

Grant Agreement N°653373

SPiCY Deliverable D5.6

Announcement about the manufacturing of Cells

WP	5	Manufacturing implementation
Task	5.6	Announcement about the manufacturing of Cells

Dissemination level¹	PU	Due delivery date	31/04/2016
Nature²	O	Actual delivery date	30/06/2015

Lead beneficiary	CEA
Contributing beneficiaries	TUM-PROLLION

Document Version	Date	Author	Comments ³
00	15/06/2016	G.Palcoux (CEA)	Creation
01	17/06/2016	J.Schmalz/ L.Richter (TUM) contribution	TUM design
Final	22/06/2016	W.Porcher (CEA)	Review

¹ Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

² Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

³ Creation, modification, final version for evaluation, revised version following evaluation, final

Deliverable abstract

Announcement about the GEN0 cells manufacturing. Main characteristic: capacity, weight, shape, energy density.

According to the cells specifications (SPICY deliverable D1.2), Gen0 cells have been manufactured.

Four different design have been provided by 3 partners: Cylindrical wound hard packaging cells, prismatic wound hard packaging cells, prismatic stacked hard packaging cells, and prismatic stacked soft packaging cells.

The main characteristics of the cells are described.

Deliverable Review

Reviewer #1: Willy Porcher.....			Reviewer #2:		
Answer	Comments	Type*	Answer	Comments	Type*
Is the deliverable in accordance with					
the Description of Work?	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a	<input type="checkbox"/> Yes <input type="checkbox"/> No		<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a
the international State of the Art?	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a	<input type="checkbox"/> Yes <input type="checkbox"/> No		<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a
Is the quality of the deliverable in a status					
that allows it to be sent to European Commission?	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a	<input type="checkbox"/> Yes <input type="checkbox"/> No		<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a
that needs improvement of the writing by the originator of the deliverable?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a	<input type="checkbox"/> Yes <input type="checkbox"/> No		<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a
that needs further work by the Partners responsible for the deliverable?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a	<input type="checkbox"/> Yes <input type="checkbox"/> No		<input type="checkbox"/> M <input type="checkbox"/> m <input type="checkbox"/> a

* Type of comments: M = Major comment; m = minor comment; a = advice

Table of content

1. Introduction	4
2. Cells Manufacturing	4
2.1. Components & Conditioning	4
2.2. Prismatic stacked hard packaging cells.....	4
2.3. Wound cylindrical and prismatic hard packaging cells	6
2.4. Prismatic stacked soft packaging cell	9
3. Results	11
3.1. GEN0 cells characteristics.....	11
3.2. GEN0 cells capacity distribution	11
3.3. Cells characteristics	13
3.4. Gen0 cells : Weight contribution of each components	17
4. Conclusion	20
5. Annex.....	21

1. Introduction

Taking into account the cells specifications defined in the document D1.2, Gen 0 cells have been manufactured.

4 different designs have been provided by 3 partners:

30 cylindrical wound hard packaging cells manufactured by PROLLION

30 prismatic wound hard packaging cells manufactured by CEA,

29 prismatic stacked hard packaging cells manufactured by TUM,

24 prismatic stacked soft packaging cells manufactured by CEA.

The main characteristics of the manufactured cells are described in this document.

2. Cells Manufacturing

2.1. Components & Conditioning

In order to compare the different designs, all the Gen0 cells have common components (electrodes, separator, electrolyte) and have been conditioned with the same protocol. In particular, all the cells have been manufactured with LFP/ graphite electrodes provided by Prollion in October 2015, from the same batch of raw material. To remind, the characteristic of the electrodes (loading, thickness...) are described in D5.5. The separator is a tri-layers Celgard 2325 grade. The electrolyte is a blend of EC: PC: DMC in volume proportion (1:1:3) with 1M of LiPF_6 and 2%wt of VC.

The conditioning cycle is described in Annex.

2.2. Prismatic stacked hard packaging cells

The prismatic stacked hard packaging cells were assembled by TUM. Cells were delivered in May 2016 after some issues as for example the drying of the electrode which has been adapted to the LFP graphite chemistry. 29 cells were delivered.

