

## Recent developments in Li-ion prismatic cells

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### Abstract

The development of new materials is required to improve the energy density of Li-ion batteries. A new graphite type with optimised physical–chemical characteristics has been studied and developed to improve negative electrode performance. Lithium ion charge and discharge acceptance have been improved by the enhanced intrinsic properties of the material. The new material has higher efficiency electrode porosity/tortuosity, and increases electrical conductivity. This allows better charge performance at low temperatures and discharge performance at high rates.

Combined with an optimised electrolyte composition, it also gives low and reproducible fading, good discharge performance in very low temperature conditions, and long term storage at high temperatures.

Due to this and other design modifications that will be discussed, a 22% improvement in energy density is obtained in the new generation of Saft Li-ion medium prismatic cells (MP).

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**Keywords:** Lithium ion; Prismatic; Graphite; Low temperature

### 1. Introduction

Li-ion electrochemistry is now mature and is the most used in portable power sources all over the world. Nevertheless progress is still required regarding the essential performance such as energy, power, life expectancy, cycling, safety, etc.

Saft manufactures high performance and high reliability Li-ion medium prismatic cells (MP) dedicated to high technology application like military, medical, instrumentation, measuring, space, telecom, etc. To answer more and more demanding needs, Saft R&D teams currently work on improving active materials. The recent development of a new graphite type in co-operation with a material manufacturer led to increase capacity by 17%, and improve other performances such as cyclability and low temperature operation.

### 2. Experimental

#### 2.1. Cell design

Technology of Saft's medium prismatic Li-ion cells is based on winding electrodes on a flat mandrel to produce an oblong

“jelly roll” coil. Fig. 1 shows the structure of a MP 176065 cell. Containers are made of stainless steel, laser-welded can and cover. The cover features an electrolyte fill port closed with a metal ball, a low pressure circuit breaker and a safety vent in case of extreme temperature situation. The circuit breaker acts on overpressure due for example to overcharge failure, without cell opening and electrolyte leaking. The volume left outside the cell within the cover shape can accommodate the electronic protection circuit.

The negative electrode is made of a 12  $\mu\text{m}$  thick copper foil coated on both sides with a mixture of high tapped density artificial graphite and non fluorinated binder.

The positive electrode is made of a 20  $\mu\text{m}$  thick aluminium collector coated with a mixture of  $\text{LiCoO}_2$ , high surface carbon black and high molecular weight PVDF binder.

The positive and negative electrode porosities are in the 25–35% range, respectively, which allows a good compromise between energy and power.

The insulation between the electrodes is provided by a 20  $\mu\text{m}$  trilayer laminated PP/PE/PP microporous separator with a micropore “shut down” capability at 125–130 °C.

Electrolyte is a organic solvents blend of ethylene carbonate, dimethyl carbonate and ethyl acetate with 1.5M  $\text{LiPF}_6$  as salt and vinylene carbonate as an additive, in order

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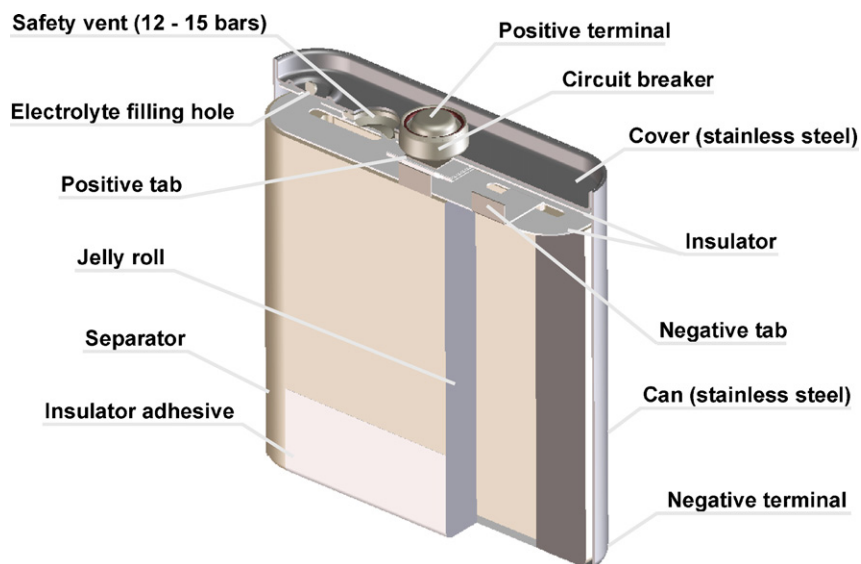


Fig. 1. Structure of Saft MP cells.



