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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Geneva, 1-9 December 2008
Item 12 of the provisional agenda

PROGRAMME OF WORK FOR THE BIENNIUM 2009-2010

Work on the inclusion of ultra capacitors in the UN Model Regulations

Transmitted by the expert from France

The expert from France welcomes the request of KiloFarad International to join the Sub-Committee (INF.14) and supports the idea of including the classification of ultra capacitors in the program for the next biennium.

As stated in the report of the informal working group on lithium batteries (see INF.35 par.15) appropriate transport provisions should be defined for these specific articles.

To help the Sub-Committee the expert from France would like to provide some synthetic information on ultra capacitors in the annexed power point presentation.

ABUSE TESTING OF SUPERCAPACITORS AND RELATED ASSEMBLIES AT INERIS

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UN Informal group on batteries and supercaps meeting, Washington DC, 11 to 13 November 2008

Introduction

Although the principle for the storing of electrical charges in a supercapacitor is rather old, commercial use in high power applications is quite recent when highly promising

As for Li-ion and other type of batteries for application in transport, the use of supercapacitors (also called ultracapacitors), mostly of EDLC type, is expected to expand very fast and benefits regularly from technological progress.

Classification of such devices for transport has become an emerging issue

- classification rules must avoid acting as a barrier against technological development when reflecting correctly actual risk profile to transport

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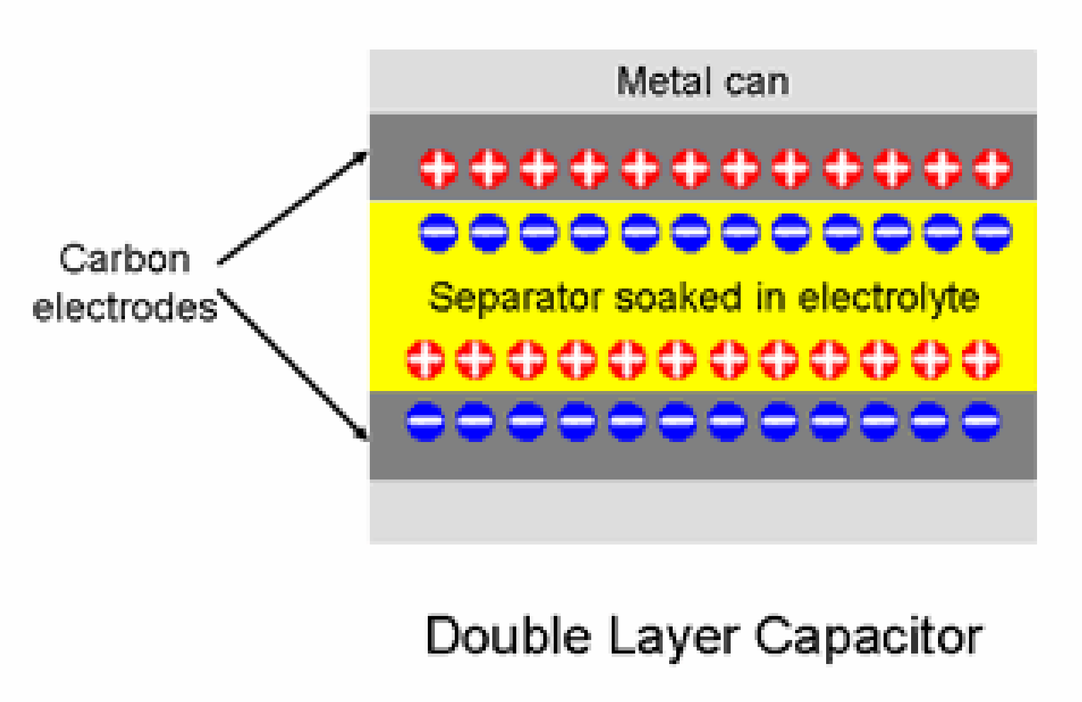
EDLC: the most common type of supercapacitor for power applications



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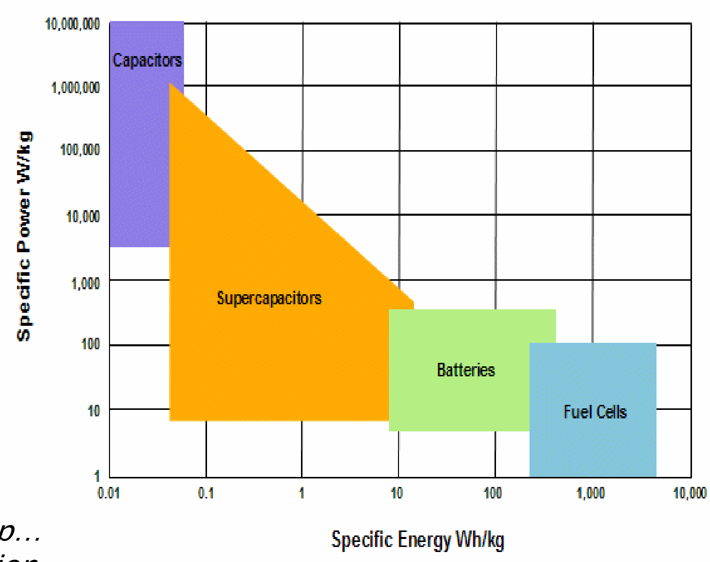
Differences between ultracaps and batteries

