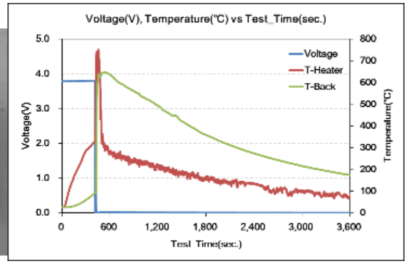
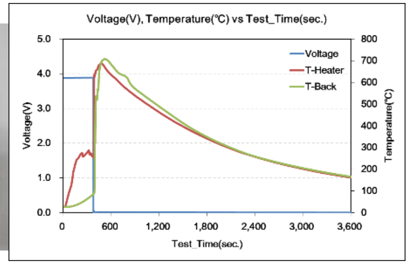
State of Charge (SOC):

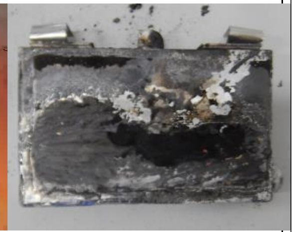
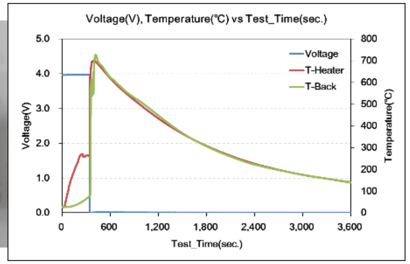
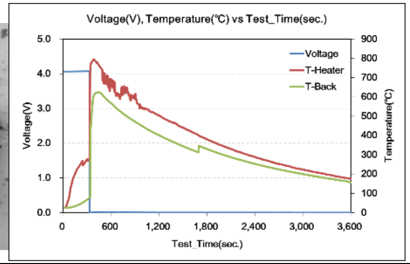
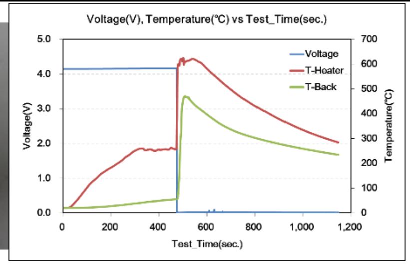
Refers to the available capacity of a battery or cell, usually expressed as a percentage of the rated capacity of the battery and cell. (Refer to ST/SG/AC.10/C.3/2004/96 and ISO 6469-1:2019).

Annex I

Thermal runaway test results of the NCM batteries with different state of charge (SOC) by heating

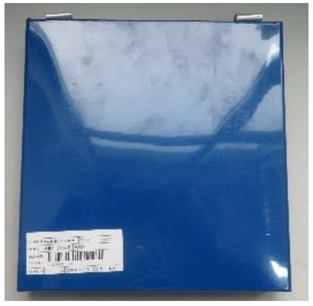
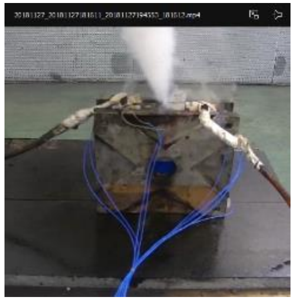
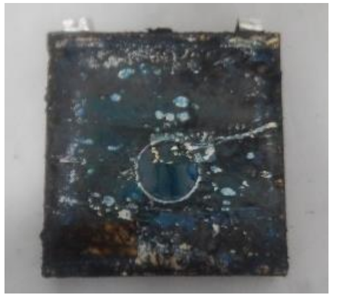
No.	State of charge (SOC)	Photo before triggering	Photo of thermal runaway	Photo after triggering	Voltage and temperature curve	Test result
1	10%					White smoke, no sparks and no fire;
2	20%					White smoke, no sparks and no fire;
3	30%					White smoke, no sparks and no fire;

4	40%					A lot of white smoke mixed with black smoke
5	50%					A lot of white smoke mixed with sparks
6	60%					Fire
7	70%					Fire

8	80%					Fire
9	90%					Fire
10	100%					Fire

Annex II

Thermal runaway test result of the LFP battery triggered by heating

No.	State of charge (SOC)	Photo before triggering	Photo of thermal runaway	Photo after triggering	Test result
1	100%				White smoke, no sparks and no fire;

Annex III

The electric energy consumption detail list of lithium ion batteries transportation and application

No.	Process	Start	Ending	Condition	Estimated consumption SOC
1	Batteries storage and transportation	Lithium-ion batteries manufacturers	Application manufacturers	International transportation: 60 days, 45℃	6%
2	Batteries storage and assembly equipments	Application manufacturers	Application manufacturers	45 days	3%
3	Application Testing	Application manufacturers	Application manufacturers	Function test	6%
4	Application storage and transport to Dealers	Application manufacturers	Dealers	90 days	9%
5	Dealers storage	Dealers	Dealers	-	6%
6	Total				30%

References

i. DGP-WG/15-IP11 IP/1: Dangerous goods panel (DGP) working group meeting (DGP-WP/15), Montreal, 27 April to 1 May 2015. *Implications of adopting a state of charge (Presented by PRBA – The Rechargeable Battery Association)* <https://www.icao.int/safety/DangerousGoods/DGPWG15/DGPWG.15.IP.001.5.en.pdf>

ii. ST/SG/AC.10/C.3/2004/96: Sub-Committee of Experts on the Transport of Dangerous Goods, Twenty-sixth session, 29 November-3 December 2004. *Changes to Special Provision 188 for Lithium Batteries and UN Manual of Tests and Criteria, Transmitted by the Portable Rechargeable Battery Association (PRBA).* <http://www.unece.org/fileadmin/DAM/trans/doc/2004/ac10c3/ST-SG-AC10-C3-2004-96e.pdf>

iii. EVS1541-616 [CHN] Thermal propagation research update, fifteenth session, 21st-23rd March. https://wiki.unece.org/display/trans/EVS+15th+session

iv. ISO 6469-2019: Electrically propelled road vehicles -- Safety specifications -- Part 1: Rechargeable energy storage system (RESS)