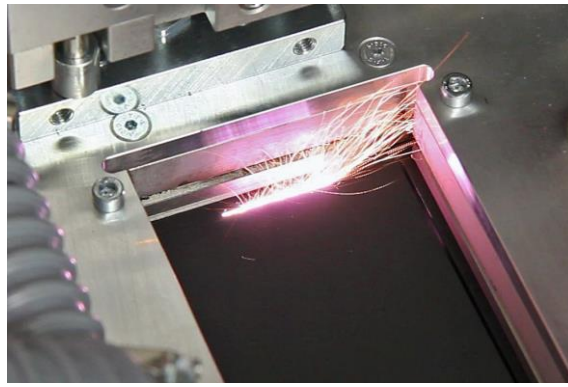


Prismatic stacked hard packaging cell (TUM); all pictures by Heddergot/TUM and iwb

The process to perform the stacks is fully done with automated equipments

- **Laser cutting of electrodes**

The electrodes were cut with a laser into single electrode sheets.



- **Z-folding with continuous separator**

In order to build the cell stack, the electrodes were stacked separately in between the z-folded separator.



- **Welding**

The stack and the taps were connected with ultrasonic welding. The cans were welded by laser welding.



- **Electrolyte filling and conditioning**

The cells were manually filled in a dry room and were conditioned subsequently inside a glove box.



2.3. Wound cylindrical and prismatic hard packaging cells

The wound and prismatic cylindrical hard packaging cells were delivered respectively in January 2016 by Prollion and in March 2016 by CEA. 2 x 30 cells were delivered. Both designs have been manufactured on the same platform, using the same equipments, except at the winding step. The equipments are designed to produce cells in series, fully automatized, except for the winding of the prismatic cells.

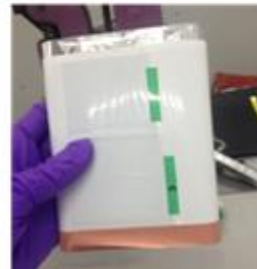


Prismatic and cylindrical wound hard packaging cell (CEA / Prollion); all pictures by Guillaudin/Cea or Avavian/CEA

- **Winding (jelly roll manufacturing)**

Electrodes and separator were wound together on a flat or cylindrical core.

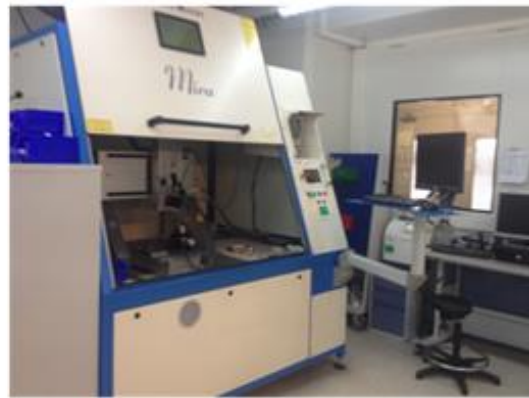




- **Cell assembly:**

The cells were assembled using different welding steps. After current collectors, top cap welding was the last assembly step.

Then, cells were ready to be filled with electrolyte using the little aperture on the cap.



- ***Electrolyte filling and conditioning:***

The cells were filled using different holders on the same machine and were conditioned outside the dry room.



2.4. Prismatic stacked soft packaging cell

The prismatic stacked soft packaging cells were delivered in June by CEA. They were the most difficult cells to produce and only 24 were successfully assembled. In fact, initially they had to be assembled using an equipment which was finally not purchased as not correctly designed. So most of the assembling was manual steps, needing a lot of manpower.



Prismatic and stacked soft packaging cell (CEA); all pictures by CEA

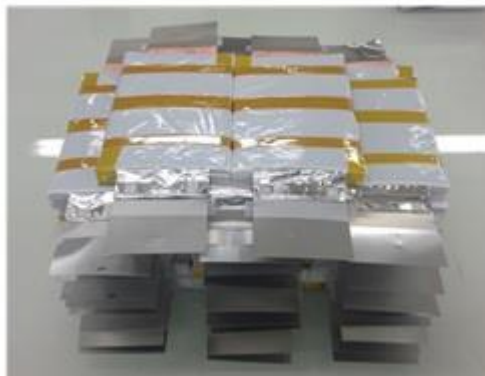
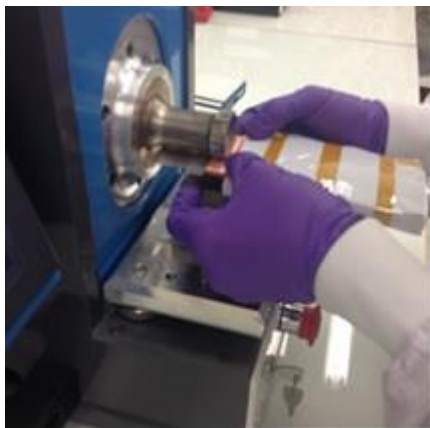
- **Electrodes and separators stacking :**

