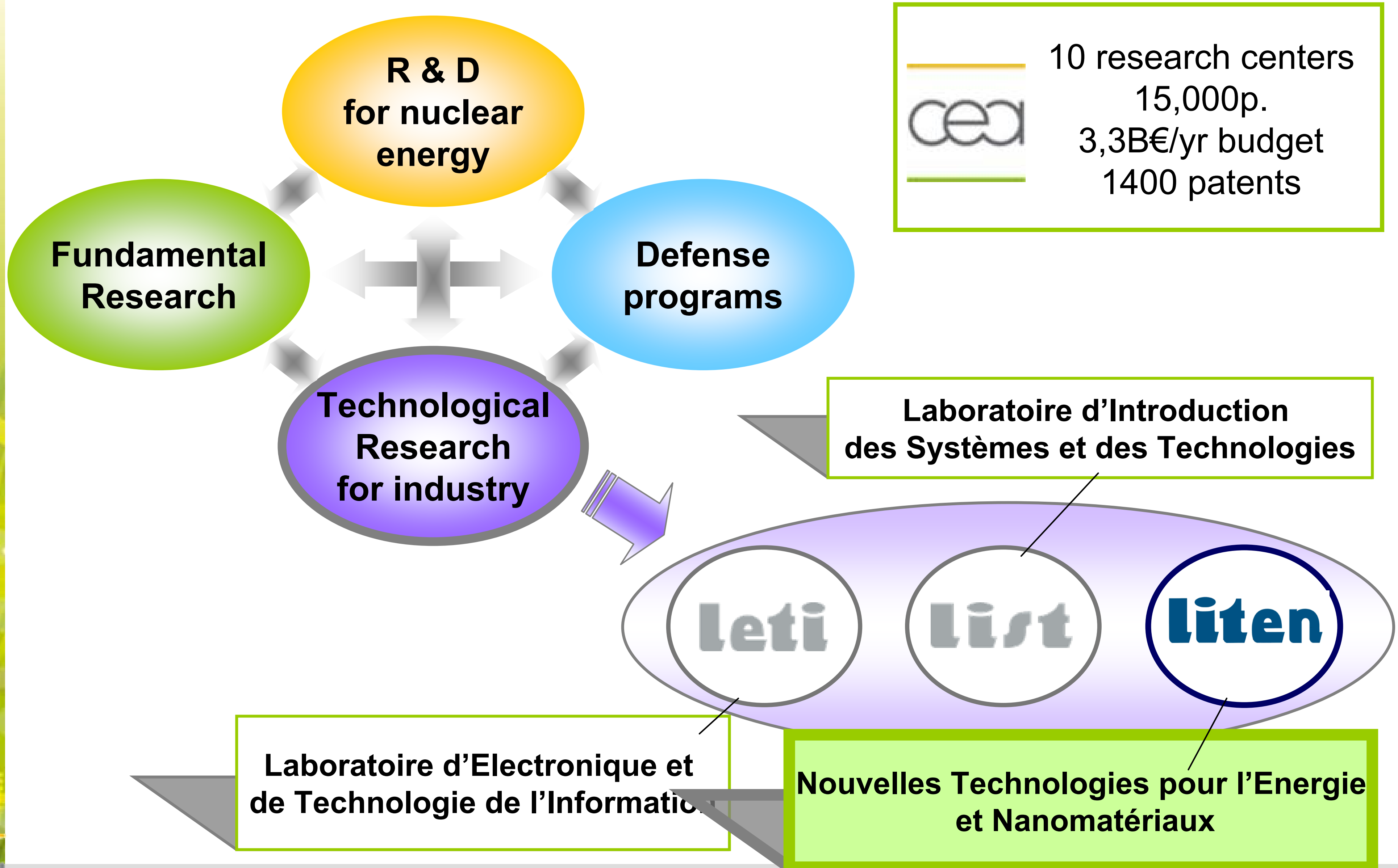
Développement des accumulateurs et µ-batteries Li-ion au CEA - LITEN

Frédéric LE CRAS

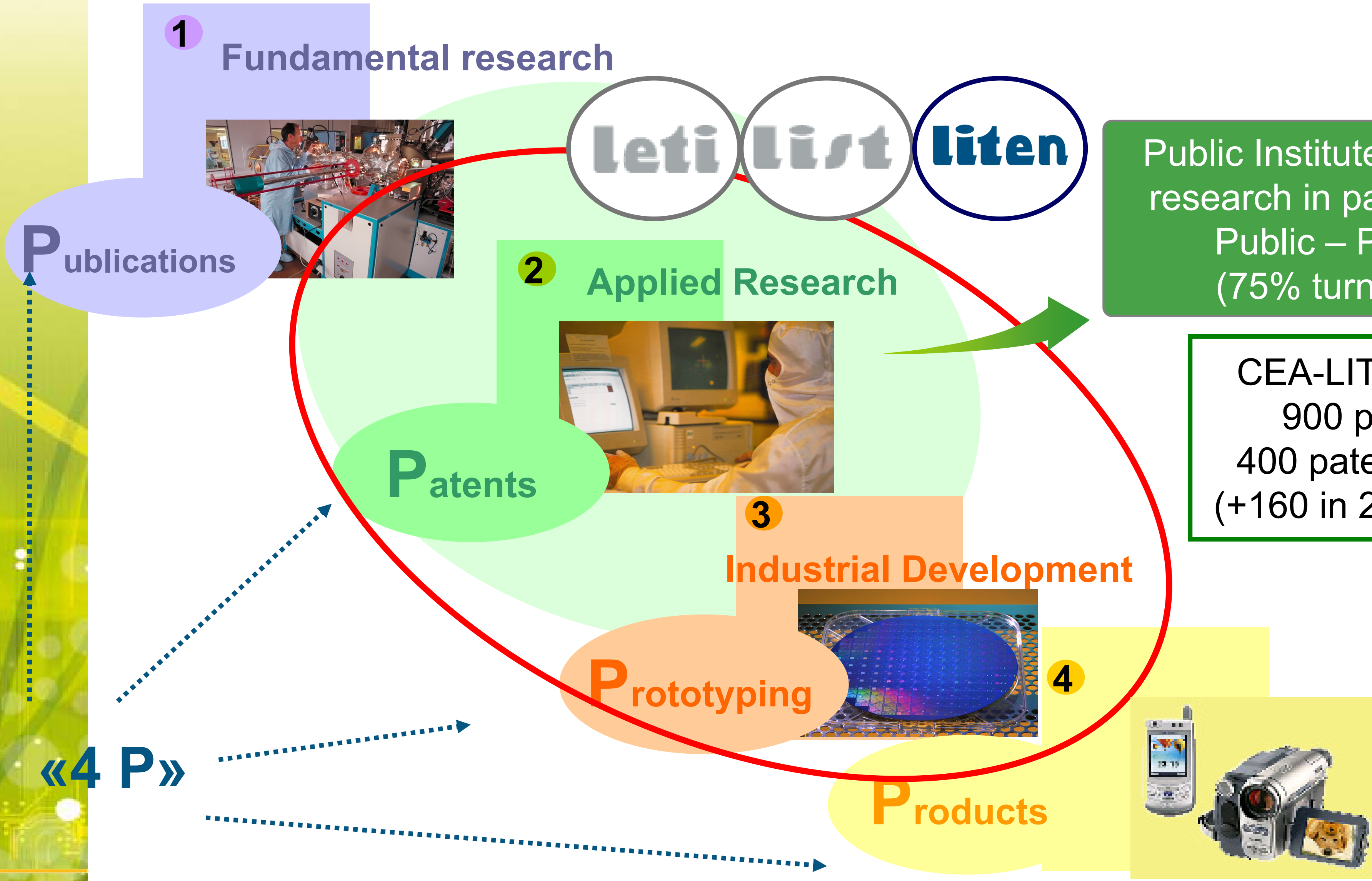
Sommaire

- Introduction : CEA Liten
- Accumulateurs Li-Ion: développements
  du prototypage à l'industrialisation
- Axes de développements des batteries Li-Ion
  → besoins :High Energy / High Power-Fast Charge Li-Ion cells
- µ-batteries au lithium et Li-ion: solutions de stockage innovantes pour l'alimentation des microsystèmes

CEA : Energie Nucléaire et Energies Nouvelles



CEA - LITEN : De la Recherche à l'Industrie



Public Institute making research in partnership Public – Private (75% turnover)

CEA-LITEN
900 p.
400 patents
(+160 in 2010)

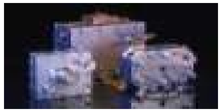
Développements au CEA-LITEN

Automotive Market	Building Market	Nomad Market	New fuel Market

New Energy for Transportation

Electrical Powered

Hybridizing
Fuel Cell / **Batteries**,
storage and delivery
Energy Saving / Storage
Electrical Conversion / management

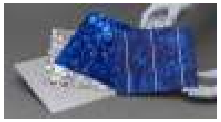



ines INSTITUT NATIONAL DE L'ENERGIE SOLAIRE

New Energy for building

Solar Energies

Thermal and
Photovoltaic cells
Electrical Systems
Energetic efficiency
Building integration

