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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

Thirty-ninth session
Geneva, 20–24 June 2011
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-eighth session, considered informal document INF.10 submitted by the expert from Japan proposing to establish a new proper shipping name for lithium ion capacitors and agreed to include the new work programme related thereto. The proposal contained in this document was prepared base on the previous proposal in informal document INF.10, taking into account comments provided in informal document INF.33 submitted by the expert from France at the said session and those received intersessionally from the representative of the KiloFarad International.

2. Asymmetric capacitors have been developed and commercialized recently and its demand is spreading rapidly for applications to effectively utilize renewable energy, energy recovery systems and so on. As a result of this increasing demand, a new proper shipping name and specific provisions for transport of asymmetric capacitors are needed.

Background information on asymmetric capacitors

Definition and working principle of asymmetric capacitors

[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).

3. An asymmetric capacitor is an electrochemical capacitor in which the positive electrode and the negative electrode are comprised of different active materials and charge and discharge can be repeated by different mechanisms at the positive and negative electrode. Typical asymmetric capacitors, such as lithium ion capacitors (LICs) and Ni-Carbon capacitors (Ni-C capacitors) are discussed below.

LIC

4. A LIC cell is mainly comprised of a positive electrode, a negative electrode, a separator and an electrolyte. (Fig.1)

5. LIC is an asymmetric capacitor which can store the electrical 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 and so on which permit intercalation and deintercalation of lithium ions. Li4Ti5O12/carbon composite may be used for the negative electrode. The electrolyte used in LIC is a lithium ion salt organic solution. (Fig.2)

6. The intercalation of lithium lowers the negative electrode potential, which raises a cell output voltage. LIC can store larger amounts of energy than EDLCs due to the large capacity of the negative electrode compared to that of the positive electrode. (Fig.3)

7. LIC shows higher working voltage and higher energy density with similar power density compared to EDLC. (Fig4) As shown in the discharge curve (Fig.5), the voltage of LIC changes with charge stored, which is a typical characteristic of capacitors. LIC shows excellent cycle durability the same as EDLC.

Ni-C Capacitors

8. Ni-C 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 ($NiO(OH) + H_2O + e^- = Ni(OH)_2 + OH^-$) .

9. For Ni-C capacitors, the positive electrode is comprised of Nickel based materials similar to those used in alkaline batteries, and the negative electrode is comprised of carbon materials. The electrolyte used in Ni-C capacitors is an alkaline electrolyte similar to that used in alkaline batteries.

10. Asymmetric capacitors have lower voltage limits, below which, the cells are damaged and lose their function. For example, lower voltage limits of LICs typically range from 1.4V to 2.2V while lower voltage limits for Ni-C capacitors typically range from 0.4V to 0.6V. Therefore, for asymmetric capacitors it is not possible to lower the terminal voltage to 0V without adversely affecting the capacitor and for this reason it is not possible to transport them in a completely uncharged state as is the case with EDLCs.

Application of asymmetric capacitors

11. Asymmetric capacitors with different energy levels have been commercialized as laminated or cylindrical cells. (Fig.6) Like EDLCs, asymmetric capacitors are often used in modules, which comprise cells connected in series and/or parallel to obtain proper voltage and energy necessary for the specific application. (Fig.7)

12. Asymmetric capacitors are quite suitable for applications which require a high energy density, a high power density and excellent durability. Potential applications for asymmetric capacitors are as follows:

- Back-up power sources, such as voltage sag compensation and uninterruptible power supplies (UPS);
- Storage of renewable energy generation, such as wind and photo voltaic power generation;
- Energy recovery systems for industrial machinery and transport systems;
- Engine starting systems with capacitors alone or in combination with existing starting batteries.

Possible risks in transport and safety assessment of asymmetric capacitors

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

(a) Energy storage device in a charged state;

An asymmetric capacitor has a lower voltage limit, below which, the cell is damaged and loses its function. Therefore, asymmetric capacitor cells must be transported in a charged state in excess of the low voltage limit; and

(b) Energy storage device containing flammable liquids;

As with EDLCs, there are cases where flammable liquids are used in the electrolyte solution; and

While LIC contain lithium ions to transport charge, they contain no metal oxides in a positive electrode and thermal runaway is not a potential hazard.