Fig. 2. Saft MP Li-ion cells.

to achieve both very low temperature and high cycle life number.

The Saft range of three medium prismatic Li-ion cells is displayed on Fig. 2, which main specifications are summarised on Table 1.

## 2.2. Physico-chemical characterisation

### 2.2.1. Powders characterisation

The pictures were made with a JSM-6340F JEOL Scanning Electron Microscope. The granulometry, expressed by the par-

Table 1  
Saft MP Li-ion cells specifications

Model	Thickness (mm)	Width (mm)	Height (mm)	Weight (g)	Nominal capacity (Ah)	Operating conditions	
						Discharge	Charge
MP 144350	13.8	43	50	70	2.7	Up to 2C	$C_{max}$
MP 174865	18.0	48	65	120	5.3	-50 to +60 °C	-20 to +60 °C
MP 176065	18.0	60	65	155	6.8	Cut off 2.5 V	4.20 V

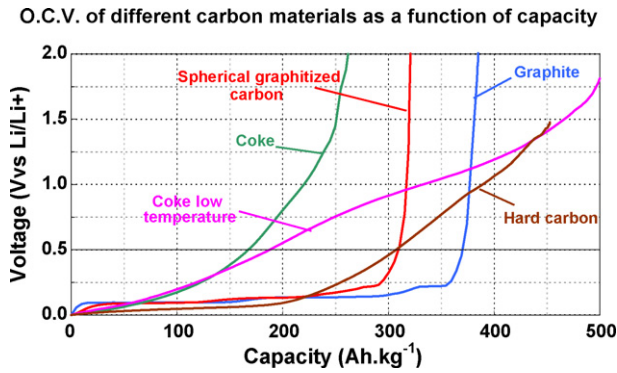


Fig. 3. O.C.V. of different carbon materials as a function of capacity.

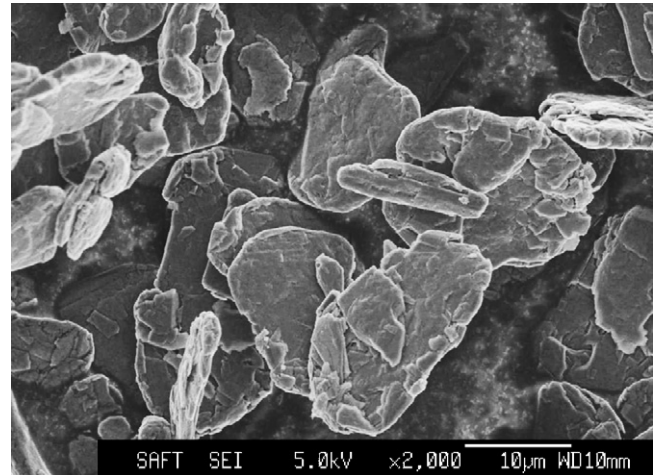


Fig. 5. SEM picture of the new selected graphite.

Particle size of the particles at 10%, 50% and 90% in volume (D10, D50 and D90, respectively) was measured the dry way with a MALVERN MASTERSIZER 2000.

### 2.2.2. Electrode characterisation

The pore size distribution of the different electrodes was measured by Hg porosimetry (MICROMERITICS PORE SIZER 9310).

The electrical transversal conductivity was measured under varying pressure on double-coated electrodes with four probe conductivity measurements.

### 2.3. Negative electrode and active material

More and more applications for Li-ion batteries request outstanding performance in terms of power, fast charge and/or low temperature operation without sacrificing energy, on which the negative electrode plays a major role [1–8].

A good carbon for use as negative active material in Li-ion cells is a carbon with:

- low cost;
- good processability;
- good performance, including high capacity in the working electrochemical window [0–0.5 V].

So, as shown on Fig. 3, graphites are good candidates for use as negative active material in Li-ion cells.

