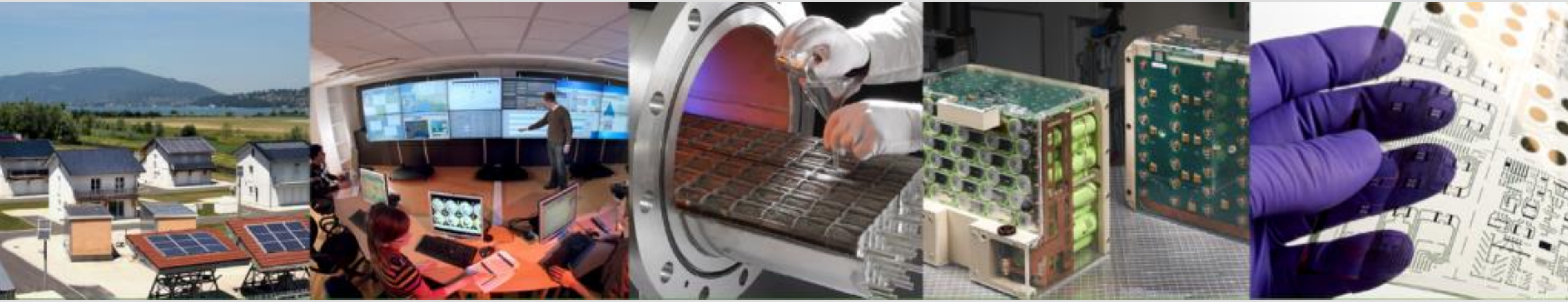


DIGITAL PRINTED LI-ION BATTERIES

Basmati Workshop | 23rd of November 2016 | Thomas Yohann

SUMMARY

1. INTRODUCTION
   - CEA / DRT / LITEN
   - RESEARCH PROGRAMMES
   - ELECTROCHEMICAL SYSTEMS
   - STRATEGY AND APPROACH

2. DIGITAL PRINTED LI-ION BATTERIES
   - OVERVIEW
   - INTERDIGITATED DESIGN
   - INK-JET VS. AEROSOL JET

3. RESULTS FROM BASMATI PROJECT

FROM ATOMIC RESEARCH TO RENEWABLE ENERGY

Defence Security

Defence Applications Division

French strategic independance

Nuclear Energy

Nuclear Energy Division

French energetic independance

Research & Technology

Technological Research Division

French economic competitiveness

TECHNOLOGY

4 500 employees

550 M€ annual budget

500 patents / year

50 start-ups

Fundamental Research

Material Science Division / Life Science Division

SCIENCE

16 000 employees
10 Research centers
4B€ annual budget

580 priority patents filed / yr.
120 new high-tech companies created since **1984**

A MULTIDISCIPLINARY APPROACH TO R&D: LITEN, LETI & LIST – A VIRTUOUS CIRCLE

2005 - Grenoble / Chambéry

INES – INSTITUT NATIONAL DE L'ENERGIE SOLAIRE

Staff 1 400 - 170M€

new energy technologies and nanomaterials

liten

list

software-intensive systems

Staff 800 - 70 M€

2003 - Paris Sud

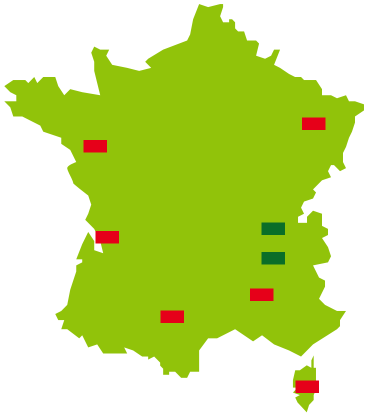
leti

micro-nanotechnologies and system integration

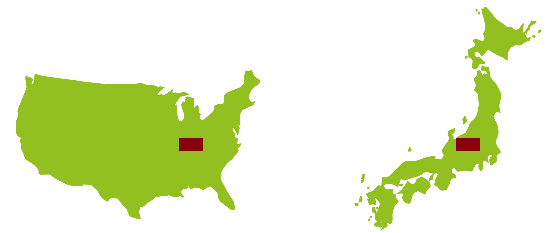
Staff 1 800 - 240 M€

1967 - Grenoble

LITEN : KEY FIGURES



- 2 Principal sites *(Grenoble, Chambéry)*
- 5 local sites*(CEA-Tech, Cadarache + Corse)*
- 2 commercial offices abroad *(America, Japan)*



