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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 **23 November 2010**

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Item 5 of the provisional agenda
Electric storage system

New proper shipping name for lithium ion capacitors

Transmitted by the expert from Japan

Introduction

1. Lithium Ion Capacitor (LIC), which has been developed and commercialized recently, is an asymmetrical capacitor 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 LIC transport are needed.

Background information on lithium ion capacitor

Definition of LIC

2. LIC is an electrochemical capacitor in which charge and discharge can be repeated by adsorption and desorption of ions at the positive electrode, and by intercalation and deintercalation of lithium ions at the negative electrode. The positive electrode is comprised of carbon material with a large surface area such as activated carbon, and the negative electrode is comprised of carbon materials and so on which is possible to intercalate and deintercalate with lithium ions. The electrolyte used in LIC is a lithium ion salt organic solution.

Constituent of LIC and working principle

3. LIC cell is comprised of a positive electrode, negative electrode, separator and electrolyte. (Fig.1) LIC is an asymmetrical 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. (Fig.2)

4. For LIC, which is currently commercialized, activated carbon material similar to that of electric double layer capacitors (EDLC) is used for the positive electrode, and carbon material with small surface area similar to that of lithium ion batteries (LIB) is used for the negative electrode, which is intercalated with non-metallic lithium ions in advance.

5. The intercalation of lithium lowers the negative electrode potential and realizes a high cell output voltage. In addition to high cell output voltage, LIC can store large amounts of energy in the cell compared to EDLC due to large capacity of the negative electrode compared to that of the positive electrode by intercalation of lithium ions. (Fig.3) Since LIC cell, which is currently commercialized, has a lower voltage limit (2.0V to 2.2V) below which the cell loses its function same as LIB, it cannot be discharged to 0V.

Features of LIC (Comparison with other energy storage devices）

6. LIC has the following features compared to LIB and EDLC: (Table 1)

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

2. The major difference between LIC, LIB and EDLC is that LIC and LIB have lower voltage limits below which the cell lose their function, whereas, EDLC can lower the terminal voltage to 0V without any inconvenience; and

3. A major difference between LIC and LIB is that activated carbon is used for LIC, while Li metal oxide is used for LIB as the positive electrode. (Table 1）When Li metal oxide is used as a positive electrode, thermal runaway reactions may occur by generation of free oxygen due to the decomposition of Li metal oxide upon rising cell temperature. Since activated carbon is used as a positive electrode for LIC, thermal runaway reaction does not occur.

Applications of LIC

7. LIC with different energy levels (40F to 5000F) has been commercialized as laminated or cylindrical cells.(Fig.6) LIC is often used configured in modules, which comprises cells connected in series and/or parallel to obtain proper voltage and energy necessary for the specific application. (Fig.7)

8. LIC is quite suitable for applications which require a high energy density, a high power density and excellent durability. Potential applications for LIC 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; and
- Energy recovery systems for industrial machinery and transport systems.

Possible risks in transport and safety assessment of LIC

9. The following three potential transport risks of LIC are listed:

1. Transport risk of energy storage device in a charged state;

LIC has a lower voltage limit (2.0V to 2.2V), below which, the cell loses its function. Therefore, LIC cells must be transported in a charged state;

2. Transport risk of energy storage device containing flammable liquid; There is a case that flammable liquids are used in the electrolyte solution; and

3. Transport risk of energy storage device contained lithium ions;

Like LIB, LIC uses lithium ions.

10. Safety assessment for possible 3 risks is as follows:

1. Transport risk of energy storage device in a charged state; since LIC has a lower voltage limit below which the cell loses its function, LIC must be transported in a charged state. Therefore, LIC must be packed in a way to prevent short circuit. For safety confirmation, even if short-circuit occurs at the time of transport, the following test shall be applied;

- External short circuit test: no rupture, no disassembly and no fire;

2. Transport risk of energy storage device containing flammable liquid; the LIC electrolyte solution may contain some amount of flammable liquids such as Diethyl Carbonate (flash point 25°C) and Ethyl Methyl Carbonate (flash point 24°C). The following tests shall be applied to confirm safety;

- Altitude simulation (low pressure test) : no mass loss, no leakage, no disassembly, no rupture and no fire in a reduced pressure of 11.6kPa or less; and

- Drop test: no mass loss, no leakage, no rupture and no fire; and

3. Transport risk of energy storage device containing lithium ions; lithium metal oxide is not used as the positive electrode for LIC, thermal runaway reaction will not occur in LIC. Based on these facts, there is no need to pursue safety test regarding this point.