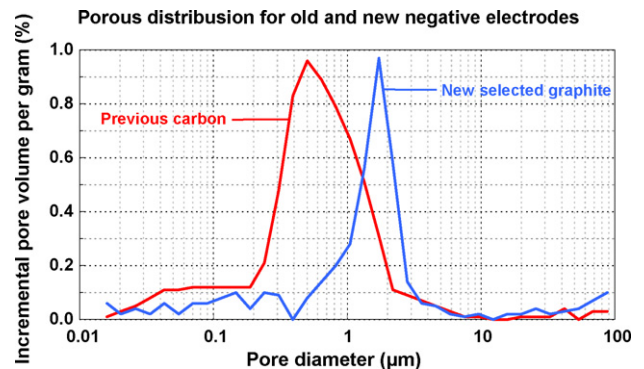


Fig. 6. Hg porosimetry of old and new negative electrodes.

To achieve a good performance in terms of power and fast charge, the negative electrode should allow a fast charge transfer at the interface electrode/electrolyte and a good conduction at the interface electrode/current collector. A good electrode should thus have a good adhesion, a high electrical conductivity, an adequate tortuosity allowing sufficient wettability by the electrolyte and good ionic diffusion. High crystallinity graphite powders from different suppliers with roughly the same granulometry were investigated [9]. A new graphite was selected after studying the correlation between physico-chemical characteri-

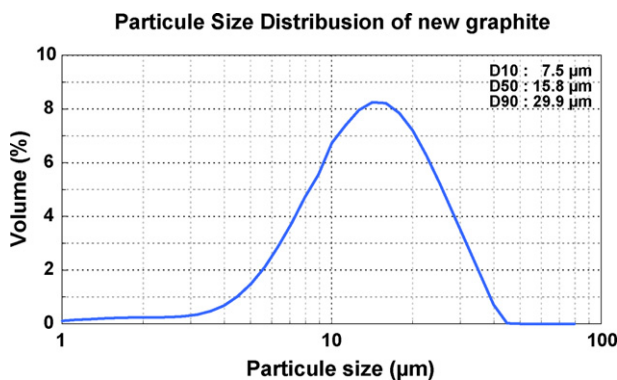


Fig. 4. Particle size distribution of the new selected graphite.

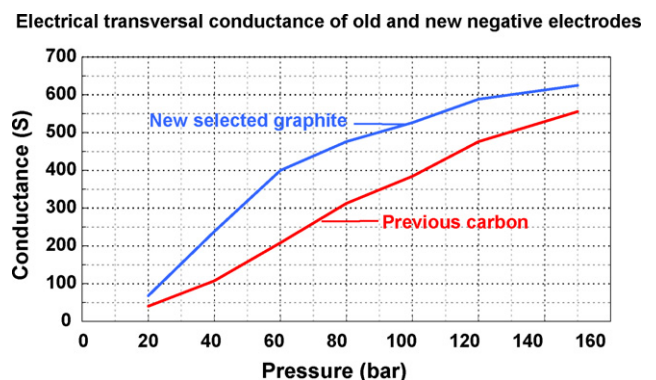


Fig. 7. Electrical transversal conductivity of old and new negative electrodes.

sation of the powders, electrode process and electrochemical performance of the different negative electrodes.

Particle size distribution and SEM picture of the selected graphite are shown on Figs. 4 and 5. The rounded-shape morphology allows an adequate electrode porosity with a median pore diameter of 1.7  $\mu\text{m}$  compared to 0.5  $\mu\text{m}$  for the previous carbon as shown on Fig. 6. In addition, the high crystallinity of the new selected graphite leads to an increase of electrical transversal conductance as shown on Fig. 7.

### 3. Results

The new Saft MP Li-ion cell generation combines the use of a new graphite, a new negative electrode design and the adjustment of the electrolyte composition. All these modifications lead to cell improvements as described below.

#### 3.1. Capacity

Increasing the capacity resulted from two separate actions: introducing the new graphite selected, as described above, and designing a new electrolyte composition to increase the charge voltage from 4.1 to 4.2 V. Maintaining the previously specified charge voltage of 4.1 V still increases the capacity from 5.8 to 6.1 Ah, while charging the cell to 4.2 V allows an improvement up to 6.8 Ah, as shown on Fig. 8, obtained from a continuous low rate  $C/5$  discharge.