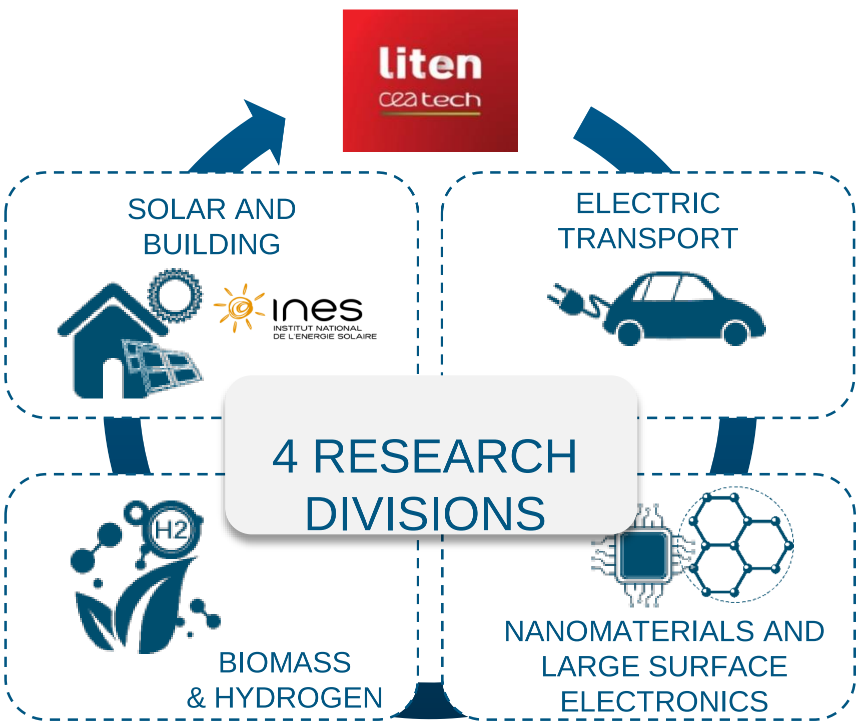
1000 researchers
- 2/3 permanents
- Average age < 40
- 28% female