Higher specific power but much lower specific energy

Physical storage of charge instead of electrochemical storage



Low power application : memory back-up…
High power application : vehicle hybridation

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Abuse testing : what are the goals ?

Anticipate overall behavior of such pieces of equipment, as an isolated cell, or as coupled in modules of several cells or as found in more complex assemblies, when charged or discharged and throughout their life cycle.

Qualify intrinsic hazards of devices in the context of transport to define appropriate safety provisions for all mode of transport that can be used

Support the industry for the development of integrated safety devices (emergency pressure relief vents…)

Ensure safety at use, once integrated in equipment (public transport systems, electric hybrid cars…)

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Safety at use: the right issues as fire risk is concerned

According to normal stress during lifetime of supercaps, do the fire and explosion risks differ (e.g. rates higher ?) compared to the « standard » risk in a passenger car that does not make use of such energy storage device ?

Is the time available for the emergency services to rescue trapped people in the event of a post crash fire any shorter before untenable conditions are reached in the cabin ?

- (from thermal or toxic threat).

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Safety in transport

Industrialization at large scale may lead to mass transportation by road and rail, and likely also by other modes of transport (air, maritime)

How far should the current TMD regulations be changed for best account of related risks?

How far may we draw experience from the case of batteries in the field to develop a pertinent test series (if needed) ?

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Type of abuse testing

Of electric nature :

- Overcharging
- Response to Internal short-circuit
- Response to external short circuit

Mechanical

- Response to crash or impact
- Response to vibrations

Thermal

- Resistance to heat stress (when charged or discharged)
- Fire behavior

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Experimental means available at INERIS for testing supercapacitors

Major equipements

- Same as for testing batteries as far as fire testing is concerned

Dedicated equipment for electrical and mechanical testing under consolidation

- Hydraulic press
- Device for applying external short circuit

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Experience achieved so far by INERIS (1/2)

Started 5-6 years ago, at early stage of supercaps development in the EU

Gained essentially for private customers

- Supercaps developers
- Supercaps integrators

Experience achieved so far mainly targeting safety at use, as no official or non official test series apply for transport of supercaps

- However, abuse testing designed for safety at use also inform on safety issues that may apply to transport

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Experience achieved so far at INERIS (2/2)

Experience achieved at INERIS encompasses:

- testing on individual cells, and on modules
- Electrical testing, mechanical testing, thermal abuse and fire response testing

Preliminary evaluation of toxicity issues (Tewarson apparatus) in well ventilated and air vitiated conditions of :

- our earliest commitment in the field

The freedom Car manual (abuse testing) has served as a guidance so far for the development of our internal abuse testing protocols

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Overview of abuse testing done so far at INERIS

Electrical

- Electric overcharging of modules
- External short circuit on cells

Thermal

- Thermal stability at various T with on-line monitoring of gas emissions (charged cells)
- Fire behavior in 80 m3 chamber of charged cells and modules
- Fire testing in the Tewarson apparatus (2 technologies)

Mechanicial

- Impact test (nail perforation)
- Crushing test (under progressive mechanical pressure)

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External short circuit on ultracapacitor cells