#### 3.2. Discharge performance

The high electrical conductivity of the negative electrode brings to the cell a very high current discharge capability, with a good capacity retention (up to 96% of the nominal capacity under  $2C$  continuous discharge) as shown on Fig. 9.

Although not specially designed for power, this high energy cell is still able to supply high pulse discharge of up to  $4C$  rate at room temperature over the complete cell discharge.

Low temperature operation is particularly required for military applications. Because diffusion phenomena are the limiting factors in these conditions, electrolyte properties play the main role in the performance obtained.

C/5 discharge performance comparison of different MP176065 definition.

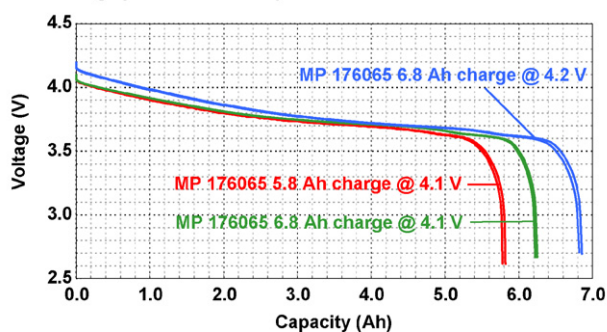


Fig. 8. Discharge performance comparison of different MP 176065 definition. Discharge at room temperature under  $C/5$  (cut off 2.7 V) after charge at  $C$  floating 4.1 or 4.2 V.

MP 176065 6.8 Ah discharge performance at room temperature.

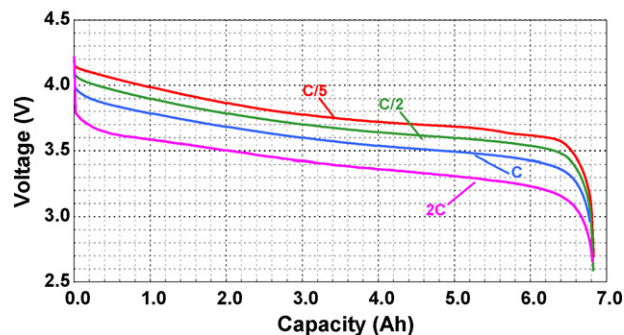


Fig. 9. MP 176065 6.8 Ah discharge performance at room temperature. Discharge at room temperature under different  $C$  rate (cut off 2.7 V) after charge at  $C$  floating 4.2 V.

A proprietary modification of the electrolyte was applied to obtain low viscosity and high conductivity at very low temperature, while maintaining the stability with both negative and positive electrodes, required to obtain a good cyclability and calendar life. The SEI layer stability is enhanced by addition of vinylen carbonate (VC) at the appropriate concentration [10,11], and high voltage of 4.2 V can be sustained on the positive electrode by correct selection of both  $\text{LiCoO}_2$  and electrolyte purity.

Significant performance improvement is obtained at temperatures as low as  $-40^\circ\text{C}$ , as shown on Figs. 10 and 11, and even  $-50^\circ\text{C}$ , as described on Fig. 12. Although the voltage increase at high drain is due to cell self heating (total increase is  $40^\circ\text{C}$  during complete discharge at  $-40^\circ\text{C}$  under  $C/2$ ), the power capability is high enough to start the discharge process at this very low temperature. Fig. 13 shows the variation of discharge profile at  $C/5$  over the complete temperature range from  $-50$  to  $+60^\circ\text{C}$ .

#### 3.3. Charge performance

Fig. 14 describes the charging characteristics at ambient temperature, at several rates, from  $C/5$  to  $C$ . At  $C$  rate, 90% of the capacity is charged within 1 h.

The optimised negative electrode formulation associated to the low temperature electrolyte improves the charge ability of the new cell at low temperature. As shown on Fig. 15, more

C/2 discharge performance comparison at  $-40^\circ\text{C}$  of different MP176065 definition.