Almost 1300 patents
- 230 generated in 2015

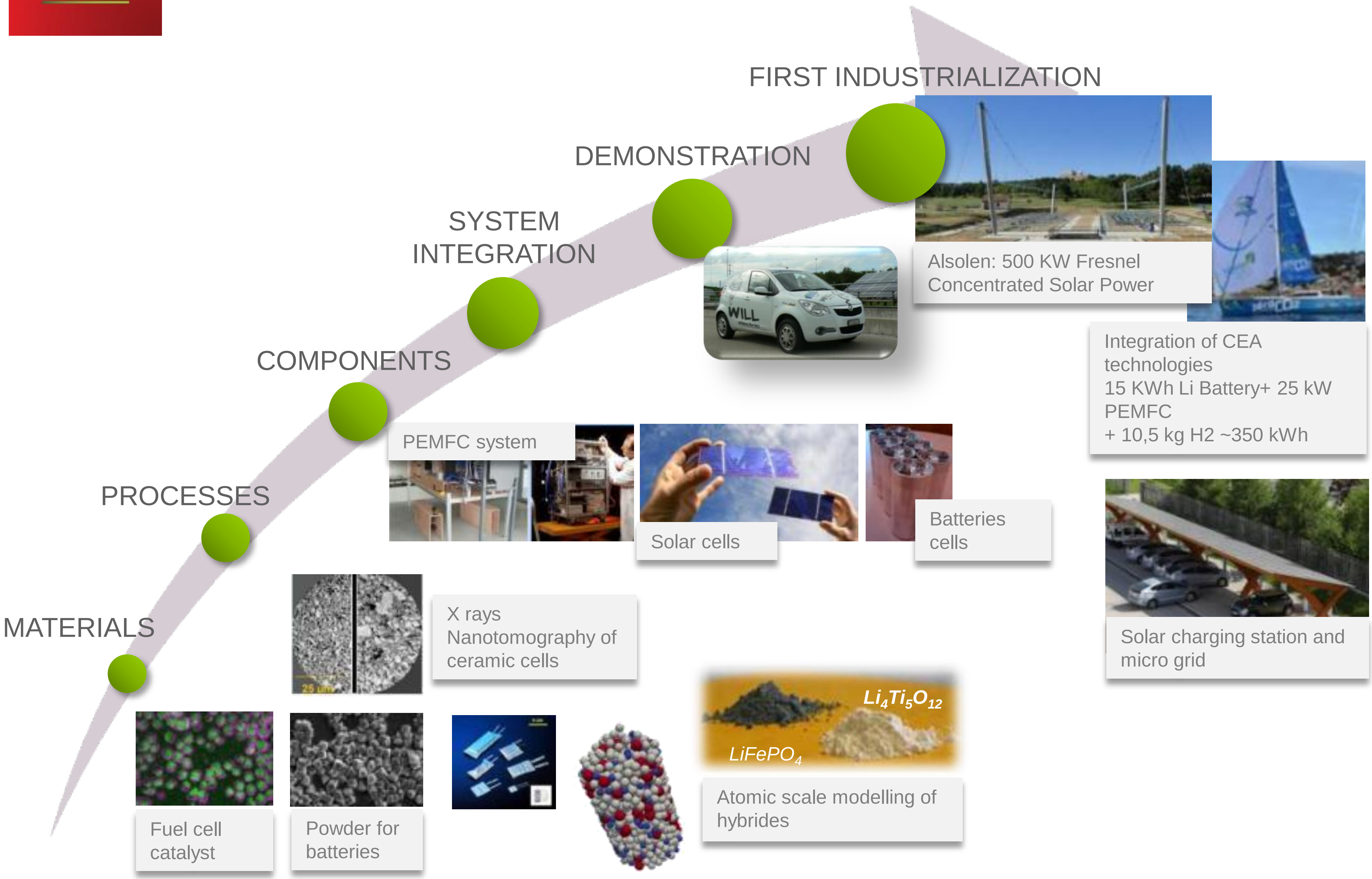
> 350 industrial partners

140 M€ budget

Bilateral research contracts
- 50% large companies
- 50% SMEs



VERTICAL INTEGRATION: THE VALUE CHAIN



LITEN RESEARCH PROGRAMMES

Electric Transport

Lithium batteries

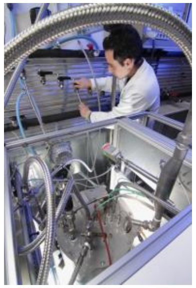
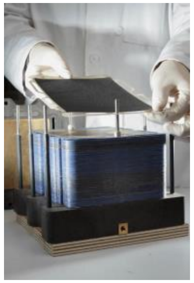
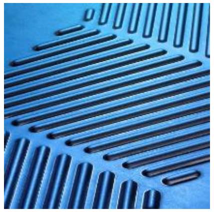
Materials & processes
Design, prototyping & test of battery systems
Pack architecture
BMS





PEM Fuel cells

Design, prototyping & test of FC systems
Materials & processes
Components - stacks