New Energy for nomad devices

Hybrid components

Micro-Power Sources
*incl.*Organic components
based on
NanoTechnologies



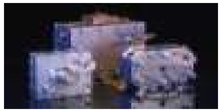
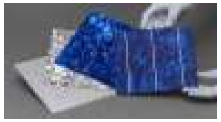
New Energy from biomass

Novel fuel

Biomass to liquid,
Massive hydrogen
production
Hydrogen storage


More than <u>150</u> people developing Li-ion batteries
from the materials and their characterization to electrode coating, cell prototyping, battery management systems, testing, modeling, LCA,…

Développements au CEA-LITEN

Automotive Market	Building Market	Nomad Market	New fuel Market
New Energy for Transportation	**New Energy for building**	**New Energy for nomad devices**	**New Energy from biomass**
Electrical Powered	**Solar Energies**	**Hybrid components**	**Novel fuel**
Hybridizing Fuel Cell / **Batteries**, storage and delivery Energy Saving / Storage Electrical Conversion / management	Thermal and Photovoltaic cells Electrical Systems Energetic efficiency Building integration	Micro-Power Sources *incl.*Organic components *based on* NanoTechnologies	Biomass to liquid, Massive hydrogen production Hydrogen storage
 	 	  	 

More than <u>150</u> people developing Li-ion batteries
from the **materials** and their characterization to electrode coating, **cell prototyping**, battery management systems, testing, modeling, LCA,…

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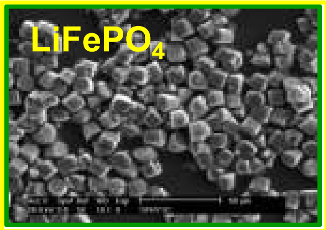
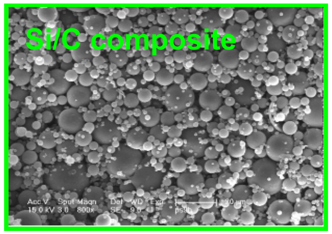
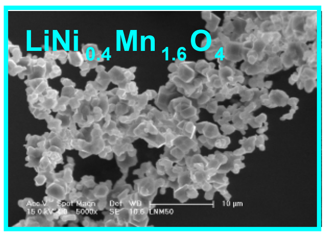
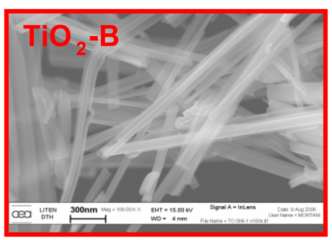
Li-ion material development and characterization









Electrodes materials synthesis

Positive electrode
- *Safe Polyanionic materials ($LiFePO_4$…)*
- *High Voltage Spinel oxides*
- *High Capacity Layered oxides*

Negative electrode
- *High Power Titanium Based Compounds*
- *High Capacity Si/C composites*

Electrolytes

salts, solvents, additives, ILs

Membranes

new materials

New systems

Li/Sulfur, Li-air, Li-water,..

TEM,…

Hydrothermal synthesis

Spray drying

Lab, Pilot

Microwaves

Ball/jet milling

30g

Freeze-drying

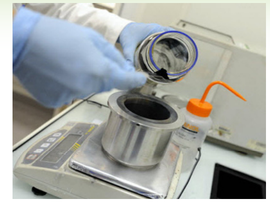
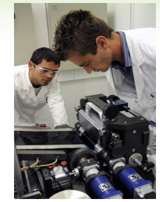
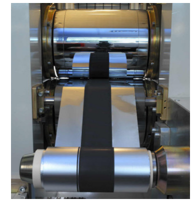
200g

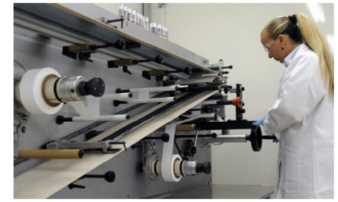
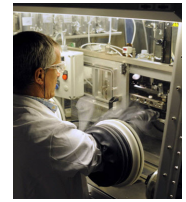
Furnaces

1–2 kg

5-10kg

Li-ion batteries prototyping

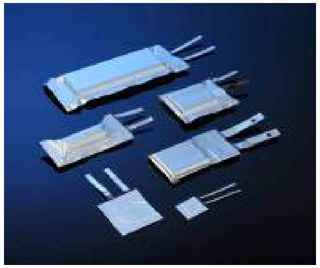
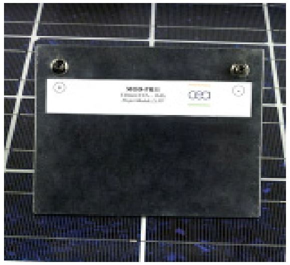




Electrodes / Cells prototyping

Electrode formulation and rheological characterization, coating
Electrode calendering and slitting
Cell winding, assembly
Electrolyte filling, crimping, welding

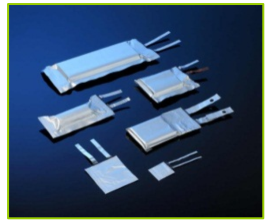
A 130m² dry room with 3 areas
Dew points: -20°C and -40°C
Line capability from 5 to 15kWh/month

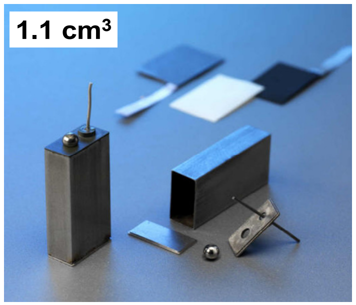
On-demand Li-ion batteries :


Li-ion batteries prototyping : On-demand Li-ion batteries at CEA-LITEN

From 1mAh to 40Ah cells (including bipolar technology)





SAFT chemistry inside

Sensors

3.2V - 40 mAh
-0.01% / cycle
$LiFePO_4$-B/Graphite
Efficiency > 99%

Medical Implants

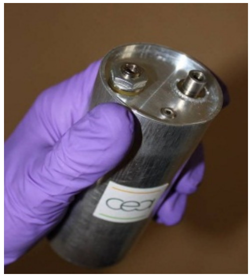
3.7V - 50 mAh - 2.45 g
10 years at 37°C
4000 cycles
Layered oxide/Graphite

Safety tests performed successfully

Strong weldings
High tightness

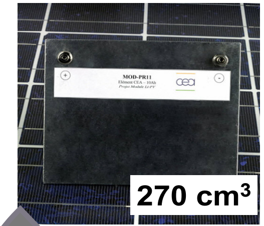
After nail test

Overcharged cell



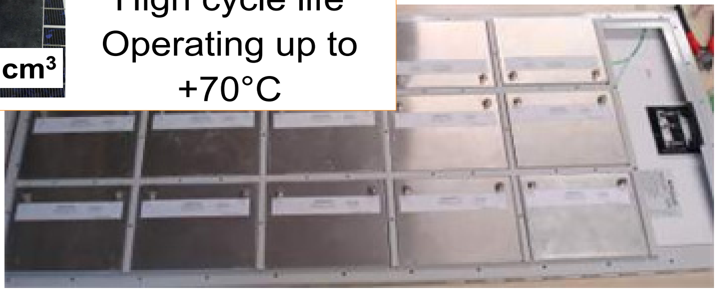
EVs

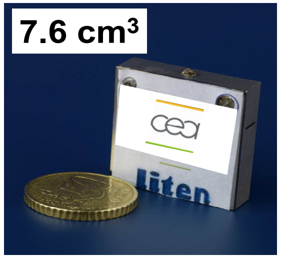
1.9-4.3V
-
20 Ah



Photovoltaic

3.2V - 10 Ah
High cycle life
Operating up to
+70°C





Spatial Sensor

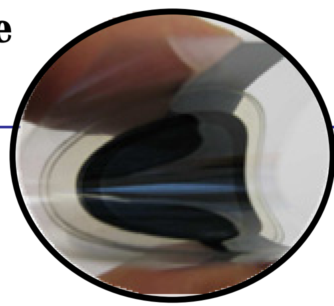
3.7V - 350 mAh
Cell for extreme
conditions

Lithium-Ion

Thin Film Batteries (TFB)

(Thin, Conformable-Flexible & Printed Batteries)

Advantages	**Flexible** · **Green** · Low cost · **Rechargeable** · **Mass production** · **Multiform** · 2-D Product integration · Thickness · Multi substrate · **OTHERS ??**



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Thin Flexible Batteries

	Cathode / Anode	Electrolyte/Membrane	Current collectors	Substrat
Materials	■ $LiCoO_2$ / Graphite ■ $LiCoO_2$ / $Li_4Ti_5O_{12}$ ■ $Li(Ni_xMn_yCo_z)O_2$ /Graphite ■ $Li(Ni_xMn_yCo_z)O_2$ /$Li_4Ti_5O_{12}$ ■ $LiFePO_4$/Graphite ■ $LiFePO_4$/$Li_4Ti_5O_{12}$	■ Liquid electrolyte with separator (PvdF…) ■ Gelled electrolyte	■ Cupper, aluminum ■ Conducting polymers …	■ Bent or plane surface ■ Glass ■ Wood ■ Plastic ■ Textile ■ Paper ■ Metal ….