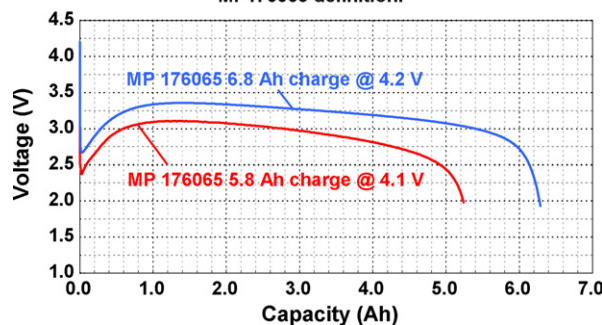


Fig. 10.  $C/2$  discharge performance comparison at  $-40^\circ\text{C}$  of different MP 176065 definition. Discharge at  $-40^\circ\text{C}$ , after 12 h storage, under  $C/2$  rate (cut off 2.0 V) after charge at RT floating 4.1 or 4.2 V.

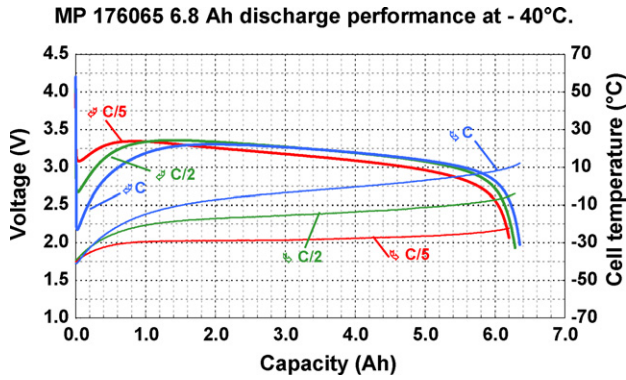


Fig. 11. MP 176065 6.8 Ah discharge performance at  $-40^{\circ}\text{C}$ . Discharge at  $-40^{\circ}\text{C}$ , after 12 h storage, under different  $C$  rate (cut off 1.5 V) after charge at RT floating 4.2 V.

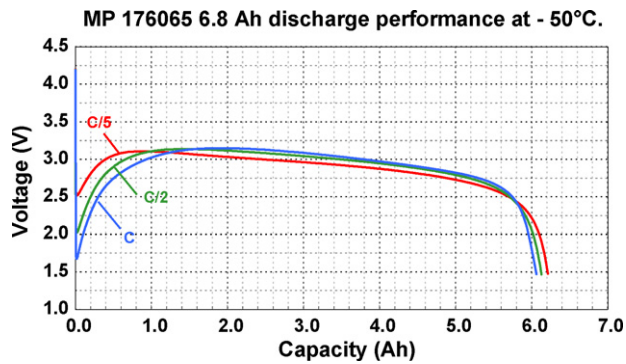


Fig. 12. MP 176065 6.8 Ah discharge performance at  $-50^{\circ}\text{C}$ . Discharge at  $-50^{\circ}\text{C}$ , after 12 h storage, under different  $C$  rate (cut off 1.5 V) after charge at RT floating 4.2 V.

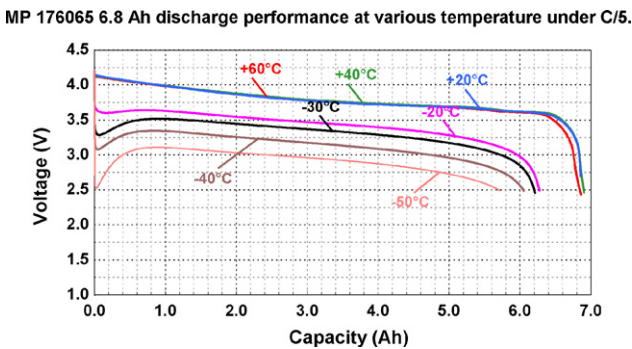


Fig. 13. Discharge after 12 h storage at  $T (^{\circ}\text{C})$ , under different  $C/5$  rate (cut off 2.5 V) after charge at RT floating 4.2 V.

