

# Perspectives of Li-lon technology developments

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ASPROM - December 3rd and 4th 2013



# **Presentation of CEA & LITEN**



#### French Atomic and Renewable Energy Commission



#### CEA : 10 R&D Centers in France

#### 4 main research priorities

- Defense & Global Security
- Energy
- •Health and Information Technology
- •Fundamental Research

#### Key figures (2011-12)

- •Staff : 15 982
- •Budget : 4,2 b€
- •613 priority patents applications field

« Laboratory for Innovation in New Energy Technologies and Nanomaterials »



- $\Rightarrow$  Solar energy & smart building
- $\Rightarrow$  Transport technologies
- $\Rightarrow$  Energy sources for portable electronics
- $\Rightarrow$  Nanomaterials
- ⇒ Biomass & Hydrogen Technologies

- •Staff : 1200
- •Budget : 170 M€ (140M€ turnover)
- 840patents
- •>250 p on batteries

http://www.cea.fr/ http://www-liten.cea.fr

# Li-Ion Cell Pilot Line: Production representative environment



Semi Industrial Line: Dry room ~ 1000m<sup>2</sup> (Dew points: -20°C & -40°C)



- A stabilized design to investigate chemistries with capability to produce prototypes in a production relevant environment
- Stable Prototypes Performances, Manufacturing process definition established, Process flow validated... Manufacturing yield compatible with an industrial transfer...

# Cea Battery System from TRL3 to TRL6-8

**CEA PROPRIETARY** 



**Customer Specification**  In-field monitoring Market knowledge (BEM) Application System solution Oriented TCO approach 4 Design Safety • EE Architecture Around the pack Pack design • EE Architecture Abuse tests • Temp. control RC&S Cell tests 3 In house product / process Technology expertise Thermal conditioning /

Mechanics / Electronics



Electrical test benches: High power ~300 channels Low power (Includes formation) 480 channels

Battery Modules & pack assembly with emanagement Semi automatic assembly with full components tracking

Battery Modules & Packs Assembly ~500m<sup>2</sup> ca. 20 to 40 battery packs (EVs sizes)/month

# **Li-Ion Active Material Up-scaling platform**



Upscale of Material Synthesis (solid-state route, solvothermal route...)

- > Production of ~1Kg batches
- Process Optimization (cost, perfs...)
- Differentes synthesis routes possibles

Reminder – Rough Estimation of AM per device: Cellular Phone 5-10g – EV pack 20-60kg





# **Ceal Embedded Energy : Specific Batteries**



## Customized battery development to stand drastic conditions

#### CEA Tech Competences

CEA LITEN has an **integrated approach** from materials to system dedicated to **battery** developments :



→ CEA LITEN develops customized Li-ion technologies and designs depending on technical specifications, for example :

- Safe & Stable energy or Power batteries integrating LiFePO<sub>4</sub>

- High Energy Li-ion cells integrating high capacity electrodes

- Costs care

#### Applications

→ Prototyping (TRL 3-6) have been realized in several application fields :



#### Military application

Si-C Technology 3.4V - 1.25Ah 260Wh/kg cells Reduced cyclability For 70Wh 13.6V Si Battery pack Higher autonomy at 20°C (+60%) & -20°C (+180%) versus commercial For Energy Efficient Soldier...



**Aeronautic Large** Capacity/High Energy Li-ion cells Si-C Technology 3.4V – 40Ah 300Wh/kg (C/10 @45°C)



#### Security (beacons)

NMC/Si-C Technology 3.4V - 1.2Ah, 250-270Wh/kg Operating from -20°C to 55°C In a power mode Cospas-Sarsat approval UL1642-qualified

Micro Hybrid -

Start & Stop

**Bipolar Architecture** 

**High Power** 

Fast charge

24V – 15Wh



Spatial Sensor



#### EVs. Buses. other large vehicles, stationary

Various P/E ratio 3.3V – 10Ah LiFePO<sub>4</sub> Technology 1.9V – 11Ah Li4Ti5012 Technology Designed electrolytes, components...