Process

- **Different process available inspired from printing industry in aqueous/organic media :**
  - **Screen printing**
  - **Gravure printing :**

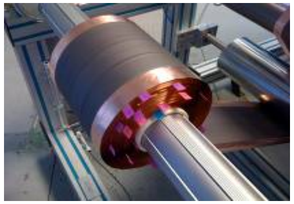
  Flexography/Heliogravure

Equipments

- **Printing Lab & Pilot tools for industrial transfer :**
  - **Coating (Slot die), 3m/min**
  - **Screen printing : sheet by sheet and Reel to Reel in dry room**
  - **Flexography/Heliogravure with/without Screen printing**

Li-ion batteries Pilot line

Semi Industrial Line – End 2010
Dry room extension > 400m²
New facilities (>1000m²)
Line capability up to 500kWh/month



Major Partnerships allowing CEA battery activity to ramp up steadily

RENAULT NISSAN PRAYON esa PROLLiON SOLVAY

and more…

PROLLiON

Li-ion Battery pack manufacturer created end of 2009

ALCEN

PROLLiON Business Model

R&D Expertise

Research, Valorization & Technology Transfer

CEA Liten

ALCEN Group

Industrial Expertise

Market Development

Defense
Aerospace
Energy
Medical

PROLLiON

Industrialization, Business development
Marketing/Sales
Customer Support

Li-ion cells and batteries systems

Company

PROLLiON develops and manufactures custom-designed cells and battery systems, from the most innovative Li-ion technologies to meet high demanding customer needs

- Breakthrough performances: autonomy, power, energy
- Severe environments: thermal, mechanical
- Volume constraints
- Reliability, safety, …

Applications

- Stationary systems: renewable energies, grid support, …
- Electric vehicles: buses, light electric trams, light vehicle fleet, …
- Defense: soldier of the future, radio communication, unmanned vehicles (UAVs, UUVs, …
- Aeronautics and Space (autonomous sensors, ...)
- Sea and Underwater applications
- Medical: implantable medical devices, …
- Distress beacons, seismic sensors
- …

Products

Li-ion Technology Cells

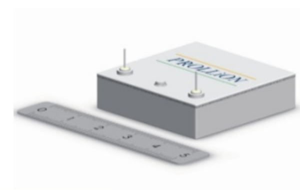
Performance :

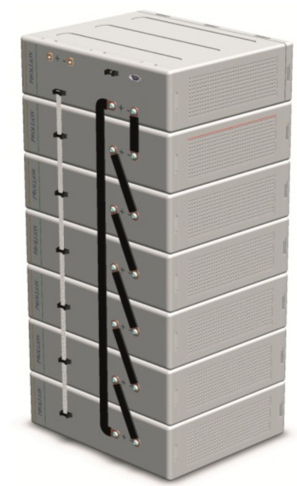
- Capacity from 10 mAh to 35 Ah
- Energy density up to 250 Wh/kg
- Specific power up to 3000 W/kg
- Ultrafast recharge up to 80% capacity recharge in less than 5 minutes
- Extreme temperatures : from -50°C to above +100°C

Li-ion Technology Battery Systems

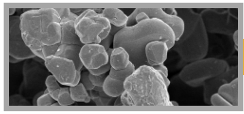
Functions et performance :

- System architecture : mechanical, thermal, electronic, electro technical
- Smart function, energy management, protection, communication, …
- Voltage up to 850 V
- Explosive atmosphere (Atex)





Manufacturing Equipments



- Mixing
- Coating
- Slitting
- Calendering
- Drying
- Winding
- Cell assembly
- Electrolyte filling
- Formation
- Sorting

- Module assembly
- Electronic integration

- Battery pack assembly
- BMM integration

Key Partners

cea

TRONICO

EPSILON GROUPE ALCEN

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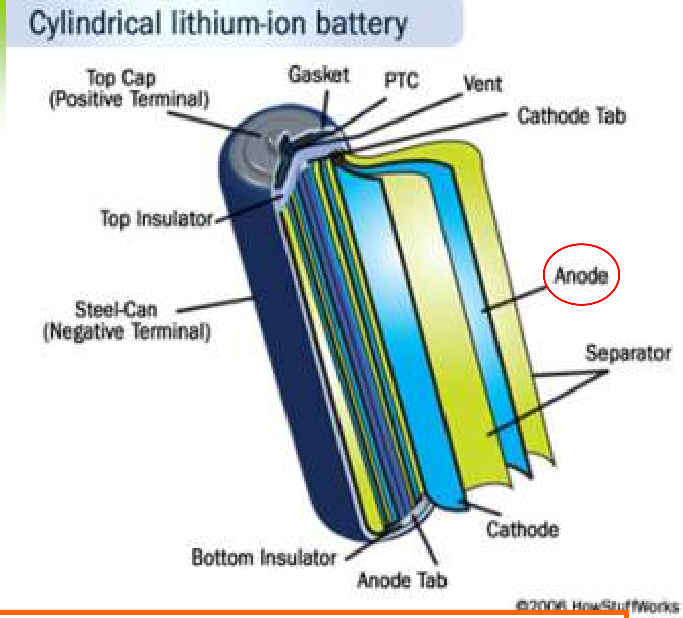
  innovantes pour l'alimentation des microsystèmes

Augmentation de l'Energie: How?



- Introducing Si-C composite negative electrode

Advantages

High capacity **3570mAh/g for Si/C vs practical 330mAh/g for graphite** :

$15\ Li^+ + 15\ e^- + 4Si \leftrightarrow Li_{15}Si_4$

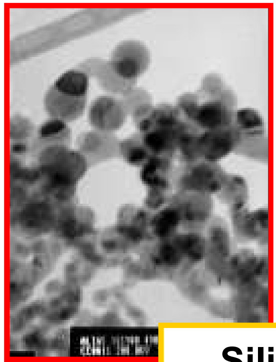
Reversible capacity « targeted » **1000 mAh/g**

Problems

- Volume changes ($Si – 0.25Li_{15}Si_4$): **+280 %**

⇒Discrepancies, disconnections from electric circuit…

⇒High irreversibility



Silicon from 20 to 50nm with carbon

Investigations

- **Nano structuration** to limit the mechanical damage, design of new binders, formulation of defined association of particles / binder for better cyclability…

Example of High Energy : Application with Si/C (-)

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

- Wound Configuration

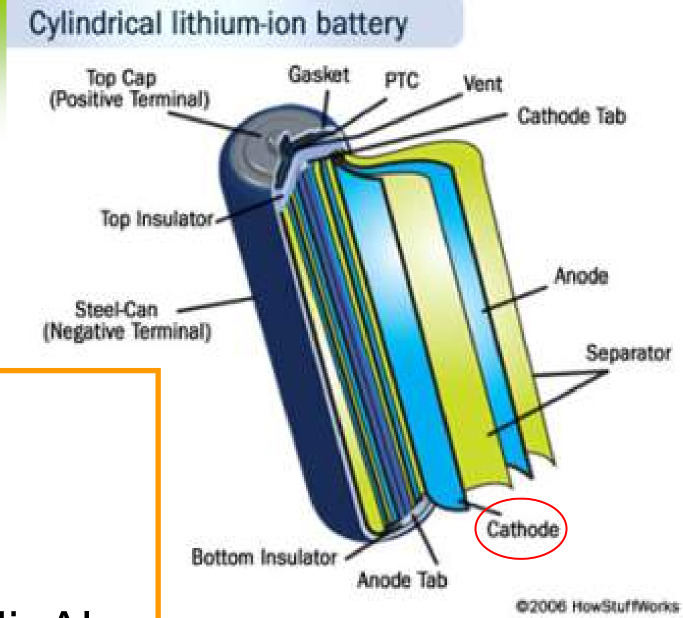
Graphite prototypes

- 850 mAh
- **200 Wh.kg^{-1}**
- 450 Wh.L^{-1}

Si-C prototypes

- 1250 mAh
- **260 Wh.kg^{-1} (+30%)**
- 600 Wh.L^{-1}
- Reduced cyclability for niche market

Augmentation de l'Energie: How?