14. Safety assessments for possible risks are as follows:

(a) Energy storage device in a charged state;

Since an asymmetric capacitor has a lower voltage limit below which the cell is damaged and loses its function, an asymmetric capacitor shall be transported in a charged state. Therefore, an asymmetric capacitor shall be protected against short circuit. The following test shall be applied to confirm safety in case the short circuit happens between the terminals.

- External short circuit test: no rupture, no disassembly and no fire;
- Energy storage device containing flammable liquids;

LIC cells may contain flammable liquids such as diethyl carbonate (flash point 25°C) and ethyl methyl carbonate (flash point 24°C) as components of an electrolyte solution. The amount of flammable liquid in a 10 Wh EDLC is approximately the same as in a 20 Wh asymmetric capacitor containing a flammable liquid.

Like Alkaline batteries, Ni-C capacitor uses an aqueous electrolyte which is not flammable. Therefore, there is no fire risk for Ni-C capacitor as for alkaline batteries.

The following tests shall be applied to confirm safety for asymmetric capacitors containing flammable liquids as an electrolyte solution.

- Altitude simulation (low pressure test): no leakage, no disassembly, no rupture and no fire under 95kPa pressure differential; and
- Drop test: no leakage, no disassembly, no rupture and no fire.

Proposal

15. The following rules are proposed for transport of asymmetric capacitors:
New entry table would read as follows:

(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)
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 held by a capacitor, as calculated using the rated voltage and nominal capacitance. All asymmetric capacitors to which this entry applies shall meet the following conditions:

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

(b) Each capacitor design type shall be subjected to an external short circuit test in which a capacitor in the fully charged state at ambient temperature (20±5ºC) shall be subjected to a short circuit condition with a total external resistance of less than 0.1 ohm for at least one hour. The capacitor must not disassemble, rupture or show evidence of fire over an observation period of 6 hours.

(c) Capacitors containing dangerous goods shall be designed to withstand a 95 kPa pressure differential

(d) 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 within the packaging or equipment in which the capacitor is installed; and

(e) Capacitors shall be marked with the energy storage capacity in Wh.

Capacitors containing an electrolyte not meeting the classification criteria of any class or division of dangerous goods, including when installed in equipment, are not subject to other provisions of these Regulations.

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 are not subject to other provisions of these Regulations when they 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 the equipment is packaged in a strong outer packaging constructed of suitable material 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."