NCA/G Technology 3.6V - 450mAh Cell mechanical design to sustain extreme environment (vibration, acceleration. vacuum...)







- Brief Introduction of Li-Ion Technology
- Introducing High Energy >250Wh/kg
- High Power Systems
- Perspectives



Electric Mobility, Stationary Applications



Professional, security, military, defense, aerospace applications

| PAGE 7

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 $\Rightarrow$  With new Li-Ion systems, more than 10,000 full cycles achievable





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| PAGE 10

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# CEA Li-ion Technology (Chemistries) for High Energy Status at Cell Level

#### Applied Research mostly to increase specific energy, to improve autonomy...



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# Cea The technology selected for Energy >250Wh/kg



**Positive Electrode – 2 possibilities:** 

 Commercial NMC – 170mAh/g or NCA – 190mAh/g

• HE-Lamellar Oxide - 250mAh/g (Dev.)

**Negative Electrode:** 

Si-C composite (500 to 1000mAh/g)





#### In soft packaging



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# Cea High Energy with High Capacity Negative Electrode



# NCA / Si-C lab prototypes

- Positive : NCA (NiCoAl Oxide)
  3.2 x 3.6 x 0.5 cm core
- Mixed carbonate electrolyte
- Wound Configuration

1000+ cells manufactured and assembled in dry room

#### **Graphite prototypes**

- 850 mAh
- 200 Wh.kg<sup>-1</sup>
- 450 Wh.L<sup>-1</sup>



# Si-C prototypes

- 1250 mAh
- 260 Wh.kg<sup>-1</sup> (+30%)
- 600 Wh.L<sup>-1</sup>
- Reduced cyclability for niche market (< 50 cycles)</li>







# High Energy Li-ion Battery for Energy Efficient Military/Soldier





Acknowledgements to **B** 



#### Table legends:

*Italic*= Calculated value

**Bold** = Corrected value due to additional interface resistance at electrical test bench (Pressure connection for the commercial battery not for HE battery) \*only between 80-50% SoC

Battery	HE (4S)	Competitor (3S)	Δ
Capacity @C/5 20°C (Ah)	5	4.2	+20%
Weight (g)	371	370	+0.3%
Nominal voltage @C/5 20°C (V)	13.6	10.8	+25%
Energy @C/5 20°C (Wh)	68	45	+50%
Gravimetric energy @C/5 20°C (Wh/kg)	183	120	+50%
Volumetric energy @C/5 20°C (Wh/L)	285	225	+25%
Internal resistance (mΩ)	220	330	-33%
Specific Autonomy 20°C (h) (μcycles 4,5A (6s) – 0,1A (54s))	8h30	7h20	+15%
Specific Autonomy 20°C (h) (μcycles of 45W (6s) – 1W (54s))	12	8	+50%
Specific Autonomy -20°C (h) (μcycles 4,5A (6s) – 0,1A (54s))	7h15	3h50*	+85%
Specific Autonomy -20°C (h) (μcycles of 45W (6s) – 1W (54s))	10	3h30*	+185%
Specific Energy density 20°C (Wh/kg)	163	103	+60%
Specific Energy density -20°C (Wh/kg)	136	48*	+180%

<u>Test protocol</u>: Repeated 1min μcycles, made of 4.5A-6s pulses corresponding to radio emission followed by CC 100mA-54s for reception or standby

-Higher autonomy at 20°C (+60%) & -20°C (+180%) compared to commercial battery -Specific pack design developed by AGLO-DEV for this « breathing » technology with high reproducibility in term of weight (<0.5%) and resistance (<0.5%)



+ Cycle life, self-discharge and power tests from -40 to +55°C

**Development of the NMC/Si technology** 

Research of electrolyte for low temperature applications (-20°C) in power mode

Development of batteries which can be stored at full charge

Impact test 50% SOC, 20°C, 9kg,

1000+ cells manufactured in dry room to evaluate silicon materials, electrode formulations, electrolyte compositions, separators