- Introducing High Energy positive electrodes

- The layered oxides (LO) for positive electrode studied since 1980 (J.B. Goodenough)

→ $LiCoO_2$ (**LCO**) – Typically 140-150mAh/g, 3.7V vs Li

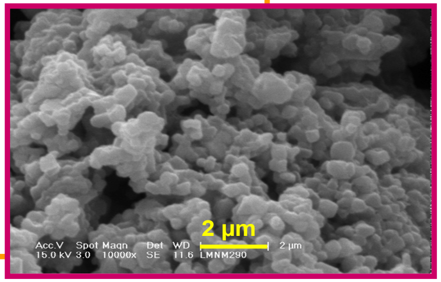
- Numerous substitutions for Co for the last 30 years (Ni, Al, Mg,…) and Mn in late 90's

→ e.g. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (**NCA**) and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (**NMC**)

- **Li-rich Mn-based layered oxides** first by the Thackeray's group at ANL, in the 00's

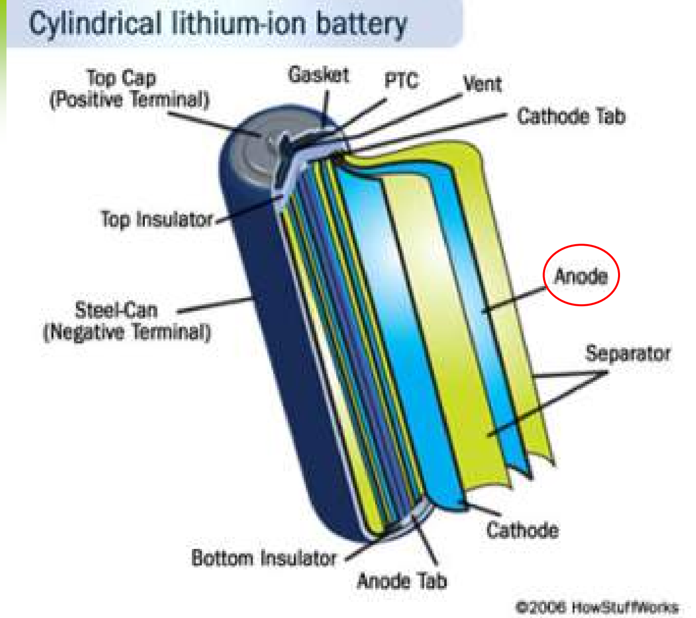
→ $xLi_2MnO_3 \bullet (1-x)LiMO_2$ with M=Mn,Co,Ni,… 3.5V vs Li

⇒ **Potential at 300mAh/g (HE-LMO)**



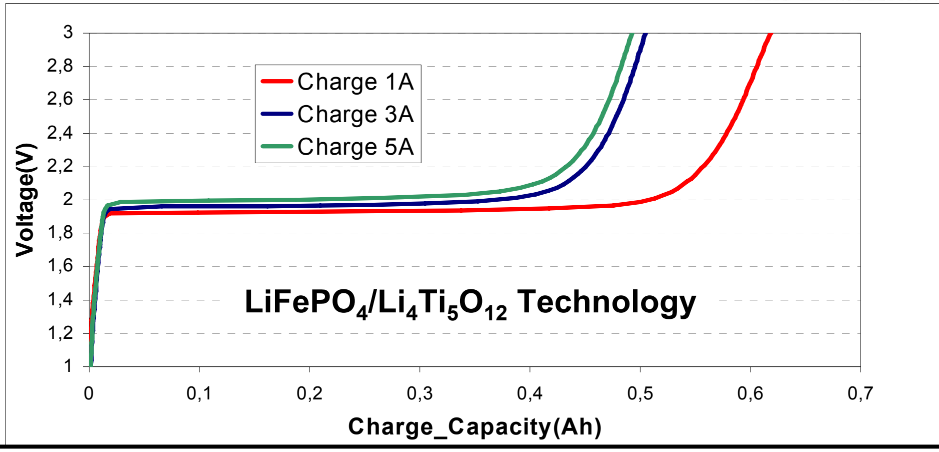
- **High voltage** $LiNi_{0.4}Mn_{1.6}O_4$ (**"5V Spinel"**) => 147mAh/g @ **4.7V vs Li**

Augmentation de la Puissance : How?



- Introducing High Power / High Rate Capability negative electrodes
- Working on cells “passive” components: separator, electrolyte, design to reduce Ri…

Negative : $Li_4Ti_5O_{12}$ to replace Graphite. Fast charge, high stability & high safety (Intercalation voltage 1.55 V/Li+/Li ⇨ no risk of Li plating even at high intercalation rate)



EV Battery Charge
Today: 6 hours
Next: 20 min (80% charged capacity, i.e. 400V)

⇒ 80 % of capacity charged in 6 minutes

⇒ Target = Full Charge in less than 3 minutes

Example of High Power : Application with LTO (-) – Mild Hybrid EV

BATTERY DATA SHEET

Technology : $LiFePO_4$ / $Li_4Ti_5O_{12}$ (1.88V)

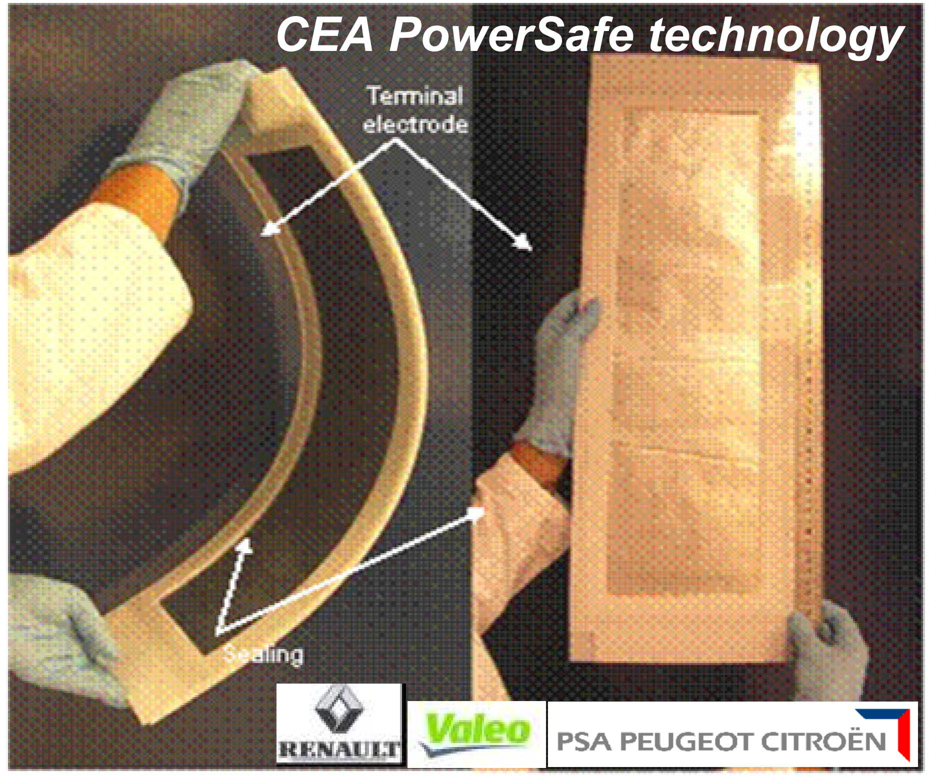
Design : Bipolar
13 unit cells

Nominal electrical data

Capacity @ C/10 target, +20°C : 0.7 Ah
Nominal voltage : 24 V
Maximum voltage (continue charge) : 33 V
Minimum voltage (continue discharge) : 6.5 V

Mechanical data (hard casing excluded)

Length : 615 mm
Width : 205 mm
Thickness : 2.5 mm
Weight : 0.7 kg



A charge at max. current 30 A and 30 V cut-off voltage : 30 A (3s) ⇔ 40 C rate

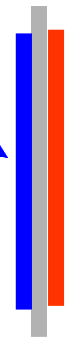
24V-15Wh Bipolar Prototype :
2-3kW/kg (**P Ref LFP/G 1kW/kg**)
At least 35-40% of usable capacity
29Wh/kg & 47Wh/L
7.5y life time in HEV profile

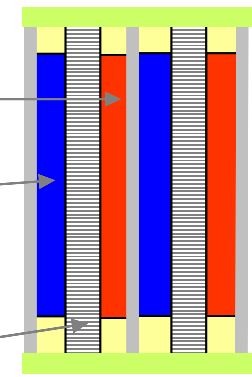
50Wh/kg reachable with **ability of regenerative and discharge power peaks around 10kW/kg for 0,5 to 1s and around 5kW/kg for 3s to 10s** without any cyclability deterioration of the cell

The bipolar technology

Aluminum is compatible with the $Li_4Ti_5O_{12}$ negative electrode

→ Light weight, Cheaper than Cu, and Double-sided coating possibility





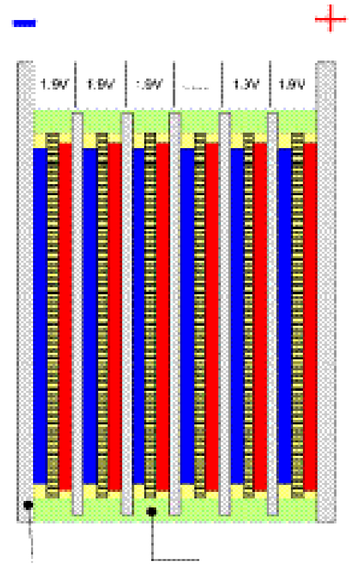
BIPOLAR CELL DATA SHEET

Technology : $LiFePO_4/Li_4Ti_5O_{12}$
Design : Bipolar 13 unit cells

Nominal electrical data :
Capacity @ C/10 20°C: 0.7 Ah
Nominal voltage : 24 V
Max. voltage (continue charge) : 33 V
Min. voltage (continue discharge): 6.5 V

