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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 (b) of the provisional agenda
Electric storage systems: lithium-ion capacitors

New proper shipping name for asymmetric capacitors

Transmitted by the expert from Japan[1]

Introduction

1. The Sub-Committee, at its thirty-ninth session, considered working document ST/SG/AC.10/C3/2011/14 submitted by the expert from Japan proposing to establish a new proper shipping name for asymmetric capacitors. A number of questions and comments were provided regarding the conditions of shipping capacitors in a charged state and Japan was asked to clarify the hazards and appropriate transport conditions, recognizing that these capacitors must be transported in a charged state. Since the 39th session, Japan has been in discussion with KiloFarad International (KFI) and others with a specific interest in asymmetric capacitor shipping requirements. The proposal contained in this document was prepared based on the previous proposal in ST/SG/AC.10/C3/2011/14 and also reflects the results of those discussions.

I. Background information on asymmetric capacitors

A. Definition of asymmetric capacitors

2. Detailed descriptions of asymmetric capacitors were provided in the previous document ST/SG/AC.10/C.3/2011/14. An asymmetric capacitor is an electrochemical capacitor with the positive and negative electrodes comprised of different active materials

[1] In accordance with the programme of work of the Sub-Committee for 2011-2012 approved by the Committee at its fifth session (refer to ST/SG/AC.10/C.3/76, para. 116 and ST/SG/AC.10/38, para. 16).

where charge and discharge are accomplished through different electrochemical processes. There are a limited number of asymmetric capacitor types currently available. One common type known as a lithium ion capacitor (LIC) is discussed below.

B. LIC

3. LIC is an asymmetric capacitor which can store electric energy by adsorption and desorption of ions at the interface of the positive electrode material and electrolyte, and by intercalation and deintercalation of lithium ions at the negative electrode. The positive electrode is similar to that of an electric double layer capacitor (EDLC) and is comprised of carbon materials with a large surface area such as activated carbon, and the negative electrode is comprised of carbonaceous materials which permit intercalation and deintercalation of lithium ions. $Li_4Ti_5O_{12}$/carbon composite may also be used for the negative electrode. The electrolyte used in LIC is an organic lithium ion salt solution.

C. Features of asymmetric capacitors

4. While asymmetric capacitors generally possess higher energy density (up to 4 times) than EDLCs, the energy density is still low in comparison to batteries.

5. Asymmetric capacitors have lower voltage limits, below which, the capacitors are damaged and lose their function. For example, lower voltage limits of LICs typically range from 1.4V to 2.2V. Therefore, it is not possible to lower the terminal voltage to 0V without adversely affecting the asymmetric capacitor and it cannot be transported in a completely uncharged state as is the case with EDLCs.

6. Asymmetric capacitors with different energy levels have been commercialized as laminate or cylindrical capacitors. Asymmetric capacitors are often configured in modules, which are assemblies of two or more capacitors, electrically connected to each other with or without additional electronics.

II. Possible risks in transport of asymmetric capacitors

7. The following two potential transport risks are posed by asymmetric capacitors.

(a) Electrical risk due to transport in a charged state:

Considering that asymmetric capacitors must be transported in a charged state, the electrical hazard should be taken into account. Without precautions, there is the potential of accidental short circuit in transport. Therefore, asymmetric capacitors should be protected against short circuit.

The safety of asymmetric capacitors, including LICs, is markedly different from that of lithium ion batteries. In lithium ion batteries, lithium metal oxides such as LiCoO2, LiMn2O4, or LiNiO2 are used in the positive electrode. Free oxygen may be generated by the thermal decomposition of these oxides upon heating over 200ºC. Thermal decomposition in batteries is accelerated by the reduction of lithium ion from lithium metal oxides in the charged state. This phenomenon may lead to an uncontrolled exothermic reaction, potentially resulting in venting of gases, fire or explosion.

LICs contain no metal oxides in the positive electrode and instead use carbon materials for the positive electrode. Thus an uncontrolled exothermic reaction due to generation of free oxygen by decomposition of lithium metal oxides does not occur.

From a transport perspective, the inherent electrical hazard in energy storage devices is best quantified by energy density. The following table provides a comparison of asymmetric capacitors with other energy storage devices.

	Asymmetric Capacitor	*Electric Double Layer Capacitor*	*Lithium Ion Battery*	*Pb-acid Battery*
Operating Voltage [V]	3.8-2.2	2.7-0	4.2-2.75	2.35-1.75
Energy Density [Wh/L]	10-50	4-15	150-600	60-100

The energy density held by asymmetric capacitors is considerably less than lithium ion battery and less than nonspillable lead acid batteries. Therefore, 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. While capacitors possess higher power density, the total energy is directly related to the amount of heat that may be generated inside a casing.