- At -20°C, high performances up to 2C rate
- 70% of the capacity recovered at -20°C
- UL1642 standard compatibility under progress

# 2012: Si-C 40Ah Prototypes Under Progress for Aerospace



#### Development of 35-40Ah cells, NMC & HELMO/Si-C for E > 250Wh/kg







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Electric Mobility, Stationary Applications



Professional, security, military, defense, aerospace applications

| PAGE 17

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Cea Ragone Diagram: High Power Cells





Missing data : Cycle Life, Discharge rates, Pulses or Continuous, Temperatures...

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# Electrochemical Storage Technologies Candidates for Power Applications



	Supercapacitor	LIC	Energy LIB
Cell voltage	2.3 to 2.75V	2.2 to 3.8V	2.75 to 4.2V
Specific Energy (Wh/kg)	5 (typical)	10 (typical)	100 to 200
Specific Power (W/kg)	Up to 10000	Up to 3500	1000 to 3000
Charge T°	-40 to 65°C	-30 to 70°C	0 to 45°C
Discharge T°	-40 to 65°C	-30 to 70°C	-20 to 60°C
Cycle life	1 million to 30000h	100 000	500 and higher
Service life	10 to 15 years	?	5 to 10 years
Cost per Wh	20\$ (typical)	?	0.50 to 1\$ (large system)

#### ✓ Suppliers Data

C22

- ✓ Lack of experience on LICs
- ✓ Self-Discharge data ? (supercapacitors: 50-100% /month)
- ✓ LIBs not High Power Sized here



# **Cea CEA Li-ion Cell Technologies for High Power**



#### **GEN1: LFP for High Power Discharge**

#### LFP/G



Lithium Iron Phosphate Technology – Cycle Life in a power mode (5C chargedischarge rates) exhibits only -0.0017% capacity loss per cycle upon 7500cycles...

# Cea Li-ion Cell Technologies for Very High Power



#### **CEA Li-ion Power Cells GEN1**



#### Lithium Titanate Technology

- $\Rightarrow$  Fast charge / Ultra High Power
- $\Rightarrow$  Long cycle life
- $\Rightarrow$  Low self-discharge
- $\Rightarrow$  Stable/Safe behavior
- $\Rightarrow$  Very good low temperature capability

 NMC/LTO also possible for higher energy density (~90Wh/kg)

LTO Technology competitive for Power modes if C-rates >15C

# GEN2: Interest in High Voltage Spinel Oxides

#### "5V Spinel"

- ➤ Generic composition is LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>
- > Theoretical capacity = 146.7 mAh/g at ~4.7 V vs. Li<sup>+</sup>/Li (Ni<sup>4+</sup>/Ni<sup>2+</sup>)
- > High cycle life, High rate capability, Energy density increase strategy



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CEA High Voltage Spinel Oxide: LiNi<sub>0.4</sub>Mn<sub>1.6</sub>O<sub>4</sub>



#### 5V Spinel/Graphite prototype:



**Target:** Similar Energy Density to current commercial Power sized cells but with Higher Power rate capability due to higher cells voltage (4.6V versus 3.6V) and lower battery oversizing due to higher discharge rate capability especially at low Temperature

#### By replacing Graphite by



- $\Rightarrow$  Fast charge / Ultra High Power
- $\Rightarrow$  Higher low temperature capability



# Li-ion Power Technologies Perspectives / Next Gen.

#### **CEA Li-ion Power Cells GEN2**

'3V' Li-ion Cell by coupling of 5V Spinel with LTO



#### **5V Spinel versus LTO**

- Higher Power capability at low temperature
- Higher DOD (higher useful capacity or lower oversizing)
- No Li plating event (safer)
- Lower Self-discharge (compared to graphite)