Vehicle integration

Integration of FC/batteries in EV/hybrid vehicles
Monitoring

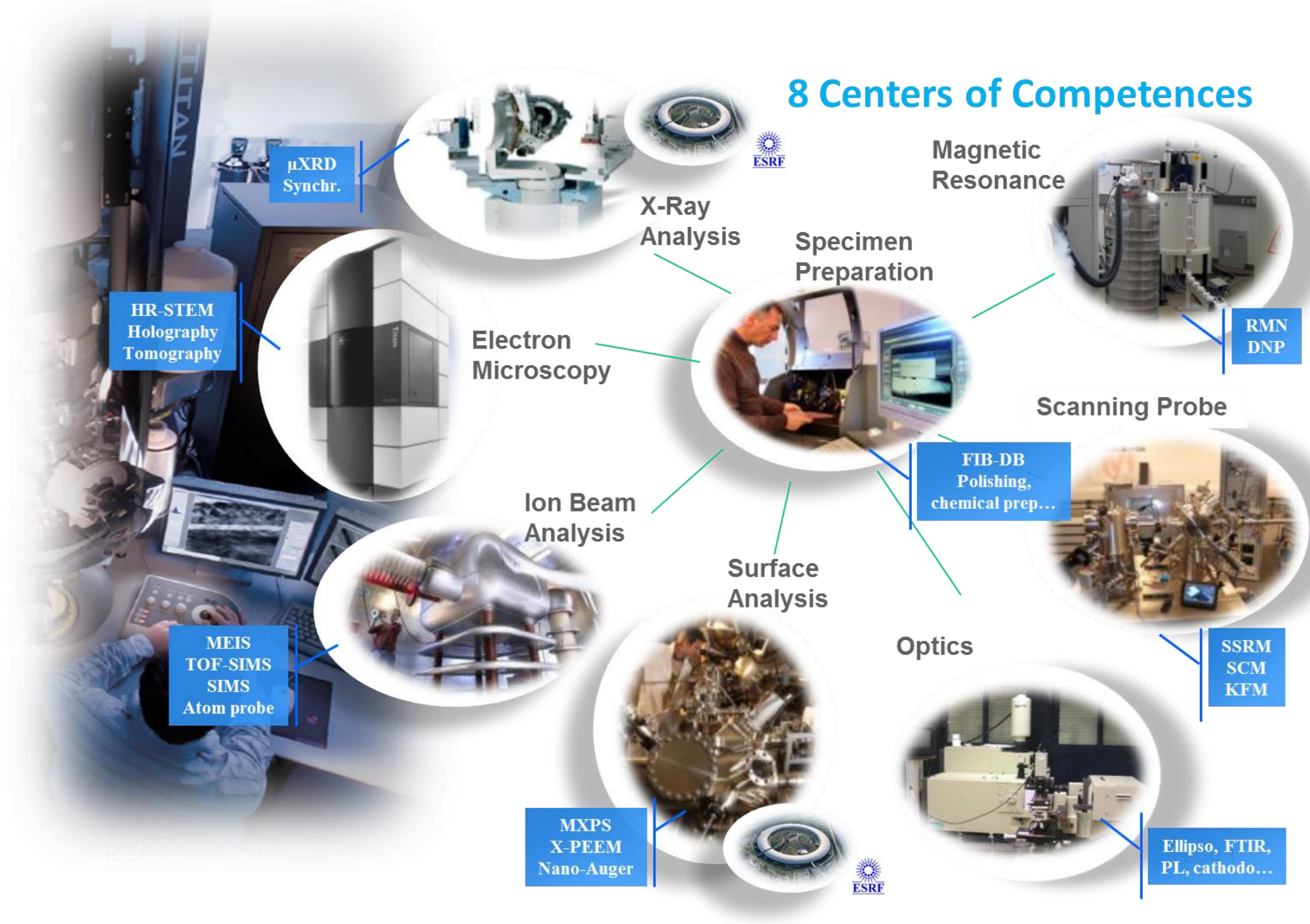

ELECTROCHEMICAL SYSTEMS AT LITEN

- **Electrochemical Systems**
  - **Fuel cells**
  - **Batteries**
    - **Primary**
    - **Secondary**
      - **Li-metal**
      - **Metal-air**
      - **Li-ion**
      - **Others**

- 20 years experience on batteries and fuel cells
- 300 patents (2/3 on Batteries)
- 250 people (2/3 on Batteries)
- Supported by (nano) characterization facilities

NANOCHARACTERIZATION PLATFORM

40 equipments / 2500m² of facilities / 3.5M€ of investments/year



- TEM / SEM
- NMR / SQUID
- XPS
- Neutron diffraction
- X ray Synchrotron
- Contact Angle
- Gas Permeation
- Profilometer / AFM
- GC/MS
- HPLC / SEC
- FTIR / UV
- X-Ray diffraction
- DSC / TGA-DTA

OUR STRATEGY FOR MATERIALS

Laboratory scale (g)

Innovation - Patents
(synthesis-composition)
Caracterization

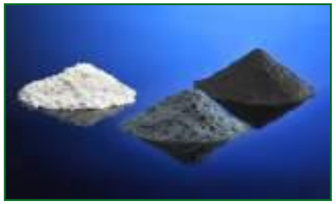
Pilot scale (kg)

Synthesis scale-up
Process optimization
Reproducibility

Technology transfer

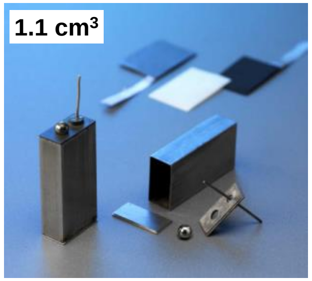
License agreement
Industrial development

LI-ION PROTOTYPE CELLS



1 mAh to 40 Ah cells

Various « fit & form » (Pr, Cy, soft packaging, hard casing…) & Specific architectures and design (bipolar cells, thin cells,...)



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

SAFT chemistry

Safety tests performed successfully

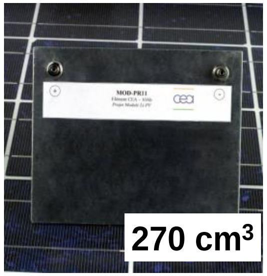
Strong weldings
High tightness

After nail test

Overcharged cell

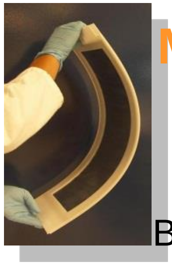
Smart-Cards, Intelligent Wears, secure personal devices, packaging, E-books, autonomous sensors...

few mAh to 800 mAh, ultra-thin packaging (< 0.4 mm)
2.3 to 3.7 V; <1g to 45g
=> *Towards fully printed Li Batteries*



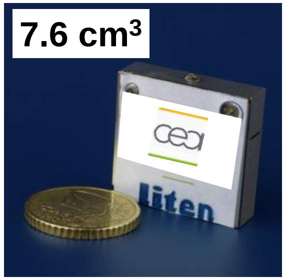
Photovoltaic

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



Micro-Hybrid

High Power
Fast charge
24V – 15Wh
Bipolar architecture



Spatial Sensor

3.7V - 350 mAh
Cell for extreme conditions

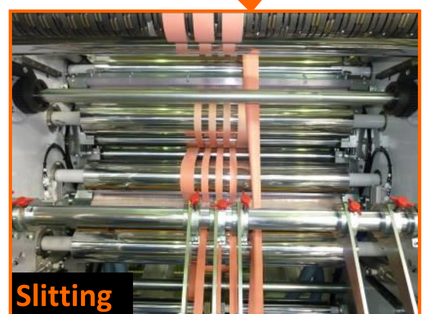
Aeronautic

3.2V- 170mAh
Thin Cell for Extreme conditions

Others

LI-ION BATTERIES PILOT LINE

1



2

3

4

5

6

Electrical, Abusive, Calendar Tests (1100 channels)