Mechanical data (hard casing excluded)
Length: 615 mm
Width: 205 mm
Thickness: 2.5 mm
Weight: 0.7 kg
Typical power electrode loading
40µm Al foils
Active area 50 x 15 cm^2

The CEA bipolar cell (24V, 0.7 Ah)



2 bipolar compartments

n bipolar compartments

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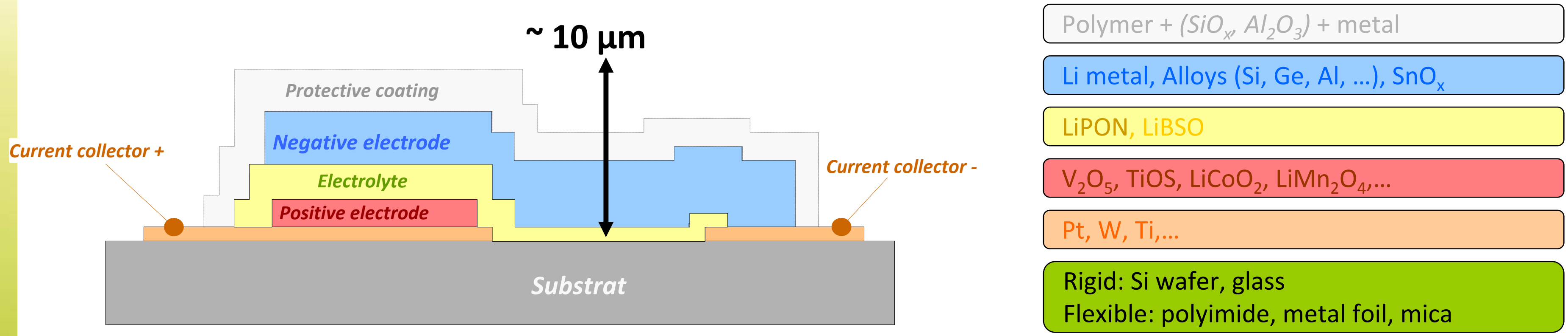
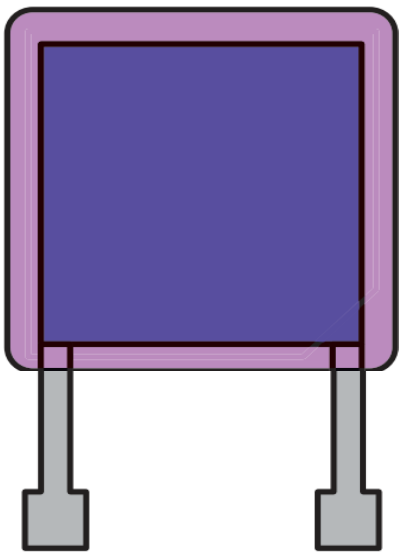
What is a microbattery ?





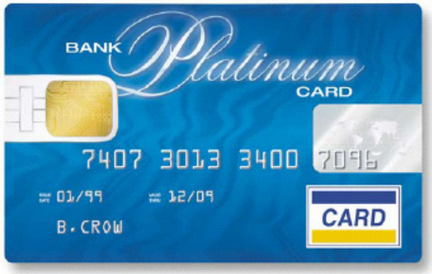
Main characteristics :

- Capacity ~ 200 µAh.cm^{-2} , 1 to 4V, power < 5 mW.cm^{-2}
- Preparation by using specific techniques (PVD, CVD…)
- Use of a solid electrolyte
- High cycle life (1k-10k cycles),high calendar life (~10 years), possibly high voltage (~5V), low self discharge (<5%/year), environment friendly
- Sustain high temperature (operation, storage)
- Easy to prepare in a variety of shapes and to any required size (mm^2 to cm^2)

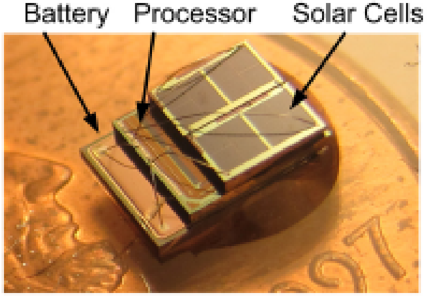
Applications

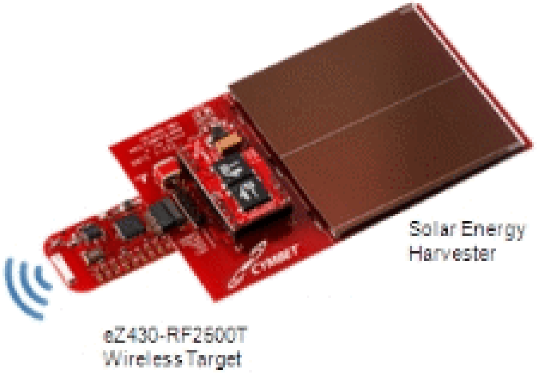
- Real-time clock (RTC)

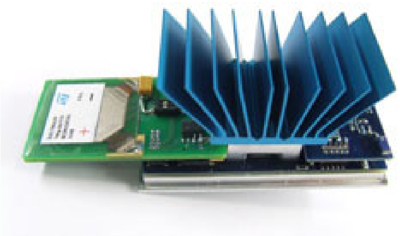
- Secured smart cards and RFID tags



- Microactuators
- Stand-alone sensors
  - µ-battery as single power source
  - Hybrid micropower source with harvesting system
    - photovoltaïcs
    - thermoelectrics