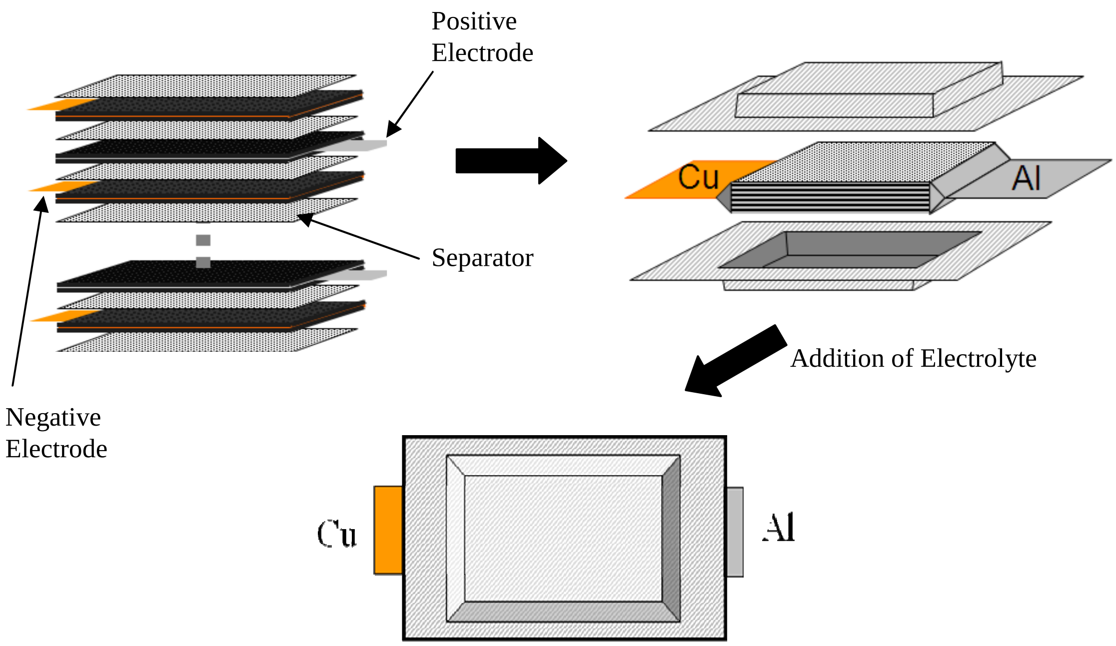

Fig.1 Constituent of LIC

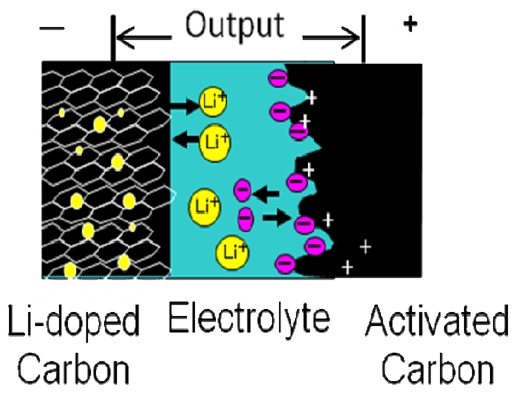

Fig.2 Schematic diagram of LIC

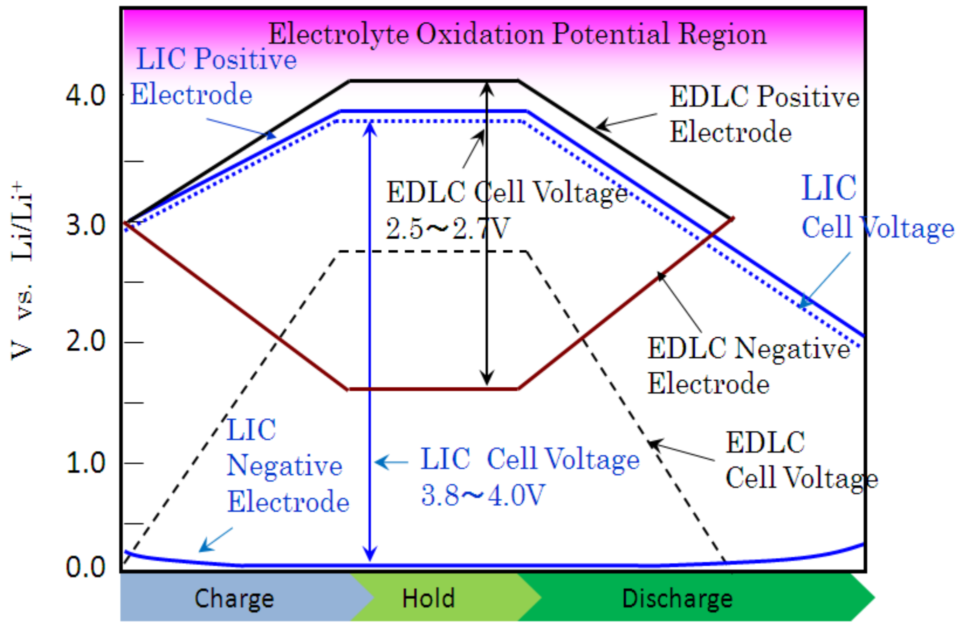

Fig.3 Operating principle of LIC（Comparison with EDLC）

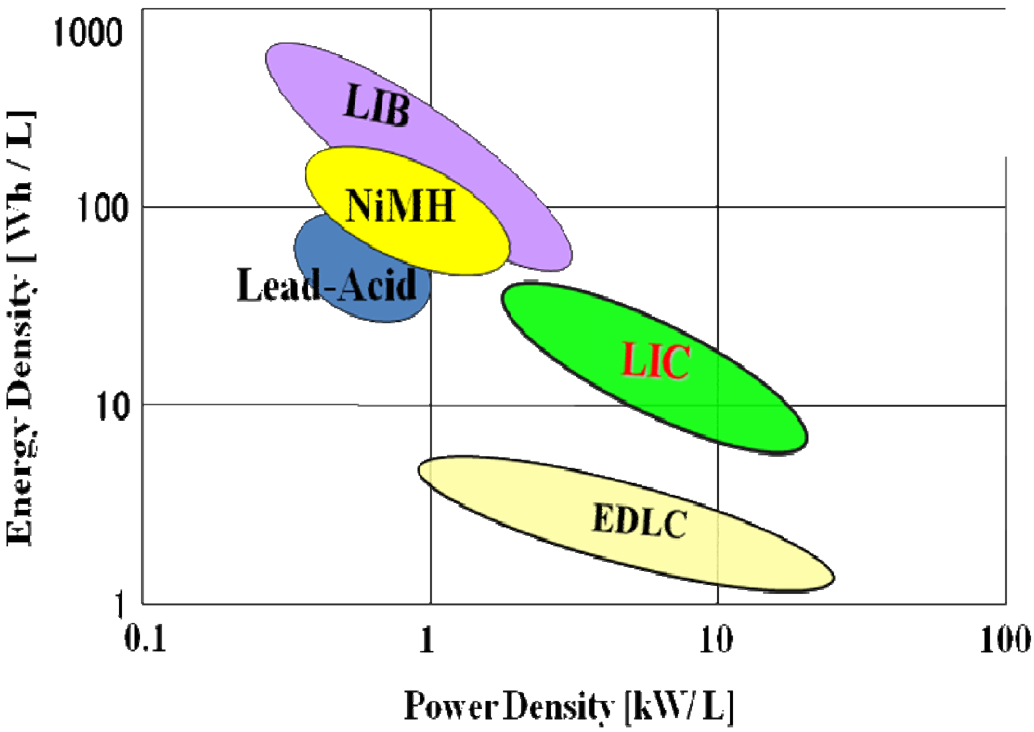