# **BUT** (Compared to Graphite)

- More cells in series to increase battery voltage
- Lower energy density <100Wh/kg</p>









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# Power Technologies versus Applications Examples Rechargeable Image Safe Ultra High Power Image Infe Safe Safe

- ✓ Autonomous Heavy Duty Vehicles >500kW, >20kWh
- Stationary ESS: Other targeted application field (not discussed here)



Source: ESA (RT Efficiency versus Cycle Life)

## In use tests

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integration and validation

Design and manufacturing of packs

- kW in 5mn => cooling / mechanical
- ✓ System integration tests on the CEA test bench. Bus integration.
- Key issues : end of bus line charge = 250
- **180 kW, 4 min (at least 20% of capacity)**. Voltage of the battery : between 400V and 600V

Electric Energy Storage with Power Capability

Demonstrating Project under progress (ElLiSup)

#### **CEA Work:**

(ca. **15000 cvcles**)





CEA Grenoble Scale 1 Demonstration



e-BUSES

# Cea LFP/G TECHNOLOGY IN POWER MODE

Embedded energy 12 kWh (Mini) discharged in 26min. Charge Max Power :



e-BUSES Electric Energy Storage with Power Capability

**Battery Design** 

- ✓ 4 battery packs, their cooling system and BMS
- ✓ 480 kW DCDC converters for the main power
- Power box (fuses, contactors)
- ✓ 4 inverters (for communication) and 1 motor for power
- $\checkmark$  2 DCDC converters for the 24V auxiliaries bus
- ✓ Vehicle central unit

#### Station Design

- ✓ Key issues : harmonics, noise, perturbation on the grid, 250 kW safe interface with the bus
- Flectrical and thermal architecture
- Power electronics definition
- Manufacturing by sub-contractor
- ✓ System tests with the bus

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# **Ceal LFP/G TECHNOLOGY IN POWER MODE**

CEA Battery Modules

250kW charging station







# **12V Li-ion Starter Battery for Stop & Start Vehicles**

Li ion Startar Patton, Spacifications

#### Concern

- Exemption Risk on Lead Starter Batteries reviewed in 2015
- Lead : Today 25-27kg (full display)
- Average current life time = ca. 5 years (i.e. : 80% of French users)
  - => Take advantage of Li-ion in term of charge sustaining (CO<sub>2</sub> reduction)

#### Performances requirements are summarized below:

**Current Design with Lead-Acid Battery** Energy C(20h) = 70 AhPower 760A (EN) Working Temp [-30°C ; 75°C] 12Vnet Fully compatible with 12V network **Battery Target Design with Li-ion** 

Typical requirement: C(20h)=(70 Ah) Typical requirement: 760A (EN) Typical requirement: [- 30°C ; 75°C] Fully compatible with 12V network



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LI-IUII Starter De	allery specifications.	
Unom = 12V		C. P.
lmax = 760	<mark>0A</mark> , 10s @- <mark>18°C</mark> 100% SOC	
47:	5A, 10s @- <mark>30°C</mark> 100% SOC	
988	8A, 1s @23°C 80% SOC	200
Umin = 7.5V 10	s -18°C @Imax	
Charge accepta	nce: 100A @0°C & 50%SOC	
	200A @25°C & 70%SOC	
Capacity: 10Ah	min EOL	
Weight: 10kg m	nax Volume: 9.14L max	Energy: 120Wh EO
Max Operating	T°: <mark>80°C</mark> (Mean 50°C)	(12Wh/kg min
Max Calendar T	°: 100°C	Pmax: 11856W





capacity

# 12V Li-ion Starter Li-ion Proposed Solution



- $\Rightarrow$  LFP/LTO solution allows responding to the needs with weight < 10kg
- $\Rightarrow$  Best chemistry in SAFETY and CYCLE LIFE for such charge & discharge rates
- $\Rightarrow$  Demonstrated by CEA under Start & Stop mission profiles with 0.7Ah 24V cells :