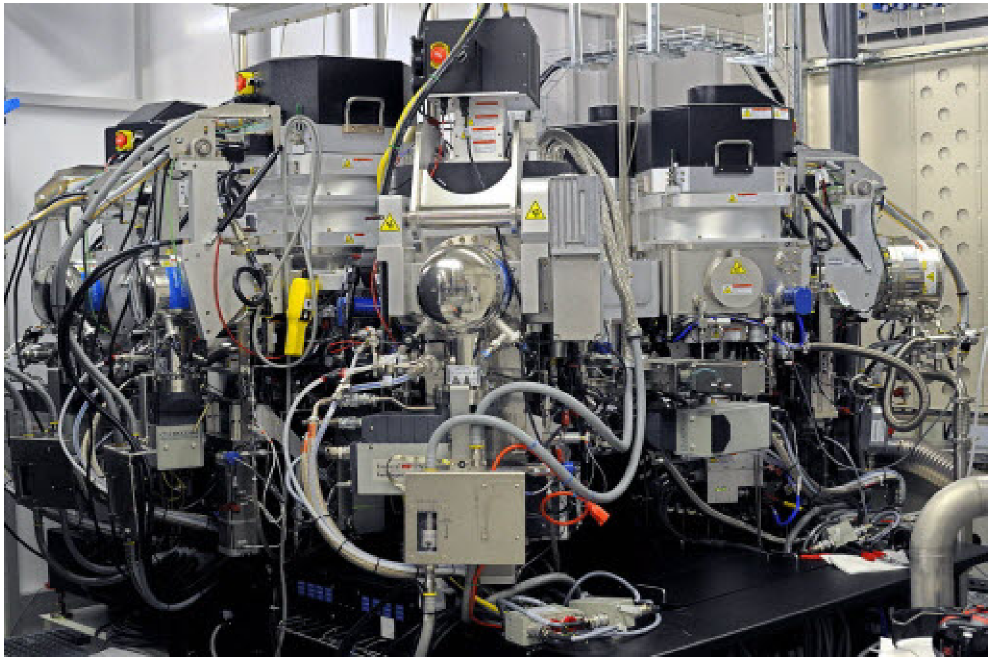




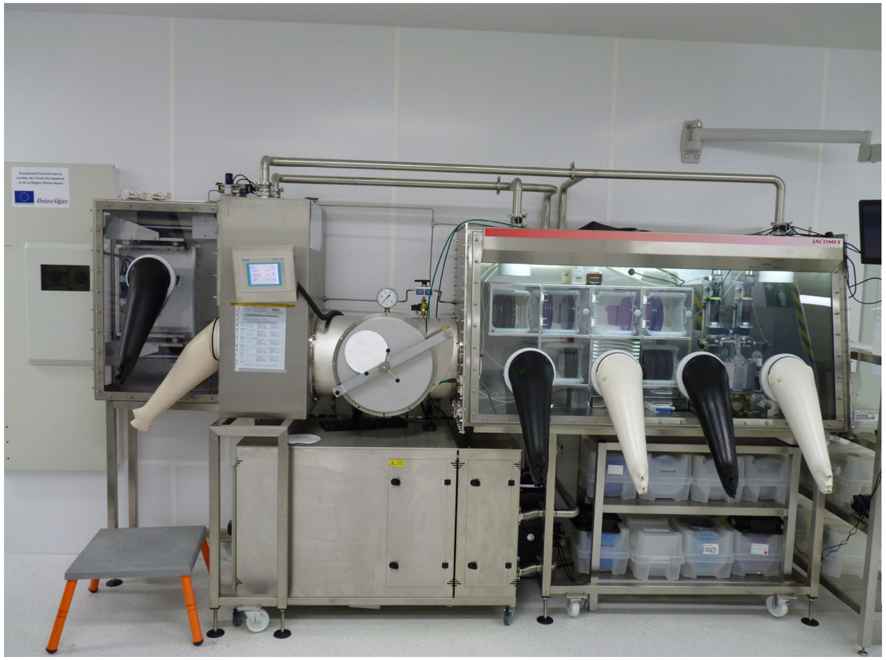


Microbattery manufacturing

- Process development on industrial tool (200mm substrates) in clean room



Endura cluster: 4 to 7 sputtering chambers

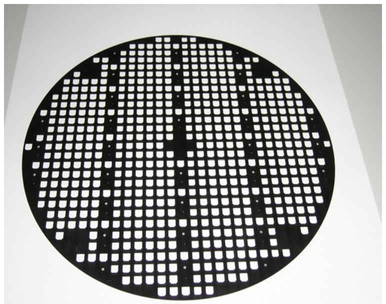


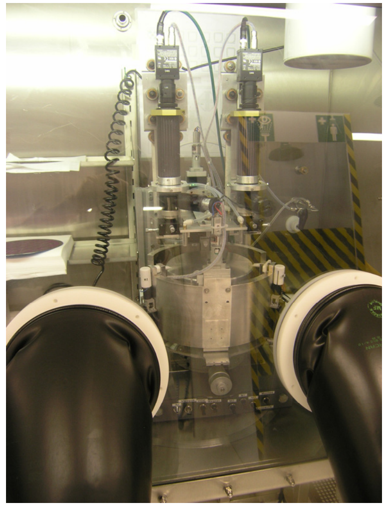
Connected Ar-filled glove box

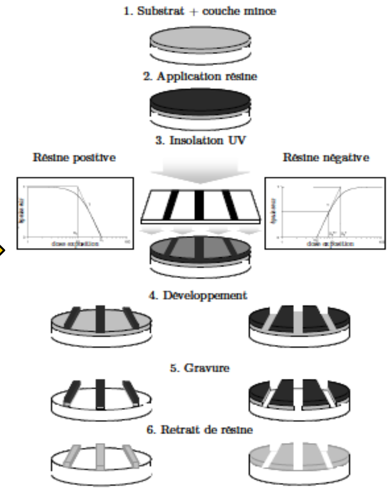
- Main partner: ST Microelectronics

Microbattery manufacturing

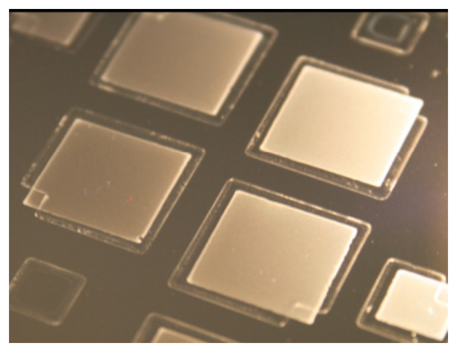
- Patterning: from shadow mask to maskless process



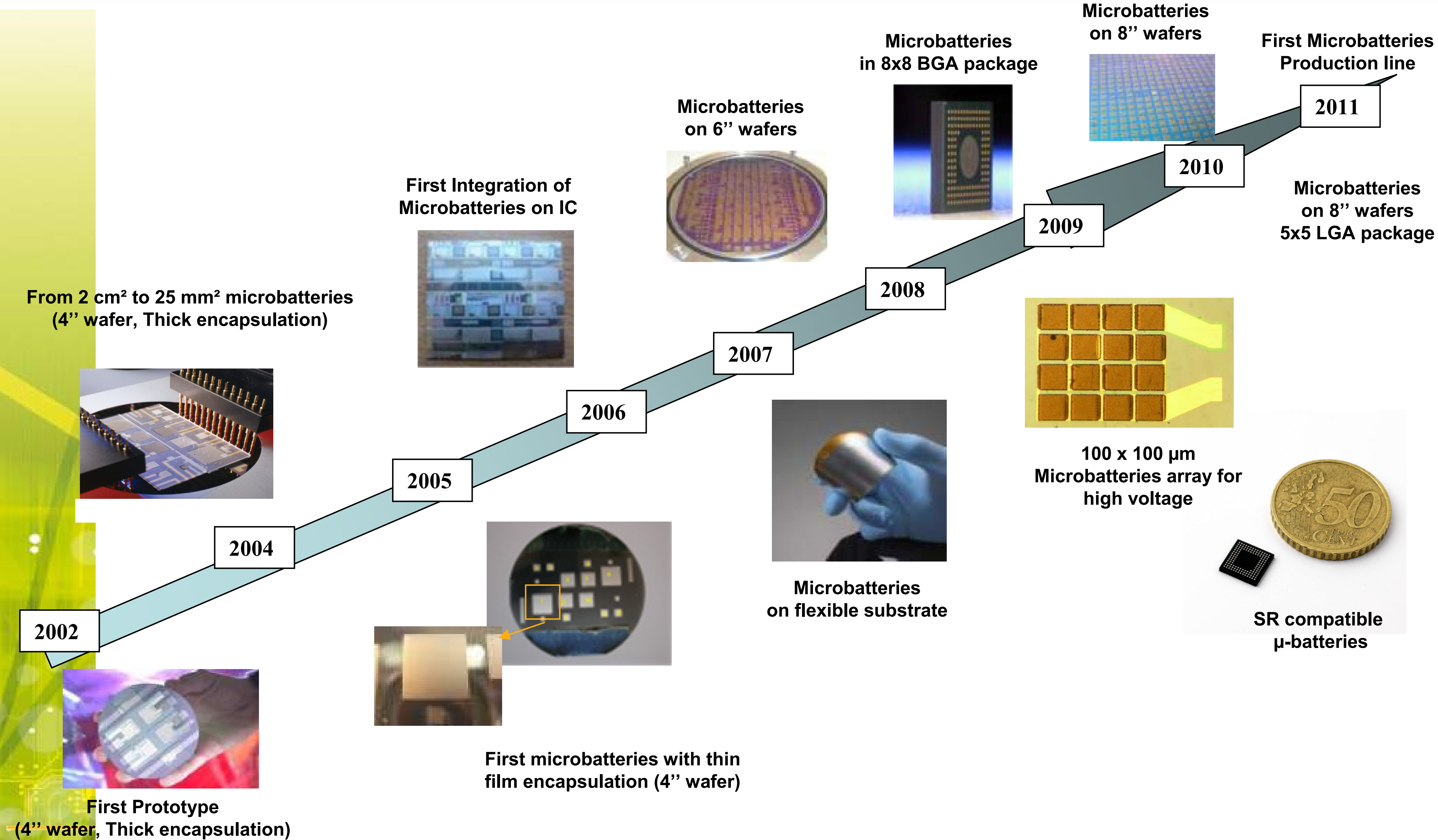




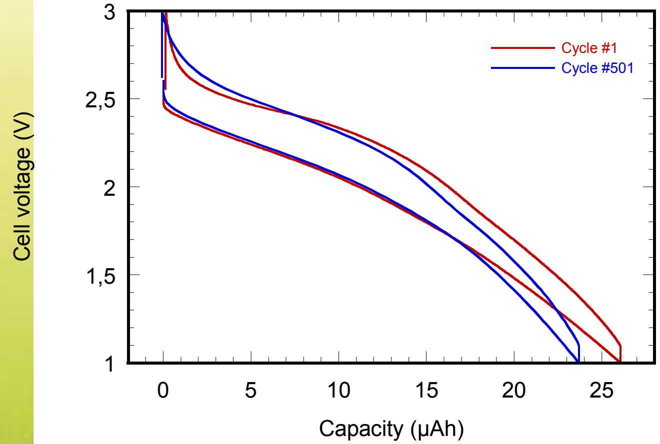
- Up to 800 microbatteries on a 8'' wafer



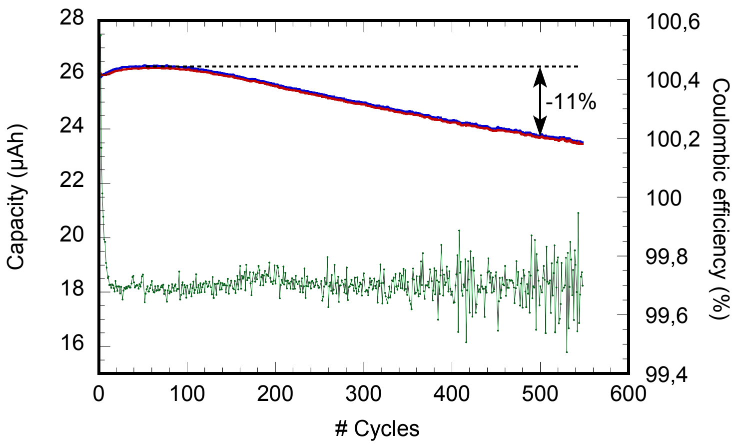
Evolution of CEA Microbatteries prototypes



