



**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****Fifty-fifth session**

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Item 4 (e) of the provisional agenda

Electric storage systems:sodium-ion batteries**Sodium-ion batteries – additional information****Transmitted by the expert from the United Kingdom*****Introduction**

1. At the fifty-third, fifty-second, fiftieth and forty-eighth sessions of the Sub-Committee the United Kingdom presented a number of documents (ST/SG/AC.10/C.3/2018/3, informal documents INF.11 (fifty-second session), INF.13 (fiftieth session) and INF.6 (forty-eighth session) regarding sodium-ion batteries. These documents:

- (a) Provided a background to sodium-ion battery technology;
- (b) Explained the differences in comparison to lithium-ion battery technology;
- (c) Explained the similarities between a shorted sodium-ion battery and a super capacitor (Capacitor, electric double layer UN 3499); and
- (d) Discussed the options for how they might be addressed in the Model Regulations.

2. These documents demonstrated that cells and batteries based on sodium-ion technology which are shorted or discharged pose no safety concern to people, property or the environment during carriage. Nevertheless, such cells and batteries may be wrongly assumed to be hazardous by people in the transport chain.

* 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).

Background

3. Whilst there was support in principle for the proposal in ST/SG/AC.10/C.3/2018/3, as noted in paragraph 76 the report ST/SG/AC.10/C.3/106, it was felt more information regarding the properties of sodium-ion batteries was needed before the proposal could be accepted. Specifically, information regarding:

- (a) The size of the batteries;
- (b) Their composition (e.g. amount of electrolyte) and similarities to lithium-ion ultracapacitors;
- (c) Their behaviour when discharged (e.g. full absence of electrical risk during normal conditions of transport);
- (d) Potential measures to prevent accidental activation i.e. how can it be guaranteed that the battery remains shorted during transport?;
- (e) Potential issues if damaged or disabled.

4. The United Kingdom would like to provide the following information in response to points (a) to (e) above:

- (a) The size of batteries range depending on their intended purpose. The United Kingdom has seen various models with sizes ranging from 100 mm x 50 mm x 15 mm (approximate) up to similar dimensions as a large car battery. A sodium-ion battery can be built in any size a lithium-ion battery can be. There is no sodium metal in a sodium-ion battery. It is present as a salt. The current classification system does not address this particular aspect of sodium-ion batteries.

The existing entry for batteries containing sodium (UN 3292) and special provision 239 are relevant to cell chemistries such as sodium sulphur and sodium metal chloride which contain metallic sodium, but do not recognise the lesser risk posed by sodium-ion cell chemistry. This situation is akin to that of lithium batteries (UN 3090) prior to the Sub-Committee's decision to recognise lithium-ion cells and batteries as being substantially different from lithium metal types. Like their lithium counterparts, sodium-ion cells contain sodium salts, NOT sodium metal.

- (b) The United Kingdom recognises that it was not made sufficiently clear in earlier documents that the electrolytes and the electrolyte solvents found in a sodium-ion cell will also be very similar to those in a lithium-ion ultracapacitor, i.e. the electrolyte salt is likely to be LiPF₆ or NaPF₆ (respectively) and the solvents will be organic carbonates. There are, however, two important additional safety features that the sodium-ion battery has over the lithium-ion ultracapacitor. In the former, the salt NaPF₆ is kinetically more stable than the lithium equivalent and in the former the high boiling-point, high flash-point of propylene carbonate (PC) can be used as a solvent. This means that the battery will need to be exposed to a higher temperature before the electrolyte solvent will boil and cause a release of gas. Furthermore, the temperature at which a spark could ignite the solvent is much higher.

This is not possible in a lithium-ion ultracapacitor because PC will react with the lithiated graphite cathode. Kuze et al. report (see footnote for reference)¹ that the sodium-ion electrolyte NaPF₆ in PC, in combination with a hard carbon anode, releases energy at a temperature 90°C above that of the lithium-ion electrolyte, LiPF₆ in EC-DMC with a graphite anode. This data again means that decomposition of the electrolyte in a sodium-ion cell takes place at a significantly higher temperature than in the lithium-ion cell equivalent leading to enhanced safety. This data is very relevant to the differences in stability of a sodium-ion battery and a lithium-ion ultracapacitor.

- (c) When discharged there is no voltage and no stored electrochemical energy. The object is NOT a battery under those conditions and there is no electrical hazard. Shorting the cells guarantees that this absence of any electrical energy will persist throughout the transport.

The key operational difference between sodium-ion and lithium technology is that sodium-ion technology can be discharged to 0 volts, without affecting the performance of the cell. Therefore, batteries using sodium-ion technology can be stored and transported in a completely discharged state, with terminals shorted if required. In this state they pose no risk from stored electro-chemical energy.

The only residual hazard comes from the flammability of the very small levels of electrolyte contained within the cells, a hazard which is equivalent to the hazard in an ultracapacitor.