- **Pilot Line with 1000m^2 of dry room extension**
- **Line capability up to 500kWh/month**
- **150-200kWh/month in practice (~3000cells)**

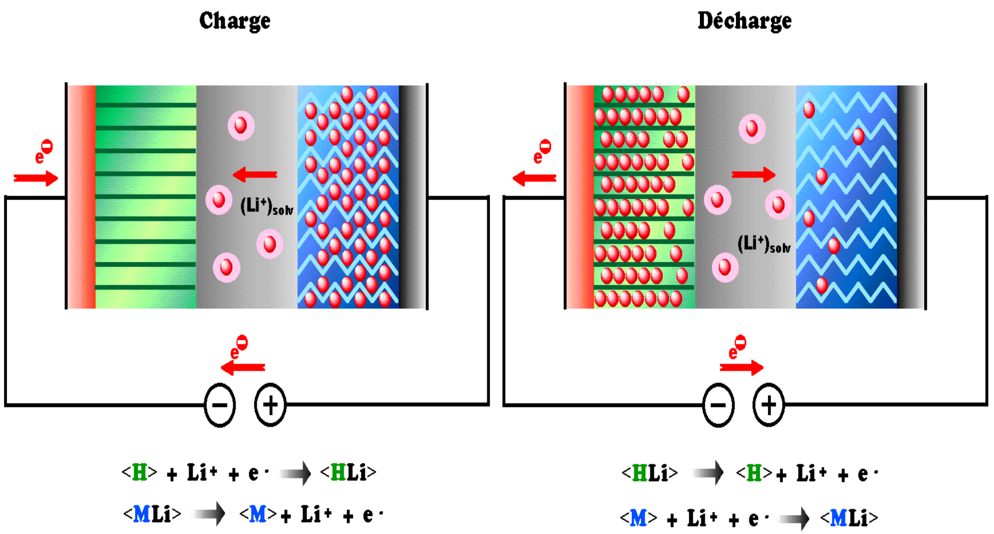
- 500 channels for formation
- 1000 channels for cycling

OPERATION OF LITHIUM SECONDARY BATTERIES

- **Conversion of chemical energy into electrical energy**

- **Reversible insertion of lithium ions in the structure of the anode material and the cathode (oxidation-reduction)**

- **Porous Electrodes (compromise impregnation / electronic percolation threshold)**
- **Electrolytic medium (electrical insulation and ionic conduction)**
- **Current collectors (metals, polymers and ceramics drivers carbons)**
- **Substrate (sealed packaging)**

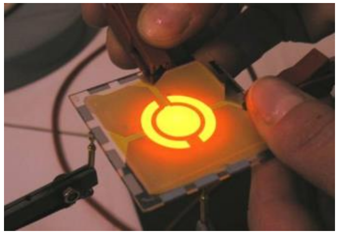
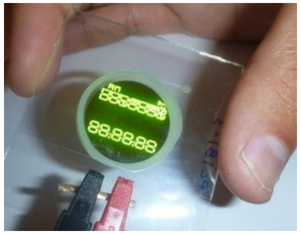
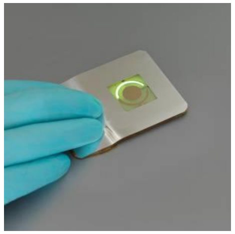
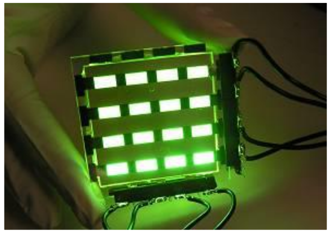
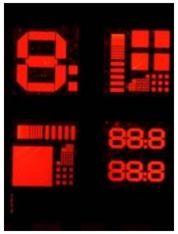
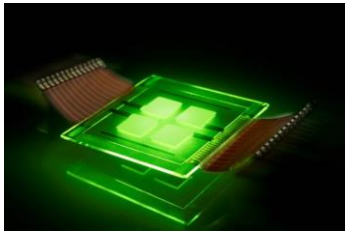


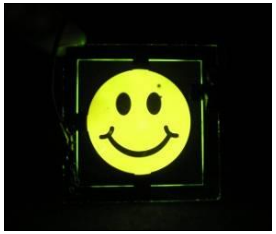
The first system lithium ion by Sony in 1991: Graphite/$LiCoO_2$ (18650) – 3.6V

PRINTED ORGANIC ELECTRONICS

PLED (Polymer Light-Emitting Diodes)

- HMI, signage
- Devices, systems
- Single digit, matrix
- Logos



Antennas

Sensors

- capacitive
- pressure sensitive


→ No rechargeable digital printed batteries !