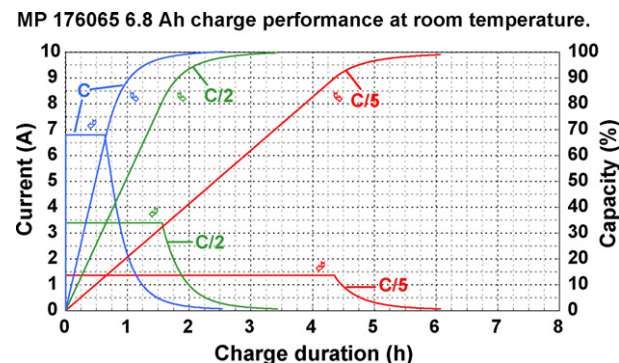


Fig. 14. MP 176065 6.8 Ah charge performance at room temperature. Charge at room temperature under different  $C$  rate, floating 4.2 V.

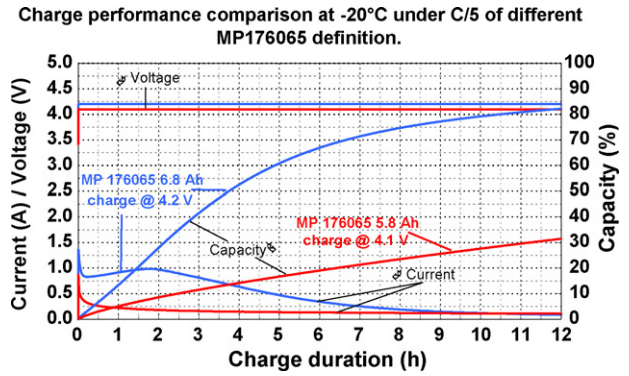


Fig. 15. Charge performance comparison at  $-20^{\circ}\text{C}$  under  $C/5$  of different MP 176065 definition. Charge after 12 h storage at  $-20^{\circ}\text{C}$  under  $C/2$  rate, floating 4.1 or 4.2 V.

than 80% of the nominal capacity can be charged at  $C/5$  and  $-20^{\circ}\text{C}$ . This represents a very large improvement compared to the previous design.

### 3.4. Cycling performance

Increasing the initial energy should not be made to the detriment of cell life, which is unfortunately often the case. Cycling ability is described on Fig. 16. During 500 cycles performed at ambient temperature (charge @  $C$  to 4.1 or 4.2 V, discharge @  $C/2$  to 2.7 V), the capacity fade is smaller than with the previous design when charged at 4.1 V. Less than 15% capacity is lost in these conditions. Charging at 4.2 V leads, however, to a slightly higher capacity fade although the capacity is always higher until 500 cycles. About a 15% average energy increase is thus obtained over the previous 5.8 Ah design during a 500-cycle life.

During cycling, the power capability should not be affected. This is however one of the main ageing mechanisms occurring in Li-ion cells [12]. Fig. 17 shows the cell resistance evolution during cycling, that remains fairly stable, insuring excellent power capability over all its cycle life. Here again, the slightly higher impedance increase of the cells charged at 4.2 V reflects the higher active material utilisation.

### Cycling performance comparison of different MP176065 definition.

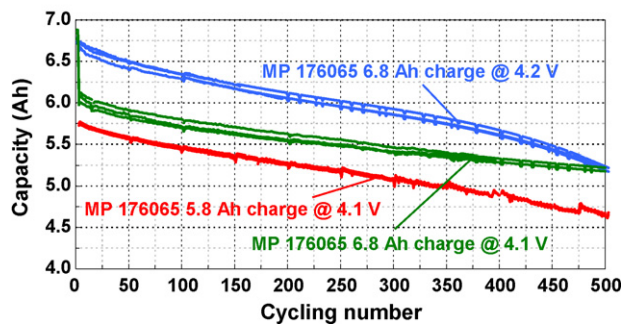


Fig. 16. Cycling performance comparison at room temperature of different MP 176065 definition. Capacity evolution during cycling at room temperature. Discharge at  $C/2$  (cut off 2.7 V), charge at  $C$  (floating 4.1 or 4.2 V).

Cycling performance comparison of different MP176065 definition.