 $\Rightarrow$  LFP/LTO accumulator allows to restitute ca. 30000 times more than 40% of its total capacity at very high rates (>>50C) in both charge and discharge modes







different temperatures (25, 40 et 55°C)

- $\Rightarrow$  Extended cycle life
- ⇒ No Capacity Loss after 6000 cycles 100%DOD@C-Rate (RT) with 20% increase of Internal Resistance
- ⇒ Very low self-discharge : 10% capacity loss extrapolated after 6 years at 20°C or ca. 20% after 3 years at 35°C
- ⇒ Safety Tests successfully passed w/o passive or active safety display

# LFP/LTO TECHNOLOGY FOR ULTRA HIGH **POWER MARKETS**



#### HEAVY DUTY VEHICLES Autonomous between stations



#### **Example of Required Specification :**

-Partial Cycling Hypothesis for >100k Cycles with ability to sustain >200k peaks @15kWh Storage Systems Sizing w/o hybridization (Super Capacitors)

#### - Parameters of interest:

Charge power / Discharge maximum level Available Energy and Restituted Energy/kWh

	CEA Pess	CEA Med	CEA Opt	Lipo	LFP-G	SC	
Energy density	60	60	60	142	107	5	Wh/kg
Max DOD for µcycles #	5	7,5	10	1	2	100	DOD %
Restituted Energy	7884	11826	15768	3731,76	5623,92	13140,00	Wh I
Requested Mini Weight	1633	1089	817	3451	2290	980	kg
Embedded Energy	98,0	65,3	49,0	490,0	245,0	4,9	kWh
(Power peaks to sustain not taken into account)							

(Power peaks to sustain not taken into account....

 $\Rightarrow$  LFP-LTO = End of life OK with needed DOD

 $\Rightarrow$  Others = need SC hybridization for life cycle > 2 500 000  $\mu$ cycles

# TECHNOLOGY DEMONSTRATION EXPERIMENTAL RESULTS FOR LFP/LTO



LFP/LTO





 $\Rightarrow$  **Power capability @+20°C :** 10C power available in charge/discharge modes quasi-stable over 20 to 90% SOC

 $\Rightarrow$  Cycling : After 2.5 months cycling (customer profile), good IR stability no significant effect of DOD%. Expected > 100 000 cycles

 $\Rightarrow$  Calendar ageing : Irreversible capacity loss < 6% upon 6 months storage at different T° (up to 40°C). Good OCV stability during storage



# **Cost of Battery Pack Analysis**



Case n°1 : e-BUS Specifications

- Pack Energy > 20kWh
- Charge power ability = 260kW, 20s.

Techno	LFP / LTO	LFP / Graphite	LFP / Graphite
Type of cell	high Power	Energy	Power
pack config.	4P x 312S	8P x 192S	6P x 192S
Nbr of cells	1248	1536	1152
cell shape	50-125 cyl.	50-125 cyl.	50-125 cyl.
cell nominal Capacity (Ah)	11	16	10
cell nominal Voltage (V)	1,9	3,2	3,2
Pack total Energy (kWh)	26	78,6	36,9
Discharge Power (kW)	213	213	213
Cell Discharge Rate (equiv. xC)	9,1	3,0	6,4
Charge Power (kW) (duration=20s)	260	260	260
Cell Charge Rate (equiv. xC)	8,6	3,0	6,4
Cost calculation , hypothesis= 500 packs/year			
Pack battery Global Cost (cells+ pack system) ( k€)	100-110	100	65
Pack battery - Cost of Energy (k€ / kWh)	4,0	1,27	1,76
Pack battery - Cost of power (€/kW)	404	385	250

- Cost of Power : LTO = about x 1,5 LFP/G power pack solution
- Pack Weight, Volume : nearly the same in case of using LFP/G power cells

Case n°2 : Simulation in the scope of a high power charge requested application

- Pack Energy > 20kWh = Unchanged
- Charge power ability = Power pick of ~900kW, up to 5-10s