→ No fully integrated battery + electronic

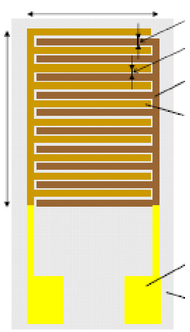
DIGITAL PRINTED BATTERY

Flexible and fully printed multi materials

Current collectors
Electrodes
Electrolyte

Non stacked configuration

simplification of interfaces (more flexibility with reduced mechanical constrains)



Interdigitated design

Nano inks

High resolution

Width of lines : 200µm
Distance between lines : <100µm (target 50µm) → electrolyte compartment

Non contact printing technique

Ink-jet

Aerosol jet printing

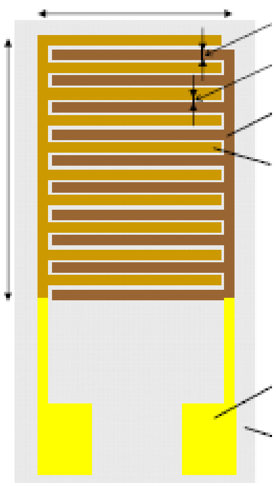
- More flexibility
  - Design
  - Interfaces
- Versatility of shapes

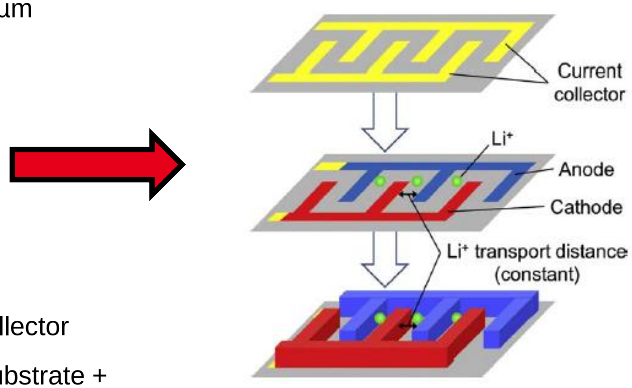
INTERDIGITATED DESIGN AND DIMENSIONS

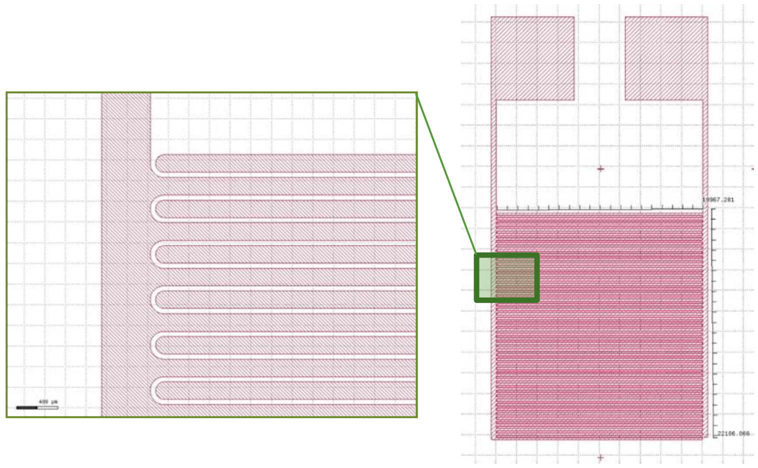
To simplify or solve several technological barriers, another battery architecture is possible: the interdigitated planar design

- **The interdigitated concept reverses at 90 ° stacked architecture**
  - ✓ Architectured current collectors on the same plane
  - ✓ Electrodes printed side by side on respective collectors
  - ✓ Separator printed between the electrodes printed on the entire surface
  - ✓ Electrolyte impregnation by the above
- **Constraints of the concept:**
  - ✓ High printing resolution(10µm +/- 1µm)

- Dimensions:
  - Width of lines : 200µm
  - Distance between lines : <100µm (target 50µm) → electrolyte compartment
- Solid electrolyte configuration
- No densification