11. From this point of view, it is necessary to transport LIC using confirmed cell safety data and based on LIC cell properties. A new proper shipping name, appropriate test items, methods and criteria should be specified.

Draft proposal

12. The following rules are proposed for LIC transport:

New entry table would read as follows:

(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)
3XXX	LITHIUM ION CAPACITOR	9			AAA	0	E0	P003		

The accompanying special provision AAA would read:

“AAA This entry applies to Lithium Ion Capacitors (LIC). All LIC to which this entry applies shall meet the following conditions:

(a) Cells or modules shall be designed to meet the requirements of the safety tests specified in sub-paragraphs (i) to (iii) below;

(b) Cells or modules shall be protected against short circuit;

(c) Cells or modules with energy storage capacity specified below are not subject to other provisions of these regulations when they meet the requirement of the safety tests specified in sub-paragraphs (i) to (iii) below;

- For cells, energy storage capacity is not more than 20Wh; and
- For modules, energy storage capacity is not more than 100Wh;

(d) On cells or modules with energy storage capacity larger than the values specified in (c) above, the energy storage capacity shall be marked in Wh; and

(e) Cells or modules installed in equipment are not subject to drop test specified in sub-paragraph (iii) below, provided that 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.

Safety tests and requirements

(i) Altitude simulation（low pressure test）

Test procedure: cell or module in fully charged state shall be stored in a reduced pressure environment at a pressure of 11.6kPa or less for at least six hours at ambient temperature (20±5ºC).

Requirement: there is no mass loss, no leakage, no disassembly, no rupture and no fire. The open circuit voltage of each test cell or module after testing is not less than 90% of its voltage immediately prior to this procedure.

(ii) External short circuits

Test procedure: cell or module in fully charged state at room temperature 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 cell or module must be observed for a further six hours for the test to be concluded.

Requirement: there is no disassembly, no rupture and no fire within six hours of this test.

(iii) Drop test

Test procedure: cell or module in fully charged state is dropped from a height of 1.2m in packed condition on a non-resilient and horizontal surface.

Requirement: there is no mass loss, no leakage, no disassembly, no rupture and no fire. ".

Action requested of the Sub-Committee

13. The expert from Japan does not request the Sub-Committee to consider this informal document proposing the establishment of a new Proper Shipping Name for LIC at this session since he intends to submit a formal proposal to the next session. The members of the Sub-Committee are kindly requested to consider the draft intersessionally and provide their comments so that a formal proposal will be able to take them into account.