Techno	LFP / LTO	LFP / Graphite	LFP / Graphite	I
Type of cell	high Power	Energy	Power	
pack config.	4P x 312S	24P x 192S	18P x 192S	
Nbr of cells	1248	4608	3456	
cell shape	50-125 cyl.	50-125 cyl.	50-125 cyl.	
cell nominal Capacity (Ah)	11	16	10	
cell nominal Voltage (V)	1,9	3,2	3,2	
Pack total Energy (kWh)	26	236	110,6	
Discharge Power (kW)	213	213	213	
Cell Discharge Rate (equiv. xC)	9,1	1,0	2,1	
Charge Power (kW)(duration=5-10s)	900	900	900	
Cell Charge Rate (equiv. xC)	30	65	7,4	Ор
Cost calculation , hypothesis= 500 packs/year				1
Pack battery Global Cost (cells+ pack system) ( k€)	100-110 = unchanged	285	180	1
Pack battery - Cost of Energy (k€/kWh)	4,0	1,21	1,63	1
Pack battery - Cost of power (€/kW)	117	317	200	1

 Cost of Power: LTO = about divided by 2 vs. LFP/G power pack solution
 Pack Weight, Volume : about 3 times higher if using LFP/G power cells
 Use of LFP/G Energy cells is clearly not competitive !!

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Electric Mobility, Stationary Applications



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| PAGE 36

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3 classes of Positive Electrodes: 3V (LFP) 4V (Std) or 5V (Dev)

➢ 3 classes of Negative Electrodes: Graphite (Std), Ti-Based (High Power, Durability), Sibased (High Capacity)

 $\Rightarrow$  "easy" to adapt to customer's specifications

\* Source GM

- $\Rightarrow$  already five of the nine combinations are commercialized
- $\Rightarrow$  Perspectives at 400Wh/kg and 1000Wh/L Volum. Energy Density >> Li-S and Li-Air  $^*$

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# Still a place for significative improvement of Li-Ion Technology



Positive Electrodes with 2 electrons per Transition Metal (Li-Rich Oxides or Polyanionic)

- Stabilized Si-Based Negative Electrode
- $\Rightarrow\,$  Perspectives at 400Wh/kg and 1000Wh/L Volum. Energy Density >> Li-S and Li-Air  $^*$

• Source GM Beyond Li-Ion 2012	Current Li-ion	Optimistic Li-ion*	Optimistic Li-Sulfur*	Optimistic Li-Air*
Specific Energy Density - Wh(total)/kg (cell)	250	530	550	710
Specific Energy Density  - Wh(total)/kg (system)	150	290	300	280
Energy Density - Wh(total)/liter(cell)	520	1050	620	760
Energy Density - Wh(total)/liter(system)	230	375	260	240

\*Assumes Li-Metal negative





 $\Rightarrow$  2020 KPIs (Ref. STRATEGIC ENERGY TECHNOLOGY PLAN © European Union, 2011) :

Li-ion Batteries KPI = 10-year battery design life and 20-year power and balance-ofsystem design life; Charge-discharge T° range: -20°C to 70°C; Charge cycles: greater than 10 000 times at 70-80% DOD; Fully installed system (All-in cost to install a step-up transformer) under 200€ per kilowatt-hour

Supercapacitors KPI = Energy densities >15Wh/kg; A cost reduction down to maximum of 10 €/kW and a specific power > 30kW/kg \* KPI: Key Performance Indicator







# Cea High Power KPIs \*/ Markets / Perspectives



Large Volumes Markets: ✓ Start & Stop: 2015 Market size \$242.6M





#### **Small Volumes High Added Value Markets:**

- ✓ Autonomous Heavy Duty Vehicles >500kW, >20kWh
- Aerospace (helicopters, launchers, radar satellites...),
   military...







# Thank you !

## **End of lecture**



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| PAGE 41