- (d) Whilst it is preferable to ensure that the short stays in place during transport, since this provides evidence that it was originally shorted, there is no safety reason to guarantee this. If a short has been professionally connected across the electrodes then any subsequent damage to the short will NOT give rise to activation unless the cell is connected to a battery charger, which is something that cannot happen accidentally. Whilst in theory miniscule currents could flow if the short is removed and the cell is left to its own devices, the level of such current will not be material.
- (e) This will depend largely on the type of damage or defect. Since we are only considering sodium-ion cells/batteries which are shorted, there will be no release of electrochemical energy and the principal hazards will be those associated with the electrolyte, which could leak from a damaged or defective cell or battery and represent a potential fire hazard (very similar to that which would be associated with an ultracapacitor).

However, this hazard is still significantly smaller than it would be in a discharged lithium-ion battery (Note - A lithium-ion battery can't be shorted and maintained at zero volts without causing damage to the battery itself). Sodium-ion cells use the high boiling point (of 242°C) and high flash point (of 116°C) solvent propylene carbonate (PC) as a major component of its electrolyte. This is not possible in lithium-ion cells because PC reacts with the anode in lithium-ion cells.

5. This document contains the same proposal as found in ST/SG/AC.10/C.3/2018/3, to introduce a special provision to UN 3292 BATTERIES, CONTAINING SODIUM which

¹ Sumitomo Chemical Co., Ltd. Tsukuba Material Development Laboratory Satoru KUZE Jun-ichi KAGEURA Shingo MATSUMOTO Tetsuri NAKAYAMA Masami MAKIDERA*1 Maiko SAKA Takitaro YAMAGUCHI Taketsugu YAMAMOTO*2 Kenji NAKANE*3 "SUMITOMO KAGAKU", vol. 2013.

permits shorted or discharged sodium ion batteries or cells from full regulation, subject to meeting certain requirements. The United Kingdom hopes that, having provided the requested additional information, the Sub-Committee will find the proposal acceptable.

Proposal

6. For UN No. 3292, insert a new special provision “XXX” in Column (6) of the Dangerous Goods List in Chapter 3.2.

7. Add a new special provision “XXX” in Chapter 3.3 as follows:

“XXX Sodium-ion cells and batteries offered for transport either loose or installed in equipment are not subject to other provisions of these Regulations if they meet the following:

- (a) Cells and batteries are transported in a shorted or discharged state; and
- (b) Cells, batteries and equipment containing cells and/or batteries are packed in packaging that meets the general provisions of 4.1.1.1 and 4.1.1.2. Large robust batteries may be transported on pallets or in suitable handling devices.”

Justification

8. The proposal made below solely addresses sodium-ion cells and batteries that are **shorted** or **discharged**. The ease with which these batteries can be shorted and the resultant minimising of any risk during transport means that this is the condition in which most commercial consignments will be transported. The inclusion of this proposal in the next revised edition of the Model Regulations would be timely for this emerging technology.

Annex

Additional background information

Key points

1. The key operational difference between sodium-ion and lithium technology is that sodium-ion technology can be discharged to 0 volts, without affecting the performance of the cell.
2. Batteries using sodium-ion technology can therefore be stored and transported in a completely discharged state, with terminals shorted if required. In this state they pose no risk from stored electro-chemical energy and it could be argued that they cease to be batteries at all.

Similarities and differences between a shorted sodium ion battery and symmetric and asymmetric supercapacitors

3. Comparisons are now made between a shorted sodium-ion battery and supercapacitors, because the safety features of these devices are strongly comparable.
4. From a transport perspective, the inherent electrical hazard in an energy storage device is best quantified by the electrical energy density. The table below provides a comparison of the electrical energy density of shorted sodium-ion batteries with other energy storage devices.
5. The amount of heat that may be generated accidentally inside a casing through an unintended short circuit is much lower for asymmetric capacitors compared to other high energy devices such as lithium ion batteries, which is why they can be transported under less stringent conditions of carriage. An electrical double layer capacitor can be shorted and shipped at zero volts. A lithium-ion asymmetric supercapacitor cannot be shorted but nonetheless the electrical energy density it contains is still an order of magnitude less than that of a lithium-ion battery.

The voltages and electrical energy densities of certain energy storage devices:

	<i>Shorted sodium-ion battery</i>	<i>Shorted electrical double layer capacitor</i>	<i>Electrical double layer capacitor</i>	<i>Lithium-ion asymmetric supercapacitor</i>	<i>Lithium-ion battery</i>
<i>Operating voltage</i>			2.7-0.4	3.8-2.2	2-2.75
<i>Electrical Energy Density Wh/l</i>	0	0	4-15	10-50	150-600

6. The electrical energy density held by a shorted sodium-ion battery is zero, less than that of an asymmetric capacitor (see UN 3508). Thus, from the point of view of the inherent electrical hazard, the shorted sodium ion battery is akin to a shorted electrical double layer capacitor (see UN 3499).