Dry batteries including alkali-manganese (390Wh/L), zinc-carbon (195Wh/L), and nickel-cadmium (146Wh/L) batteries are not subject to the model regulations provided that they are protected against short circuit. Considering the level of regulations for other electric storage devices, Japan considers that the electrical hazard for asymmetric capacitors can be properly treated by protecting against short circuit during transport.

To demonstrate the safety of asymmetric capacitors upon accidental short circuit, external short circuit test results are shown in Table 1 and Fig.1 in the Annex. The capacitor in the fully charged state was subjected to a short circuit condition at ambient temperature with a total external resistance of 3m ohm for one hour. The maximum temperature of the capacitor was 76 ºC by heat generation due to energy release. The capacitor showed a small degree of swelling, but no significant change was observed. Noting that the required resistance for lithium battery testing under 38.3.4.5.2 of UN Manual of Tests and Criteria is less than 0.1 ohm (or 100 m ohm), the short circuit test carried out on the asymmetric capacitors is considered substantially more severe.

(b) Chemical hazard due to the use of electrolyte solutions:

Asymmetric capacitors may contain an electrolyte meeting the criteria of a class or division of dangerous goods. Electrolyte solutions in LICs typically consist of lithium salts, such as LiPF6, LiBF4 in an organic solvent, which may meet the criteria for a flammable liquid. Diethyl carbonate (flash point 25°C) and ethyl methyl carbonate (flash point 24°C) are two example solvents. The electrolyte solution is absorbed onto cell constituents such as carbon materials, other cell materials and separators. Similar to EDLCs, asymmetric devices normally include small amounts of free liquid electrolyte solution to ensure complete wetting of the electrode materials.

The integrity of capacitors containing dangerous goods should be ensured. Capacitors which contain any class or divisions of dangerous goods should be required to withstand a 95kPa pressure differential to confirm the robustness of capacitor casing.

The amount of flammable liquid in LICs with a Watt-hour rating of up to 20Wh is below 0.5 litre and the amount of free liquid is about 5 ml - approximately the same amount as in an EDLC of 10Wh. On this basis, it is proposed that asymmetric capacitors containing flammable liquids with an energy storage capacity of 20Wh or less should be transported without applying other Regulations when they are capable of withstanding a 1.2 metre drop test unpackaged and can withstand a 95kPa pressure differential test. These tests are the same as those for EDLCs.

Examples of safety test results for 95kPa pressure differential and 1.2m drop test are shown in Table 2 and Fig.2; and Table 3 and Fig.3 in the Annex, respectively.

8. For asymmetric capacitors, energy storage capacity means the usable energy stored in a capacitor, as calculated according to the following equation, Wh= $1/2C_N(U_R^2-U_L^2)\times(1/3600)$, using the nominal capacitance(C_N), rated voltage(U_R) and rated lower limit voltage(U_L).

9. Examples of LICs with different energy storage levels are shown in Table 4 in the Annex. Considering energy levels of existing primary batteries such as 1.35Wh for the AAA and 3Wh for the AA alkaline manganese battery, Japan considers the risks associated with transporting asymmetric capacitors with 0.3Wh or less to be considerably lower than those batteries. Therefore, it is reasonable for asymmetric capacitors with 0.3Wh or less to be permitted to be transported without being subject to these Regulations.

10. Nickel-Carbon capacitors are asymmetric capacitors in which charge and discharge can be repeated by (K+ ions) adsorption at the double layer of the negative electrode, and by electrochemical reaction at the nickel hydroxide positive electrode (NiO(OH) + H2O +e- = Ni(OH)2 + OH-). The electrolyte used is an alkaline electrolyte similar to that used in alkaline batteries.

11. These devices contain considerable free liquid and are not hermetically sealed to avoid a failure due to a pressure increase by gas generation inside the devices. Since the structure of these devices is quite different from capacitors such as EDLCs and LICs in which the electrolytes are nearly completely absorbed by solid substances to keep free liquid to a minimum, it is recommended that Ni-Carbon capacitors should be transported under UN2795; Batteries, Wet, Filled with Alkali; Class 8 which is now applied to these devices.