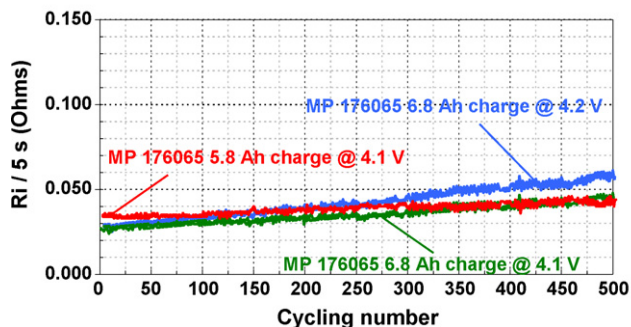


Fig. 17. Cycling performance comparison at room temperature of different MP 176065 definition. Internal resistance at 5 s evolution during at room temperature. Discharge at C/2 (cut off 2.7 V), charge at C (floating 4.1 or 4.2 V).

### 3.5. Abuse testing

Increasing energy density may also result in more important safety concerns. The most drastic and potentially occurring abuses are overcharge, short circuit and overheating.

These tests have been carried out on the new cell design, to verify the cell safety level.

#### 3.5.1. Overcharge performance

Thanks to their circuit breaker design, the MP cells can sustain abuse overcharge without any damaging event such as flames, fumes, or even electrolyte leaking. Fig. 18 describes an abuse overcharge test performed at 20 A rate representing three times the specified maximum charge rate (according to UL 1642 Standard for Safety Lithium Batteries procedure), without any additional electronic protection against overvoltage. As it can be seen, the circuit breaker activates well before the cell temperature reaches a potentially dangerous level.

#### 3.5.2. Short circuit test

A short circuit test done on fully charged cells at room temperature, according to the IEC procedure (room temperature, total external resistance of less than 50 mΩ) does not lead to either flames, fumes, or vent operation. As it can be seen on Fig. 19, the cell reacts like during a continuous discharge at very high rate (around 55 A; 8 C) with a fast increase temperature of the

MP 176065 6.8 Ah overcharge performance at room temperature under 3C.

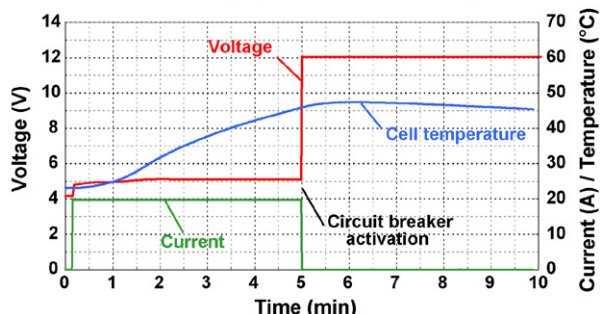


Fig. 18. MP 176065 6.8 Ah overcharge performance at room temperature under 3C. Overcharge at room temperature under 3C, after charge at C floating 4.2 V.

MP 176065 6.8 Ah short circuit performance at room temperature under 50 mOhms.

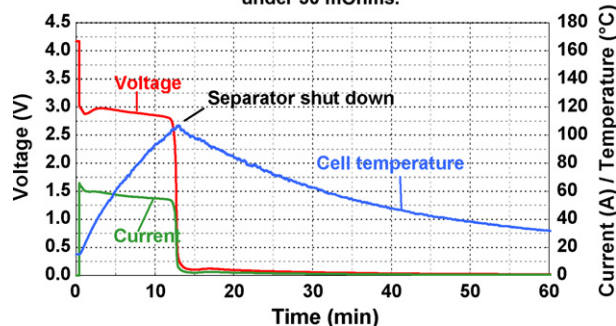


Fig. 19. MP 176065 6.8 Ah short circuit performance at room temperature under 50 mΩ. Short circuit at room temperature under 50 mΩ, after charge at C floating 4.2 V.

skin cell until the shut down effect of the separator stops the short circuit before the cell temperature reaches a potentially dangerous level.

#### 3.5.3. Heating test performance

Overheating of fully charged cells, according to the UL 1642 procedure (5 °C min<sup>-1</sup> up to 150 °C, maintained 10 min) does not lead to flames, fumes, or vent operation.

## 4. Conclusions

The development of a new graphite type with optimised physical–chemical characteristics was carried on to improve negative electrode performance. This electrode, combined with an optimised electrolyte composition, provides the new generation of Saft Li-ion medium prismatic cells with higher energy, low and reproducible fading, good discharge and charge performance in very low temperature conditions, with still a high protection level on abuse.

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