Each component, electrodes and separator of the stack was cut manually with a cutting press, then they were assembled to form the stack containing 38 anodes; 76 separators and 37 cathodes:

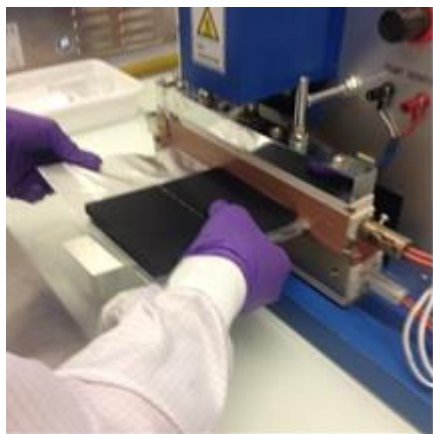


- **Welding :**

Tabs were welded on terminals.



The stacks were placed between two half shells based of aluminium and heat sealed before the filling step.



- ***Electrolyte filling and conditioning:***

The pouch cells were filled with electrolyte in a glove box and the remaining side was welded. After conditioning, the cells were degassed.



3. Results

3.1. GEN0 cells characteristics

Mean and main characteristics of the produced cells are in Table 1. It can be noticed that electrical values are not directly comparable with the specifications data. Specifications were built with C/5 C-rate, and the characterizations have been lead under C and C/10 C-rate.

It can be concluded with the values obtained at C-rate and C/10- rate that the C/5-rate specifications, which are intermediate, are reached for cylindrical and prismatic hard packaging 17Ah cells. The stacked cells, with prismatic soft and hard packaging provided by CEA and TUM, are a little under the specifications due to the design limitation.