III. Proposal

12. The following provisions are proposed for transport of asymmetric capacitors. A new entry table would read as follows:

(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*
3XXX	ASYMMETRIC CAPACITOR (with an energy storage capacity greater than 0.3Wh)	9			AAA	0	E0	P003		

The accompanying special provision AAA would read:

"AAA This entry applies to asymmetric capacitors with an energy storage capacity greater than 0.3 Wh. Capacitors with an energy storage capacity of 0.3 Wh or less are not subject to these Regulations.

Energy storage capacity means the energy stored in a capacitor, as calculated according to the following equation, Wh= $1/2C_N(U_R^2\text{-}U_L^2)\times(1/3600)$, using the nominal capacitance(C_N), rated voltage(U_R) and rated lower limit voltage(U_L).

All asymmetric capacitors to which this entry applies shall meet the following conditions:

(a) Capacitors or modules shall be protected against short circuit in transport;

(b) Capacitors shall be designed and constructed to safely relieve pressure that may build up in use, through a vent or a weak point in the capacitor casing. Any liquid which is released upon venting shall be contained by the packaging or by equipment in which a capacitor is installed;

(c) Capacitors shall be marked with the energy storage capacity in Wh; and

(d) Capacitors containing an electrolyte meeting the classification criteria of any class or division of dangerous goods shall be designed to withstand a 95kPa pressure differential;

Capacitors containing an electrolyte not meeting the classification criteria of any class or division of dangerous goods, including when configured in a module or when installed in equipment, are not subject to other provisions of these Regulations when the capacitors meet the conditions (a) to (d).

Capacitors containing an electrolyte meeting the classification criteria of any class or division of dangerous goods, with an energy storage capacity of 20Wh or less, including when configured in a module, are not subject to other provisions of these Regulations when the capacitors meet the conditions (a) to (d) and are capable of withstanding a 1.2 metre drop test unpackaged on an unyielding surface without loss of contents.

Capacitors containing an electrolyte meeting the classification criteria of any class or division of dangerous goods that are not installed in equipment and with an energy storage capacity of more than 20Wh are subject to these Regulations.

Capacitors installed in equipment and containing an electrolyte meeting the classification criteria of any class or division of dangerous goods, are not subject to other provisions of these Regulations provided that the capacitors meet the conditions (a) to (d) and the equipment is packaged in a strong outer packaging constructed of suitable material, and of adequate strength and design, in relation to the packaging's intended use and in such a manner as to prevent accidental functioning of capacitors during transport. Large robust equipment containing capacitors may be offered for transport unpackaged or on pallets when capacitors are afforded equivalent protection by the equipment in which they are contained.

Note: Electric double layer capacitors do not belong to this entry. Nickel-Carbon capacitors are subject to these Regulations as UN2795 Batteries, wet, filled with alkali.".

* * *

Annex

(English only)

I. Safety test results of asymmetric capacitors

External short circuit test

Table 1. External short circuit test results

External short circuit test	***Sample***	***Results***
Total external resistance: 3m ohm Short circuit Duration: 1h Observation: 6 h Ambient temp.20±5ºC	LIC 2200F Fully charged state (3.8V)	No disassemble No rupture No fire Max. cell temperature 76 ºC

Fig. 1(1)
Before test

Fig. 1(2)
After test

Altitude simulation (low pressure test)

Table 2. Altitude simulation (low pressure test) results

Altitude simulation	***Sample***	***Results***
Stored in Δ95kPa pressure differential for 6h at ambient temperature	LIC 1100F Fully charged state (3.8V)	No leakage No disassemble No rupture No fire

Fig. 2(1)
Before test

Fig. 2(2)
After test

Drop test

Table 3. Drop test results

Drop test	***Sample***	***Results***
1.2m drop test unpackaged	LIC 1100F Fully charged state (3.8V)	No leakage No disassemble No rupture No fire

Fig.3 (1)

Before test

Fig.3 (2)

After test (1)

Fig.3 (3)

After test (2)

Drop direction

II. Energy storage levels of asymmetric capacitors

Table 4. Energy storage levels of asymmetric capacitors (example)

Voltage （Max./Min） [V]	Capacitance [F]	Energy [Wh]	Type	Size (mm)	Appearance
3.3/1.5	0.25	0.0003	Coin	φ6.8×1.6	
3.8/2.2	40	0.05	Cylinder （lead terminal）	φ12.5×35	
3.8/2.2	100	0.13	Cylinder （lead terminal）	φ18×40	
3.8/2.2	200	0.27	Cylinder （lead terminal）	φ25×40	
3.8//2.2	1000	1.33	Cylinder	φ40×110	
3.8/2.2	1100	1.47	Laminate	138×106×4.5	
3.8/2.2	2200	2.94	Laminate	138×106×8.5