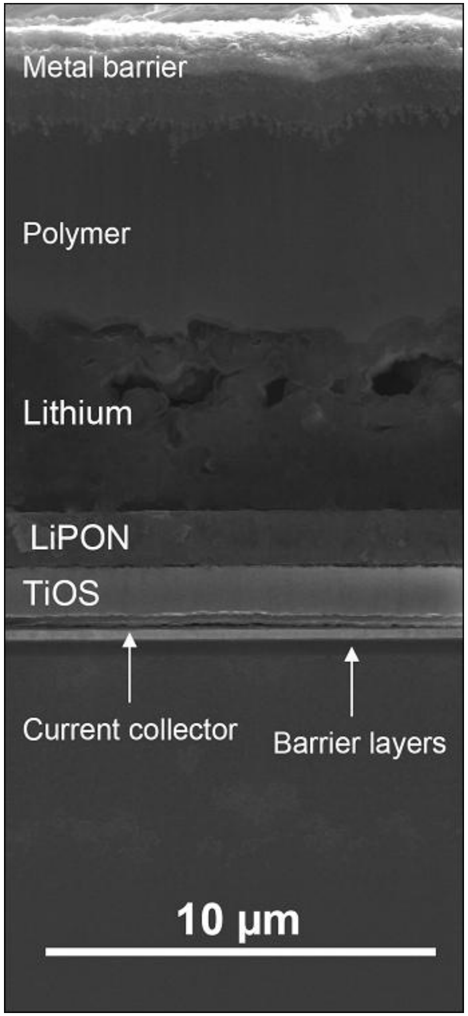
Typical lithium metal µ-battery: Li/LiPON/TiO_xS_y

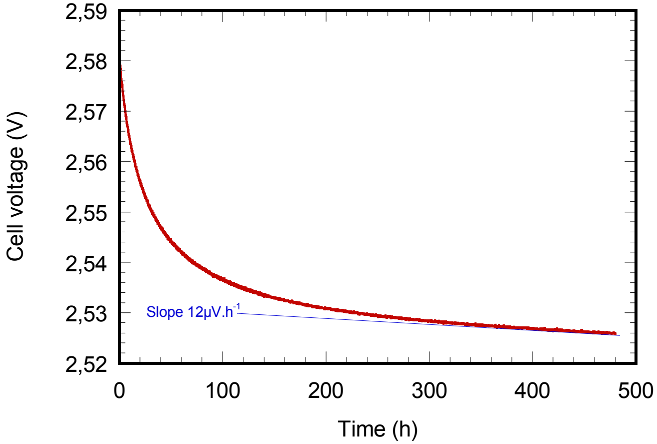


Medium voltage



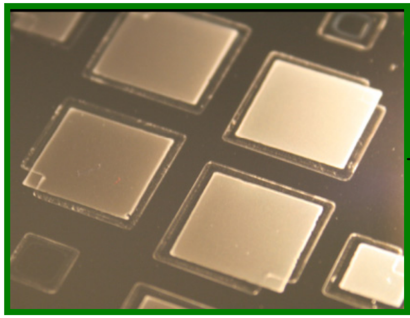
High cycle life





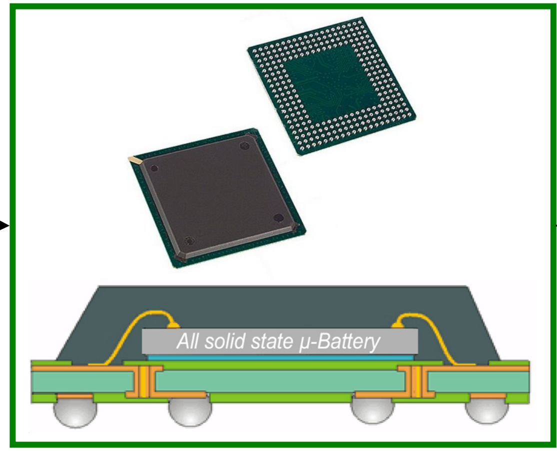
Very low self discharge
<5% / year

Reflowable µ-batteries



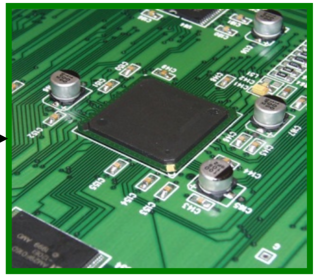
Dicing

Wire bonding
Epoxy curing



Solder reflow

T_{max} = 260°C
x3

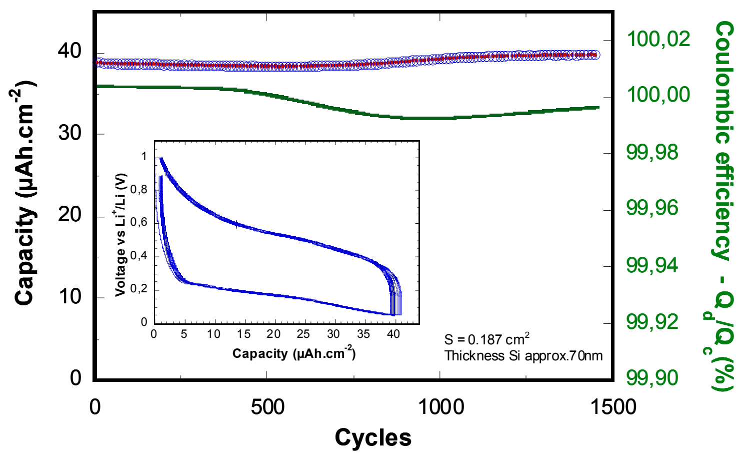


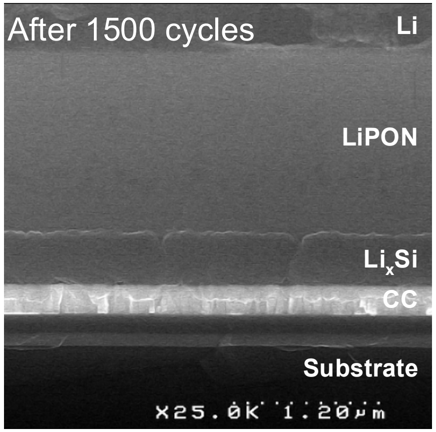
µ-batteries on Si wafer

Integration in a BGA package

Connection on the PCB

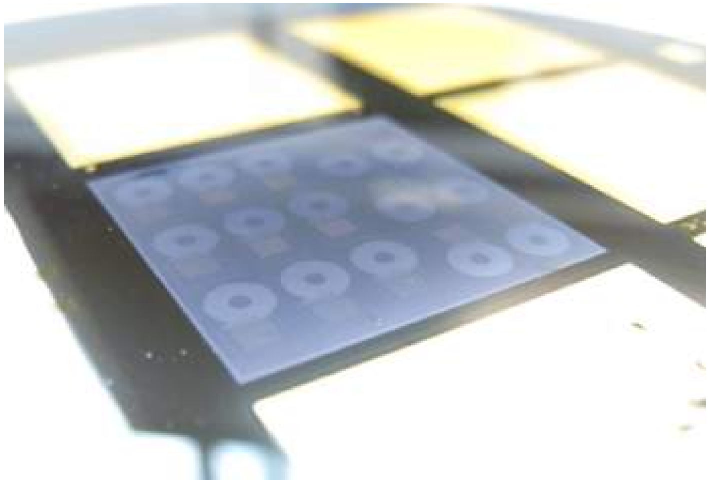
Lithium-ion cells with a highly reversible Si negative electrode

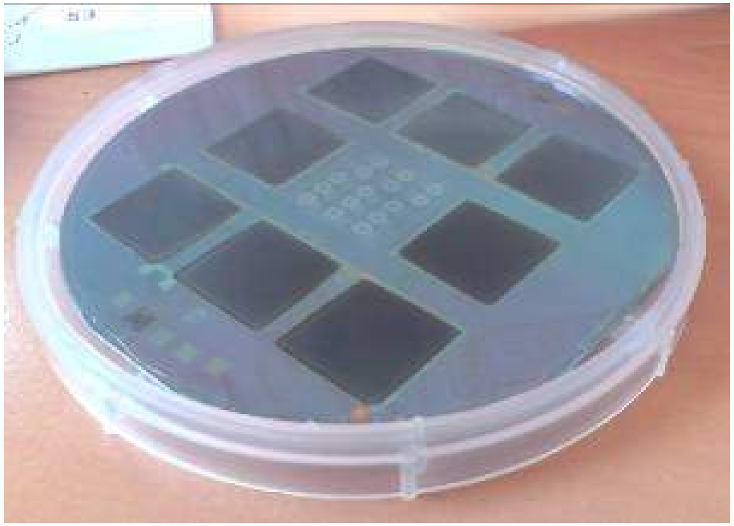




High voltage microbatteries

- High voltage energy source for actuators
  - Technology fusion between silicon actuators and microbatteries