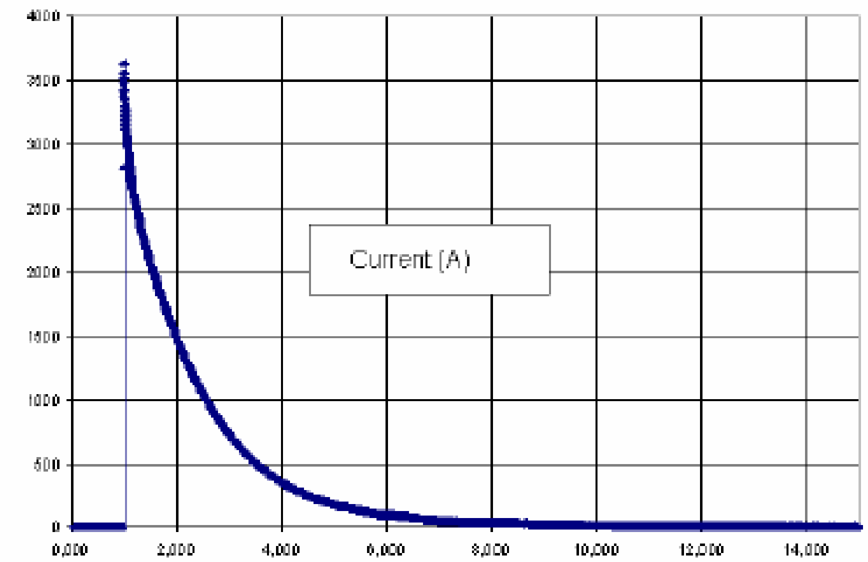

Fig. 1 : Short-circuit current versus time on supercapacitor cells

Use of switches with low resistance circuit

Results : Up to 3500 A current peak without major consequences on cell integrity (reproduced three times)

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Internal short circuits

Drill (nail penetration) test on cells

- nail of 3mm diameter at a penetration
- Fully charged cells have been penetrated with a conductive
- nail of 3mm diameter at a penetration rate between 8 and 12cm/s and at ambient temperature. Very limited consequences

Crushing tests

- Fully charged cells have been crushed by a 150mm diameter cylindrical tool in two steps :
  - (2330 N during 15 minutes) leading to deformation : no exterior sign

internal light short-circuit recorded.

  - (4170 N during another 15 minutes) leading to a 40% in height deformation : faster internal discharge without any exterior sign noted

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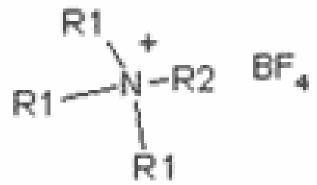
Fire behaviour of a supercapacitor cell in the INERIS 80 m3 test chamber

Assessing smoke toxicity issue of burning electrolytes



Fire bahaviour of electrolytes (complex mixtures of a ternary ammonium salt and a solvent)

- solvent flammable (CH_3CN) or at least combustible (PC, …)
- specific emissions possible due to presence of Boron and Fluorine elements in the common salts in use
- cyanides and NOx emissions ?
- smoke toxicity may be more complex to analyse as compared to building fires where carbon oxides are found responsible of fire deaths in nearly all cases
- decomposition of the electrolyte in fire conditions likely to develop under confinement (the casing of the ultracapacitor)

The FPA (coupled with FT-IR and more conventional gas analysis devices)

⇨ Unique apparatus for addresssing the issue

Recognized at ISO level by TC92 SC3 !

INERIS IS THE LEADING OPERATOR IN THE EU (since 1997)
ASTM E 2058

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Early findings on toxicity issues

Toxic emissions from electrolyte burning significantly affected by ventilation conditions

Therefore interaction with the casing of the ultracapacitors likely to play a major role:

- protective for a while,
- likely to induce fuel lean conditions.

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Technological development of Ultracapacitors

today

R&D and pre-commerciial?

	Symmetry	Material: Positive electrode	Material: Negative electrode	Category
Capacitor	Symmetric	Activated carbon	Activated carbon	EDLC (electric double layer capacitor)
		New material	New material	RuO_2 capacitor, Metal oxide capacitor
				Dual carbon capacitor
	Asymmetric	Activated carbon	carbon	Hybrid capacitor
				Lithium ion capacitor
		New material	New material	

⇨ May require, as for batteries in the past and presently, adaptation of provisions for safe transport !

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Conclusions

Same type of abuse testing may serve both safety at use and safety at transport purposes (where required)

- May serve the harmonization process of classification of such devices for transport

Consolidation of testing protocols may benefit from the case of batteries, taking account of pecularities of supecapacitors:

- EDLC transported uncharged
- Case of other technologies ?
  - Hybrid supercapacitors…
- Tests and criteria have to be defined and reported in a future version of the Manual of test and criteria to support harmonization of rules for the safe transport of such devices

Appropriate work should be introduced in the programme of work of the UN SC of experts of TDGs for the coming biennium

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Perspectives for a classification scheme for transport (INERIS viewpoint)

Future classification scheme should anticipate futher technological development

The question of level and type of testing shall be addressed consistently with what is required or desirable anyhow to guarantee safety at use

Existing UN numbers under consideration, not appropriate

- supercaps hazards not correctly reflected (overrated ?)

Best hazard class fit to host dedicated UN number(s) for supercaps seems to us division 9 for a number of reasons according to :

- Potential hazards in relation with current and future development (flammability and or corrosivity of electrolytes, Li containing electrodes, other hazardous components… ?)
- Scope of hazards divisions for transport
- Similarities with batteries (to some extent)

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Thank you!

Questions ?

Comments ?

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