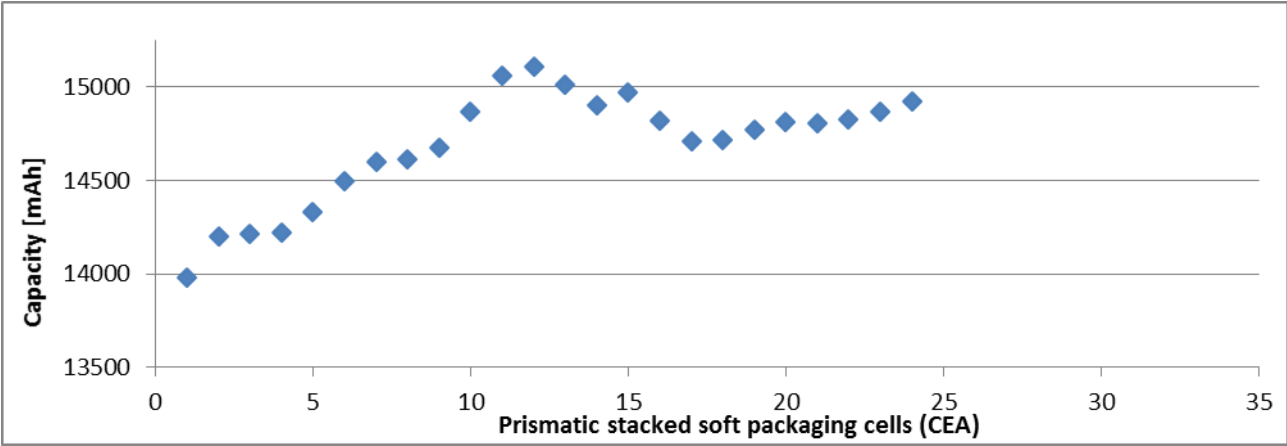
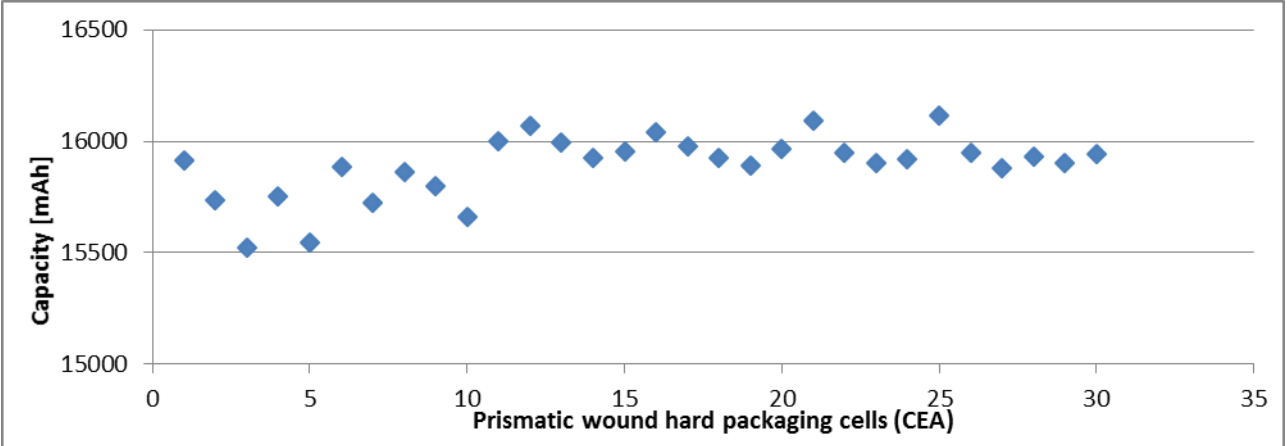
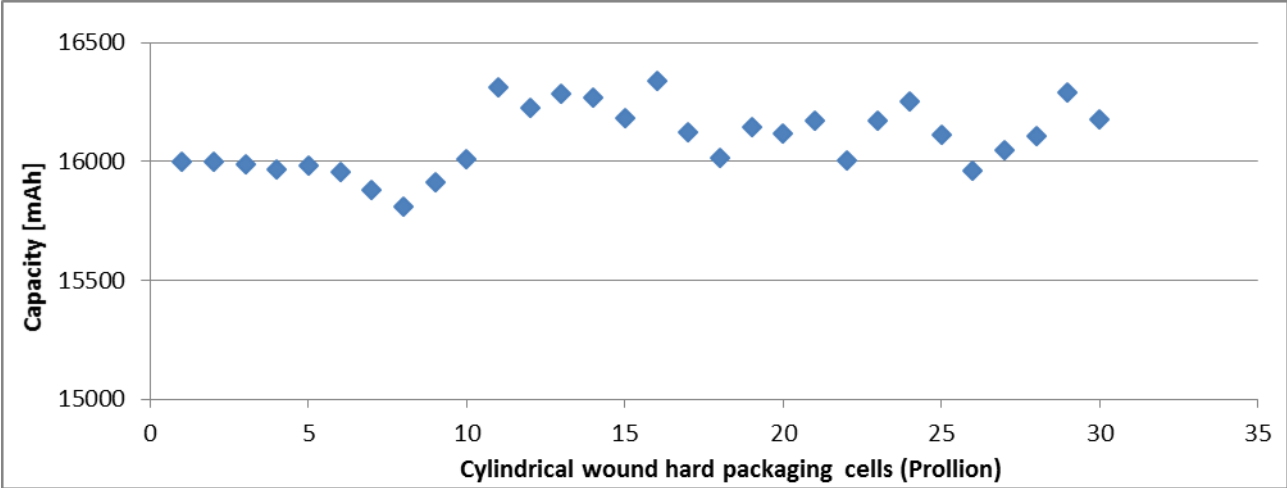
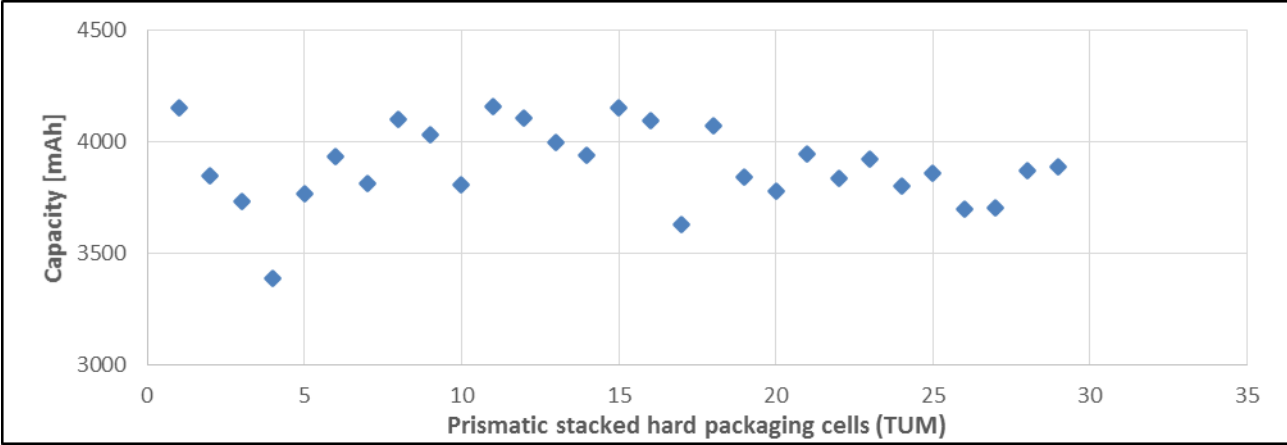
Concerning the specific energy, with a target at 130 Wh/kg with the cylindrical hard packaging, the fact that the electrochemical design was defined for a PHEV explains fully that we obtained a value of 110 Wh/kg. Noted that following the design, results are fairly different, with a casing heavier or cell less compact for a prismatic compared to a cylindrical shape with a rigid packaging. When we consider the soft packaging, with a casing so very light, more than 130 Wh/kg were obtained. For the TUM cell, the packaging is more generic and not optimized to obtain high specific energy values. Also, on a low capacity cells, the casing part is more important, explaining the value obtained.