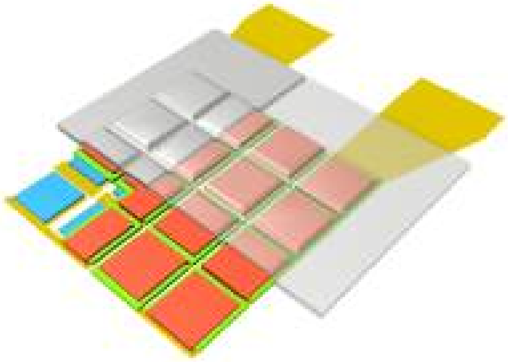


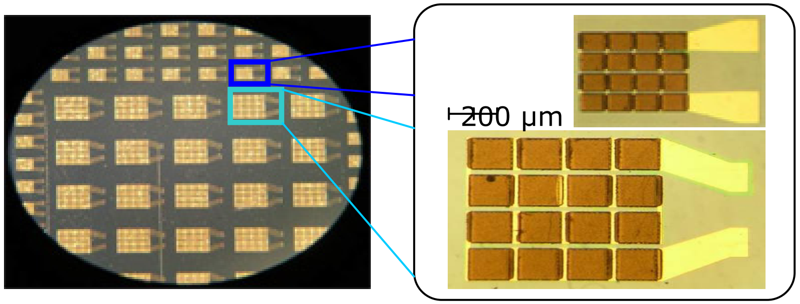


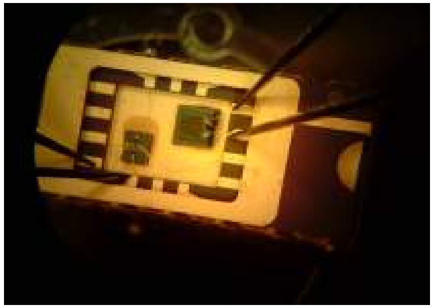
  - Applications: µUAV, avionics

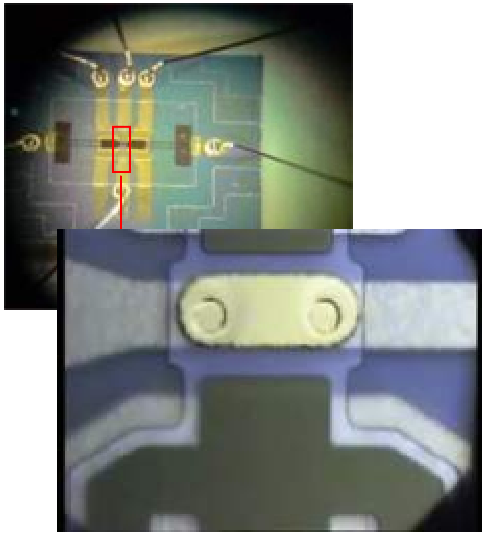
High voltage photolithography microbatteries

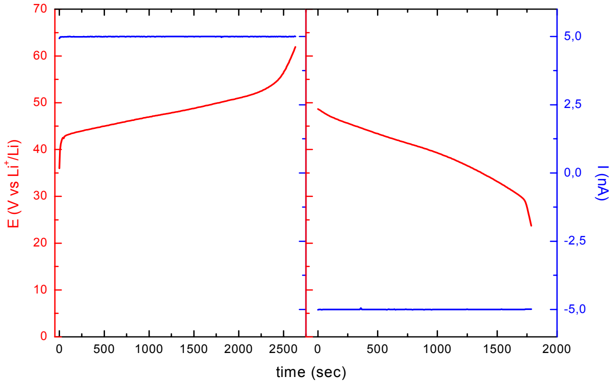
- High voltage (> 30V) energy source for RF MEMS
  - Connections in series of 16 V_2O_5 based microbatteries
  - 100 x 100 µm² microbatteries
  - Photolithographic process
  - Standard clean room environment

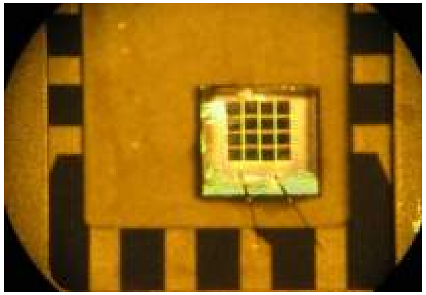






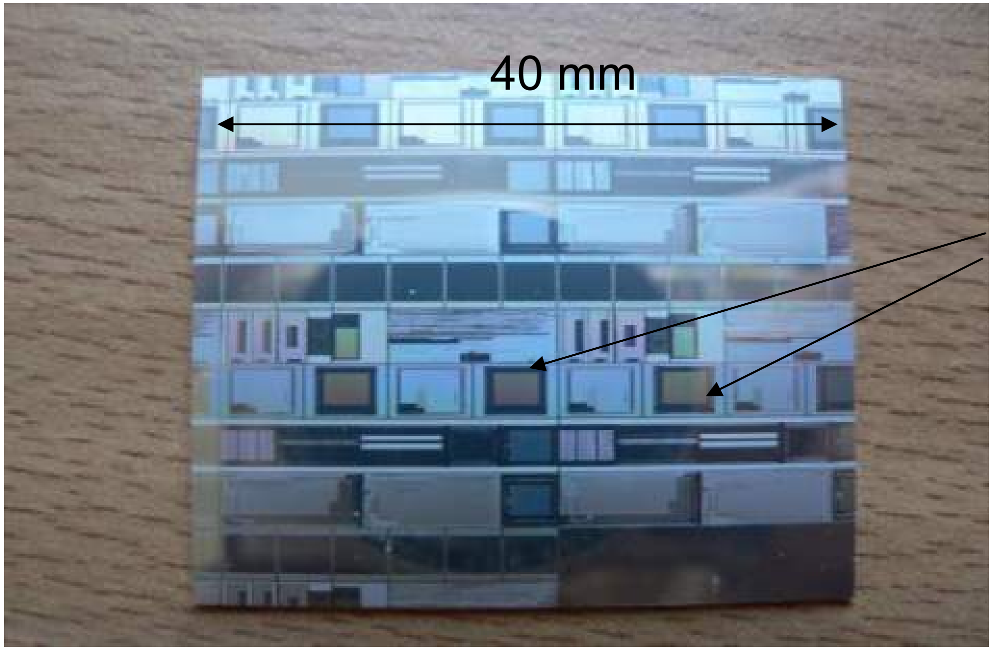






Integration: Above IC capability

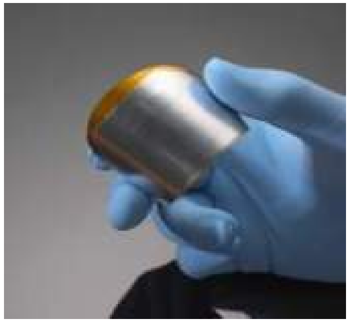
- Microbattery on integrated circuit for smart card application: security improvement

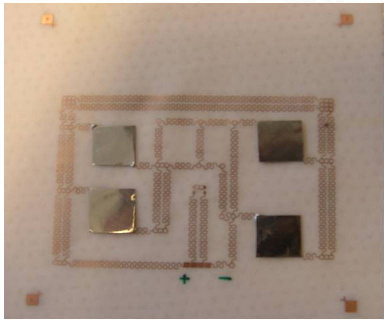


μ-batteries (23 mm²)

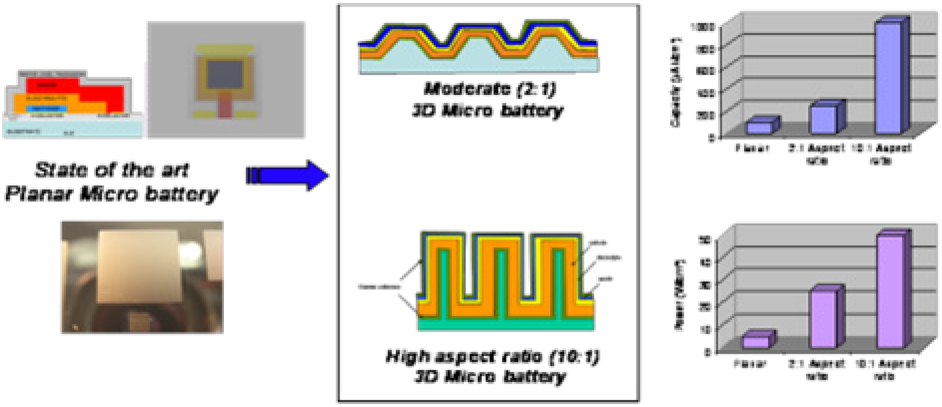
Different substrates for various applications

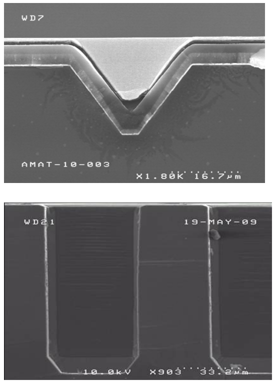
- Flexible/strechable substrates
  - Polyimide subtrates (low T process)
  - Large area for high capacity





- Textured substrates





E-STARS

http://www.estars-project.eu

- Stacked microbatteries

CEA – LITEN - Grenoble