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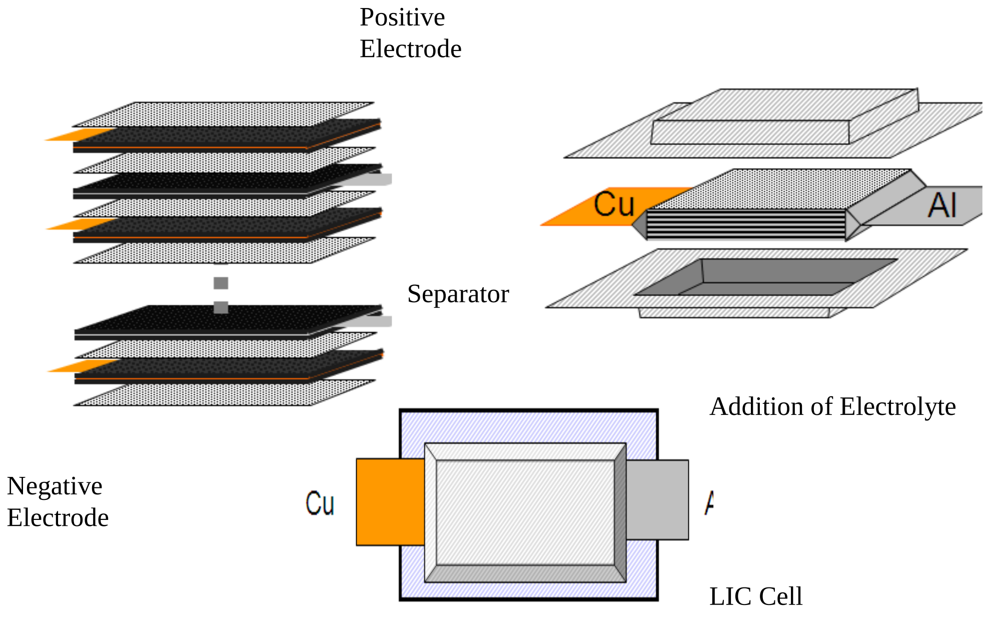