	Average Capacity (Ah)	Minimum Capacity	Weight (g)	Specific energy (Wh/kg)	Comments
Specifications (D1-2)- under C/5 C-rate	16.6	15.8	483 Cylindrical 493 Prismatic Hard P. 400 Prismatic Soft P.	110 Cylindrical 108 Prismatic Hard P. 133 Prismatic Soft P.	
Cylindrical hard packaging @ C @ C/10	16.1 16.8	15.8 16.4	474	106 116	Average on 30 cells
Prismatic hard packaging @ C @ C/10	15.9 17.2	15.2 16.8	542	91 105	Average on 30 cells
Prismatic Soft packaging @ C @ C/10	14.7 16.2	14 15.3	394	115 134	Average on 24 cells
Specifications (D1-2)- under C/5 C-rate	5	/	270	59	
Prismatic Hard packaging @ C	3.9	3.4	278	46	Average on 29 cells

Table 1. Spicy GEN0 Cells main characteristics.

3.2. GEN0 cells capacity distribution

The Gen0 cells capacity distribution are reported in the following figures. The cylindrical hard packaging cells have the better distribution with no more than 2% of deviation. The deviation is of 3.5% for the prismatic wound hard packaging.




Reference, capacity, resistance and weight of each cell are reported in the following table for prismatic stacked soft packaging cells manufactured by CEA. The tests and planned locations are also given.

[illegible]Page 13 of 21

Reference, capacity, resistance and weight of each cell are reported in the following table for prismatic stacked hard packaging cells manufactured by TUM. The test and location is also given.

Cell specifications							
Cathode material	LFP						
Anode material	GR						
Lower Voltage limit (V)	2,5						
Upper Voltage limit (V)	3,6						
Maximum charge current (A)	4 A						
Maximum discharge current (A)*	4 A*						
Temperature operation range	[0°C, +45°C]						