Fig.4 Energy density-power density relationship
（comparison with other energy storage device）

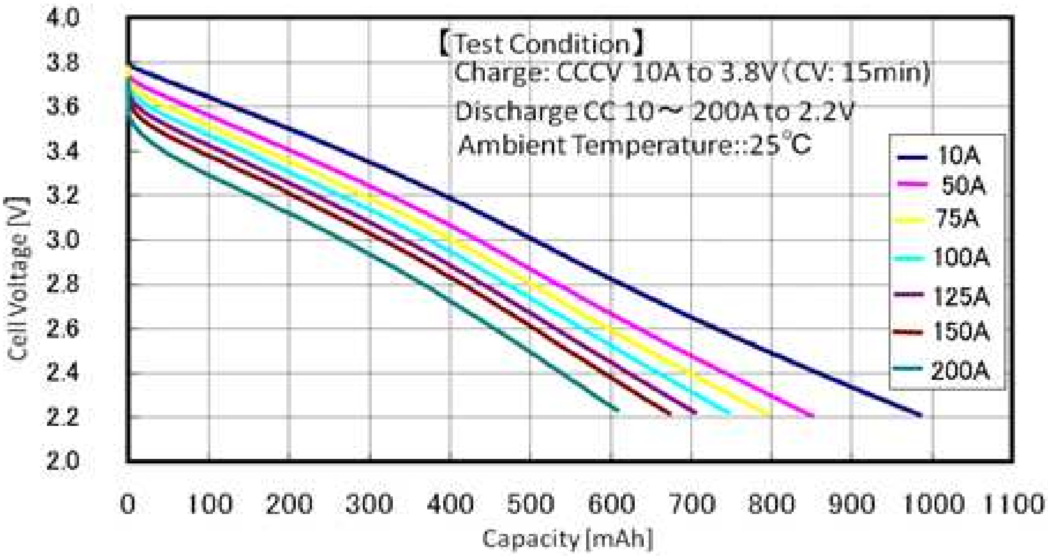

Fig.5 Discharge curve of LIC

Cylindrical cell 200F, 100F,

Cylindrical cell 1000 F

Laminate cell 1100F

Laminate cell 2000F

Fig. 6 Pictures of LIC cells

Fig. 7 Pictures of LIC modules