Fig.1 Constituent of LIC

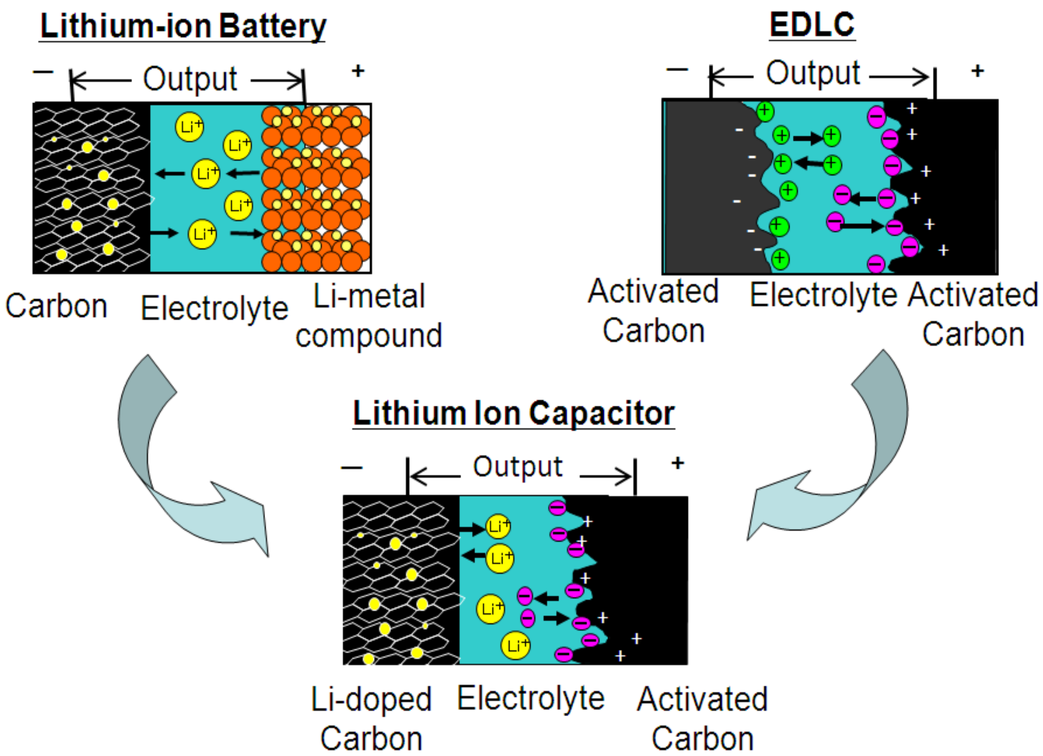


Fig.2 Comparison of LIB, EDLC and LIC

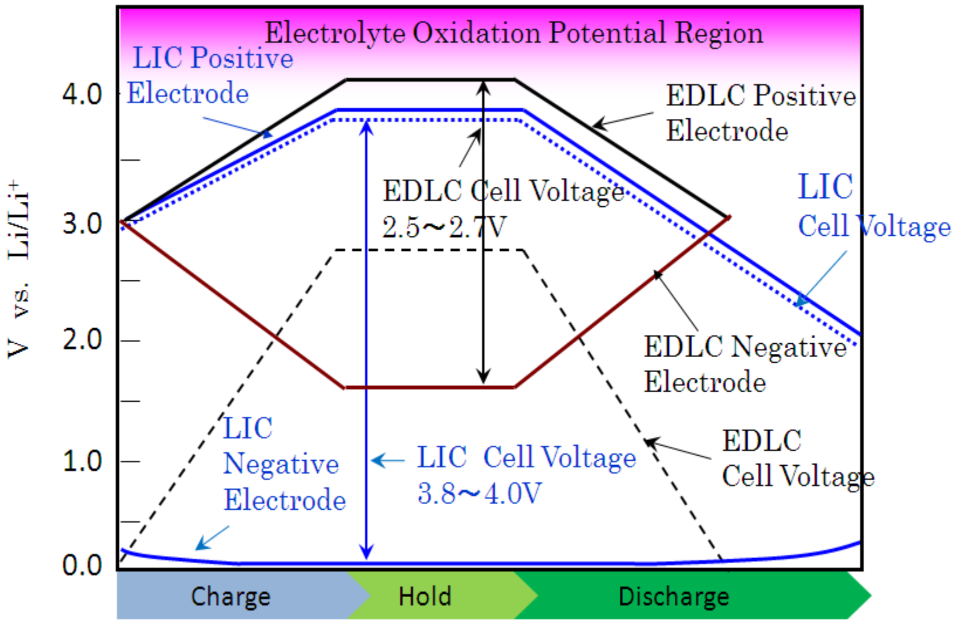


Fig.3 Operating principle of LIC（Comparison with EDLC）

Table 1 Comparison of properties, LIC, LIB & EDLC

	LIC (Lithium Ion Capacitor)	LIB (Lithium Ion Battery)	EDLC (Electric Double Layer Capacitor)
Positive Electrode	Activated Carbon	Li Metal Oxide	Activated Carbon
Negative Electrode	Carbon	Carbon	Activated Carbon
Electrolyte	$LiPF_6$/PC-EC, etc.	$LiPF_6$/EC-EMC, etc.	TEMA･BF_4/PC, etc.
Operating Voltage	4.0～2.0V	4.2～3.0V	2.7～0V
Energy Density(Wh/L)	middle(10-50)	large(150～600)	small(2-8)
Power density	large	small	large
Cycle Durability	large	small～middle	large
Discharge	Cannot discharge below lower limit	Cannot discharge below lower limit	Possible to complete discharge(0V)
Self-discharge rate	small	small	large
Working Temp. range (C)	-20～70	-20～60	-30～60