*normal cycling; rate tests up to 12 A



N°	Cell reference	Cell capacity [mAh] @ 1C	Voltage before delivery [V]***	AC resistance [mOhm]****	Weight [g]	Test	Delivery
1	102	4149	3,29	17,8	278,7	Life cycling 5°C	FZJ
2	723	3849	3,29	12,3	278,5	Storage 45°C	KIT
3	725	3732	3,29	29,8	278,6	Abuse tests	CEA
4	726	3389	3,29	16,9	279,2	Life cycling 5°C	FZJ
5	728	3767	3,29	12,3	278,4	Life cycling 5°C	FZJ
6	733	3936	3,29	16,6	278,1	Abuse tests	CEA
7	734	3810	3,29	11,7	278,5	Life cycling 5°C	FZJ
8	737	4098	3,28	11,8	278,9	Abuse tests	CEA
9	742	4031	3,28	16,6	278,5	Abuse tests	CEA
10	778	3806	3,29	10,9	279,7	Life cycling 5°C	FZJ
11	779	4156	3,29	11,2	278,3	Abuse tests	CEA
12	784	4103	3,29	16,4	277,9	Abuse tests	CEA
13	786	3995	3,29	15,2	277,3	Life cycling 5°C	FZJ
14	789	3940	3,29	14,4	278,5	Storage 45°C	KIT
15	790	4154	3,29	14,9	279,4	Autopsy	FZJ
16	791	4092	3,29	15,7	278,5	Autopsy	FZJ
17	794	3629	3,29	18,7	277,9	Initial performance	Cidetec
18	798	4074	3,29	16,2	278,3		FZJ
19	799	3842	3,27	16,0	276,8	Storage 45°C	KIT
20	804	3775	3,28	16,0	277,5	Storage 45°C	KIT
21	805	3945	3,29	16,6	278,2	Life cycling 25°C	TUM
22	808	3836	3,29	16,5	278,6	Storage 45°C	KIT
23	814	3919	3,29	17,3	278,5	Life cycling 25°C	TUM
24	815	3804	3,29	17,8	278,3	Life cycling 45°C	TUM
25	816	3860	3,29	16,5	278,7	Life cycling 45°C	TUM
26	818	3698	3,29	16,5	278,5	Initial performance	Cidetec
27	820	3705	3,29	17,8	278,6	Life cycling 45°C	TUM
28	824	3870	3,29	12,3	279,2	Life cycling 45°C	TUM
29	825	3888	3,29	29,8	278,4	Storage 45°C	KIT

[illegible]Page 15 of 21

[illegible]Page 16 of 21

3.4. Gen0 cells : Weight contribution of each components

As requested for the cost analysis and life cycle analysis in the WP8, weight contribution of components and materials are reported for every designs, for each components in Table 2. In the Table 3, materials percentage are reported for every designs.

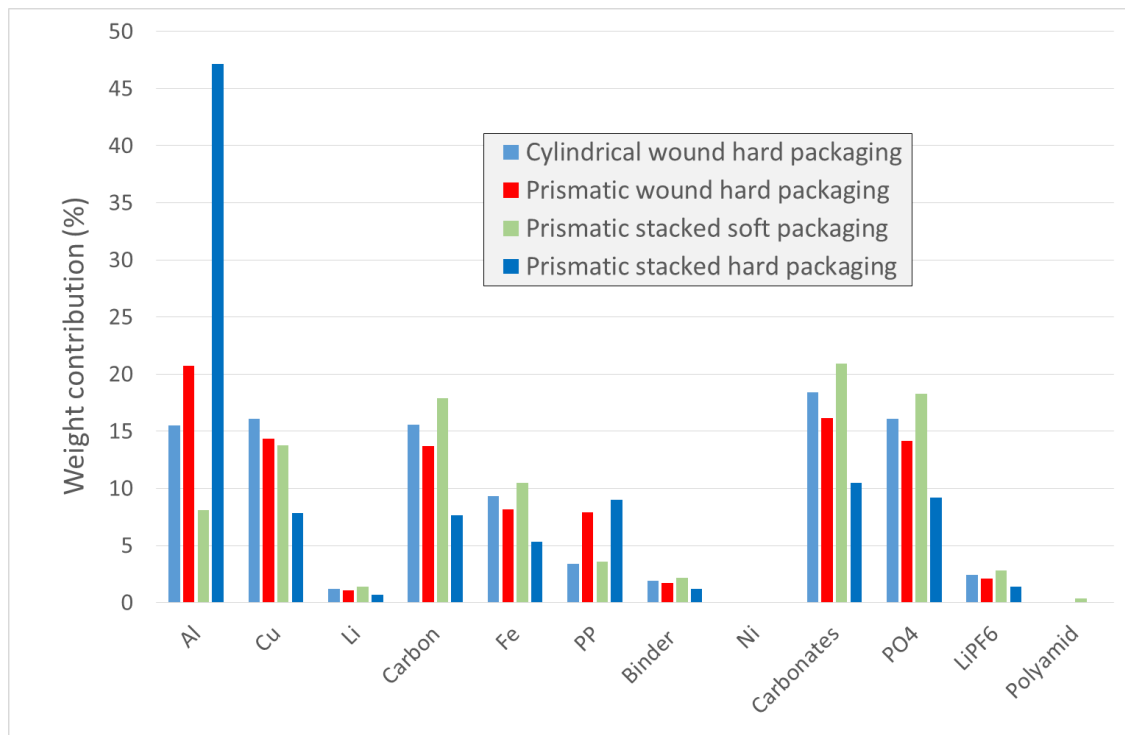
Weight (g)	Cylindrical wound hard packaging	Prismatic wound hard packaging	Prismatic Stacked Soft packaging	Prismatic Stacked hard packaging	
Electrode collector	26,78	26,78	24,49	8,24	Al
	55,53	55,53	48,59	16,81	Cu
Electrode coating					
	73,99	73,99	71,10	21,48	Carbon
	5,93	5,93	5,63	2,01	Li
	43,94	43,94	41,69	14,93	Fe
	76,43	76,43	72,51	25,96	PO4
	9,15	9,15	6,12	2,18	Binder
Separator	11,30	11,30	10,45	2,09	Polypropylene
Electrolyte					
	11,74	11,74	11,10	3,89	LiPF6
	87,40	87,80	82,90	29,08	Carbonate
Mechanical parts (packaging , collectors, core ...)					
	46,54	85,19	7,70	122,71	Al
	5,06	31,41	3,80	22,92	Polypropylene
	20,88	22,04	6,01	5,04	Cu
	0,18	0,26	0,20	0,00	Ni
			1,50		Polyamid
			0,37		Other
Total	475	542	394	278	
SPICY GEN0 cells weight average (g)	474	542	394	277	