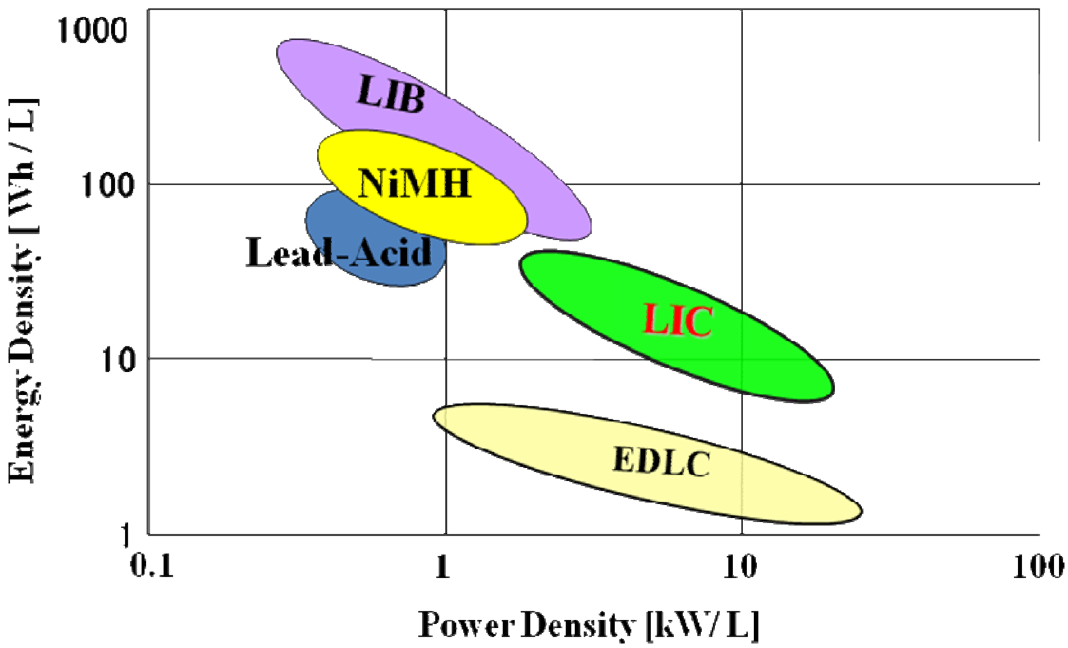


Fig.4 Energy density-power density relationship
（comparison with other energy storage device）

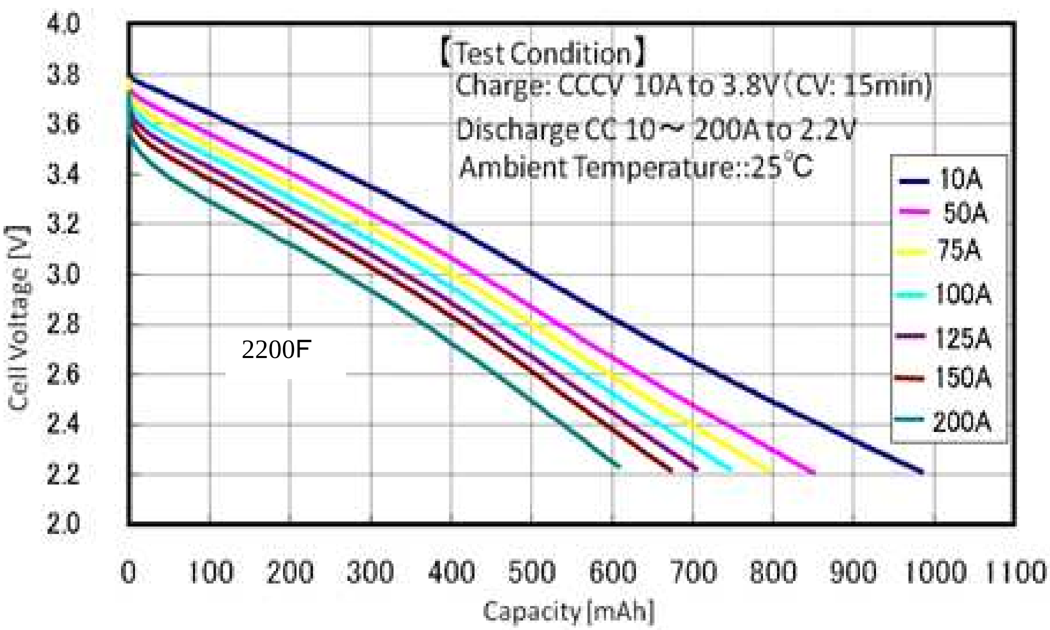
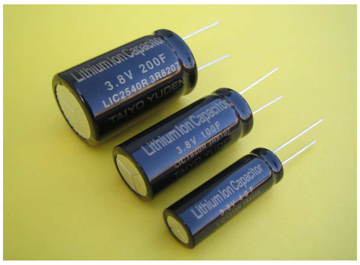


Fig.5 Discharge curve of LIC



Cylindrical cell 200F, 100F, 40F

Cylindrical cell 1000 F

Laminate cell 1100F

Laminate cell 2000F

Fig. 6 Pictures of LIC cells

Fig. 7 Pictures of LIC modules