Table 2 – Weight contribution of each component for the 4 designs

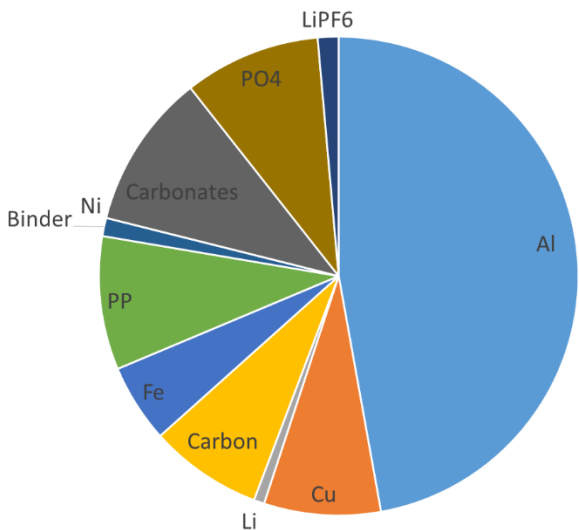
Main difference between every designs is the weight of casing first, with a strong advantage for the soft packaging. Then at a second level, the weight of the core and the internal design explain the differences.

Weight(g)	Cylindrical wound hard packaging	%	Prismatic wound hard packaging	%	Prismatic Stacked Soft packaging	%	Prismatic Stacked hard packaging	%
Al	73,32	15,5	111,97	20,71	32,19	8,11	130,95	47,22
Cu	76,4	16,1	77,57	14,34	54,60	13,76	21,85	7,88
Li	5,93	1,2	5,93	1,10	5,63	1,42	2,01	0,72
Carbon	73,99	15,6	73,99	13,68	71,10	17,92	21,48	7,75
Fe	43,94	9,3	43,94	8,13	41,69	10,51	14,93	5,38
PP	16,36	3,4	42,71	7,90	14,25	3,59	25,01	9,02
Binder	9,15	1,9	9,15	1,69	6,12	2,19	2,18	0,79
Ni	0,18	0,04	0,26	0,05	0,20	0,05	-	-
Carbonates	87,4	18,4	87,4	16,16	82,90	20,90	29,08	10,49
PO4	76,43	16,1	76,43	14,13	72,51	18,28	25,96	9,36
LiPF6	11,4	2,4	11,4	2,11	11,1	2,80	3,89	1,40
Polyamid					1,50	0,38		
Adhesive					0,37	0,09		
Total weight(g)	475		541		397		277	

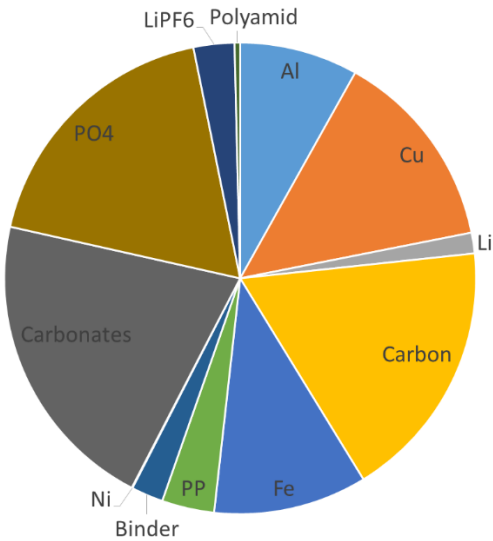
Table 3 – Weight contribution of each material for the 4 designs



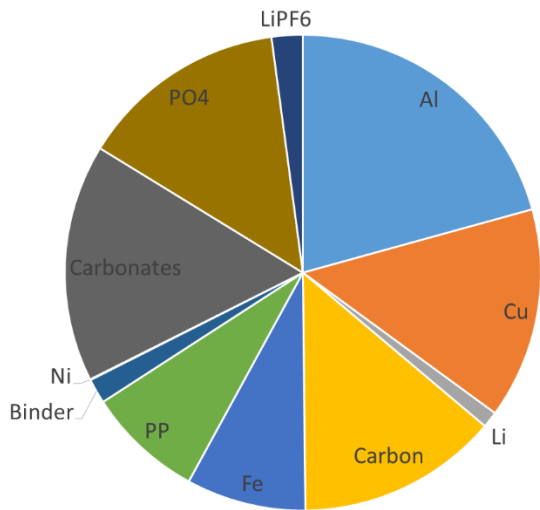
Prismatic stacked hard packaging



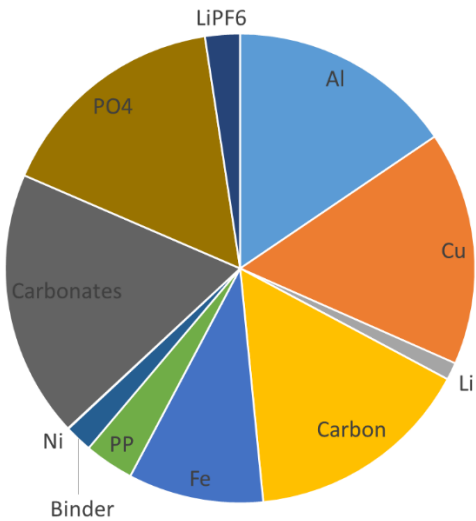
Prismatic stacked soft packaging



Prismatic wound hard packaging



Cylindrical wound hard packaging



4. Conclusion

All the cells were delivered from January to June 2016 for the 4 different designs. Even if the electrodes were reference electrode for the project, more than 6 months were necessary to assemble 2 designs:

- For the prismatic stacked soft packaging, the delay (2 months) was due to the fact that the equipment planned to make them was actually not purchased because it was not compliant with the needs. The stacks were assembled manually, required a lot of manpower and only 24 cells could be delivered. Even if this design shows the better specific energy (130Wh/kg), it is impossible to plan to make others cells for next generations with this process at CEA.
- For the prismatic stacked hard packaging, the delay (1 month) was due to the fact that TUM has to adapt its cell conception to this chemistry especially.

With all the Gen0 cells manufactured, the general distribution of capacity of the cells is globally good and should enable to have relevant evaluation of these 4 designs in WP6. The specific density energy obtained (110Wh/kg for the cylindrical hard packaging by Prollion) are compliant with what expected in D1.2, considering that the design is for a PHEV application.

Data have been provided also for the LCA in WP8, with the weight contribution of components and materials for every designs.

5. Annex

SPICY

Conditioning and Characterization cycles :

Conditioning

TUM cells: Precharge at C/10, 25°C until voltage reaches 3.0V

Other cells: Precharge at 1C for 5s

Impregnation: 10h / 45°C

Charge at 45°C and at constant current C/10 until 3.6V then charge at constant voltage until current drops to C/100

Rest 30min

Discharge at 45°C and at constant current C/10 until 2.5V

Rest ~30 min - 1h (= time to go from 45°C to 25°C)

Characterization

Charge at 1C and at 25°C until 3.6V, then charge at constant voltage until current drops to C/100.

Rest 15 min

Discharge at 1C and at 25°C to 50% DOD

Rest XXX

Internal resistance measurement (discharge 10s at C/5 then discharge 10s at C)

Discharge at 1C and at 25°C to 2.5V

Rest 15min

Charge at 1C and at 25°C to 30% SOC