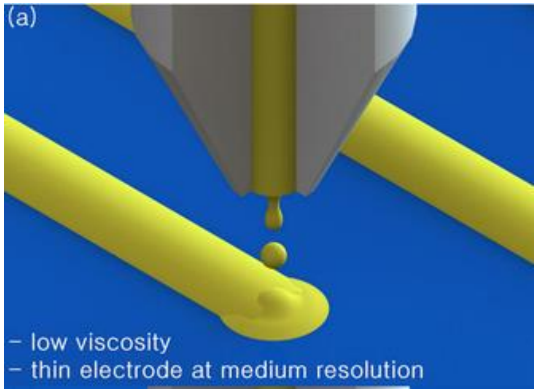


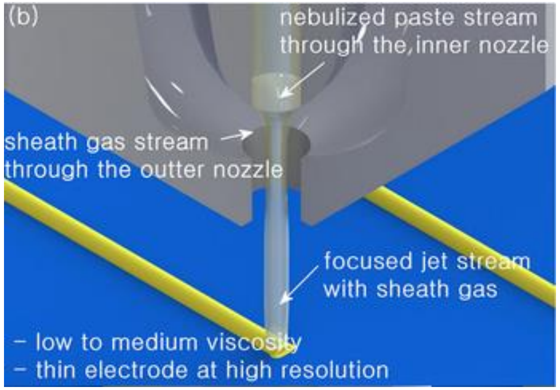
Patent BF3007206

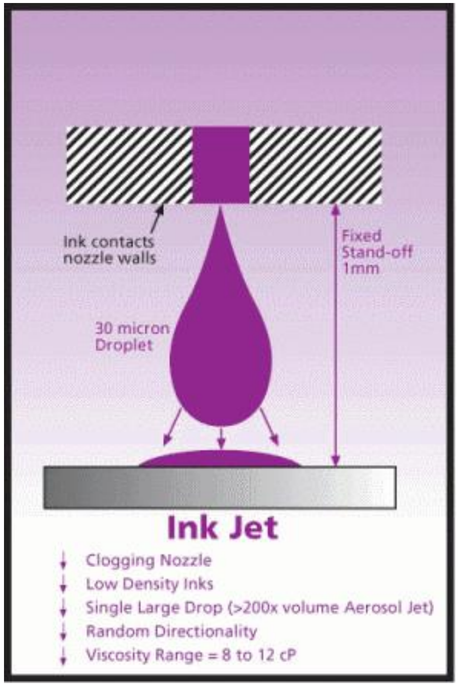
COMPARISON INK-JET AND AEROSOL JET PRINTING

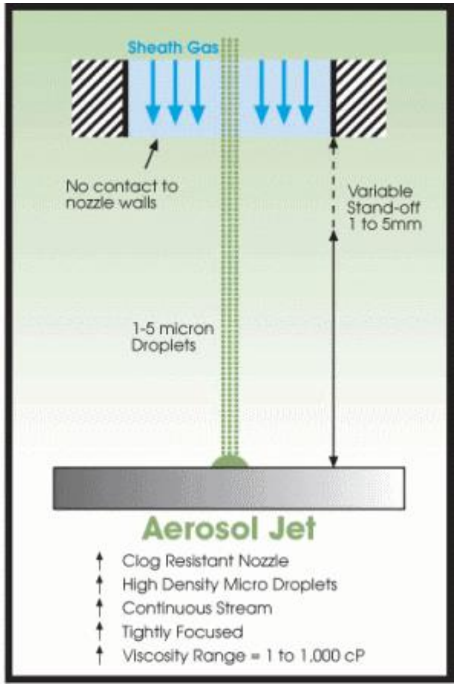
Inkjet

Aerosol jet









Advantages of aerosol jet printing:

- Less constrains on inks (viscosity, surface tension)
- Less constrains on substrates (lower spreading)
- Best resolution

Disadvantages of aerosol jet printing:

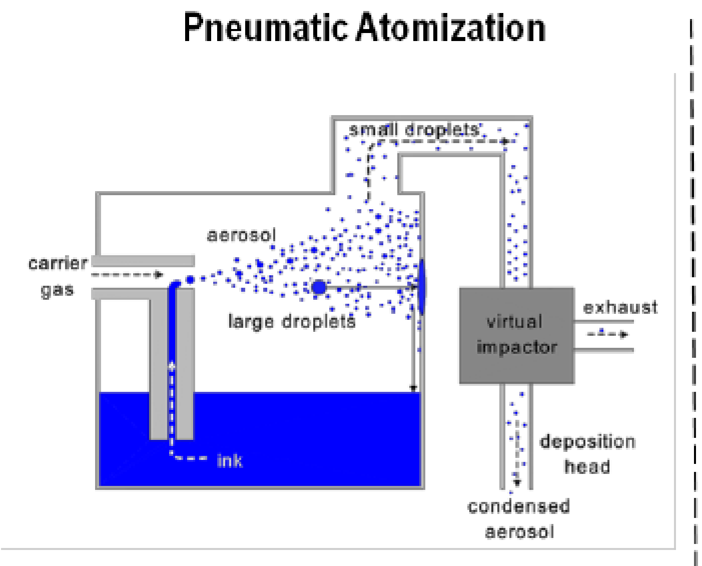
- Labscale

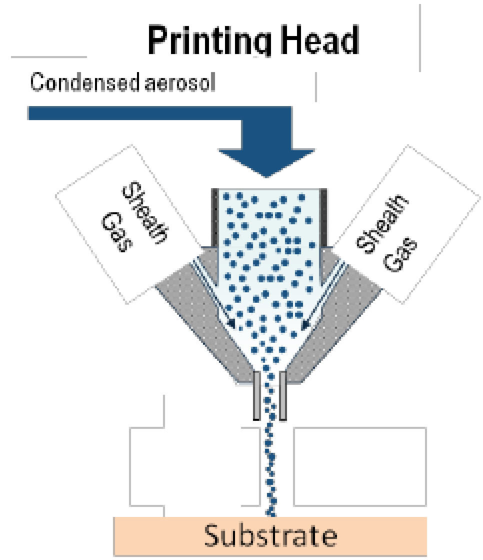
Shin et al. Scientific Reports 5:16704 · November 2015. DOI: 10.1038/srep16704

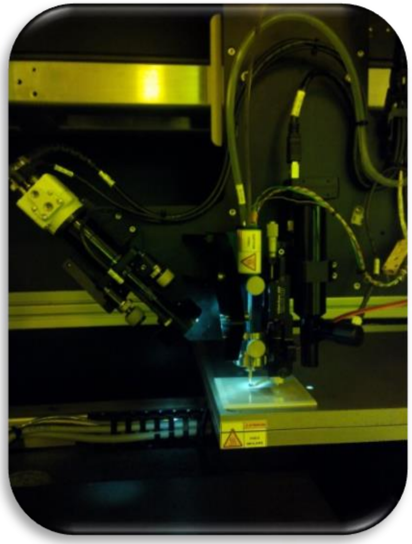
TECHNICAL SPECIFICATIONS

	Screen printing	Inkjet basic	Ink dispenser	Aerosol jetting
Particle size requested	< 100 nm	< 50 nm	< 50 nm	< 50 nm
Layer thickness (µm)	0.015-100	0.05-100	50	0.05 – 100
Definition (lines spaces) (µm)	30-100	5	10-500	2
Feature size (µm)	20-100	20-50	100	5-20
Registration (µm)	> 25	> 5	> 20	> 5
Patterning capacity	Required specific frame and hardware	Software development	Software development	Software development
Patterning Design	2D	3D	3D	3D
Ink viscosity Pa.s	0.5-50	0.001-0.1	0.02- 1	0.02 - 1
Throughput m^2/s	2-3	0.01-0.5	0.01-0.5	0.01-0.5

AEROSOL JET PRINTING







Experimental parameters (for pneumatic atomization):

- ✓ Carrier gas flow
- ✓ Exhaust flow
- ✓ Sheath flow
- ✓ Printing head temperature
- ✓ Plate temperature
- ✓ Ink temperature and stirring
- ✓ Nozzle size (100 to 300 µm)

PICTIC Platform

Shin et al. Scientific Reports 5:16704 · November 2015. DOI: 10.1038/srep16704

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3. RESULTS FROM BASMATI PROJECT

RESULTS FROM BASMATI

- **Current collectors → Cu / CNT / Ni / Gold**
  - Formulation / characterization
  - Printing
  - Sintering

- **Electrodes → LFP / NMC / LTO / graphene**
  - Material synthesis
  - Formulation
  - Testing in coin cell with jellified configuration
  - Printing (LFP)

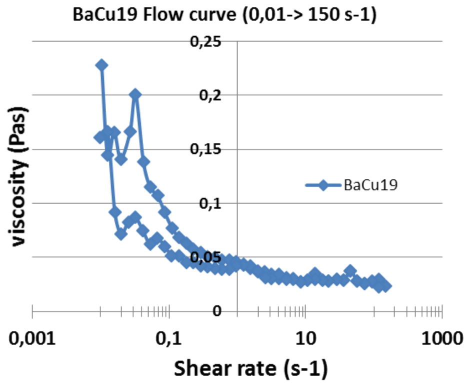
- **Multi-material printing for complete prototype (to be done)**

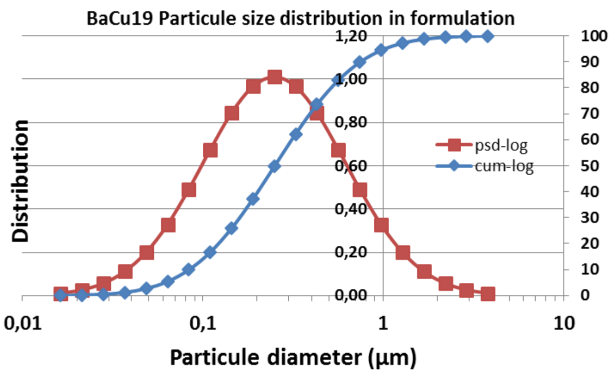
RESULTS FROM BASMATI CURRENT COLLECTORS

Copper current collector

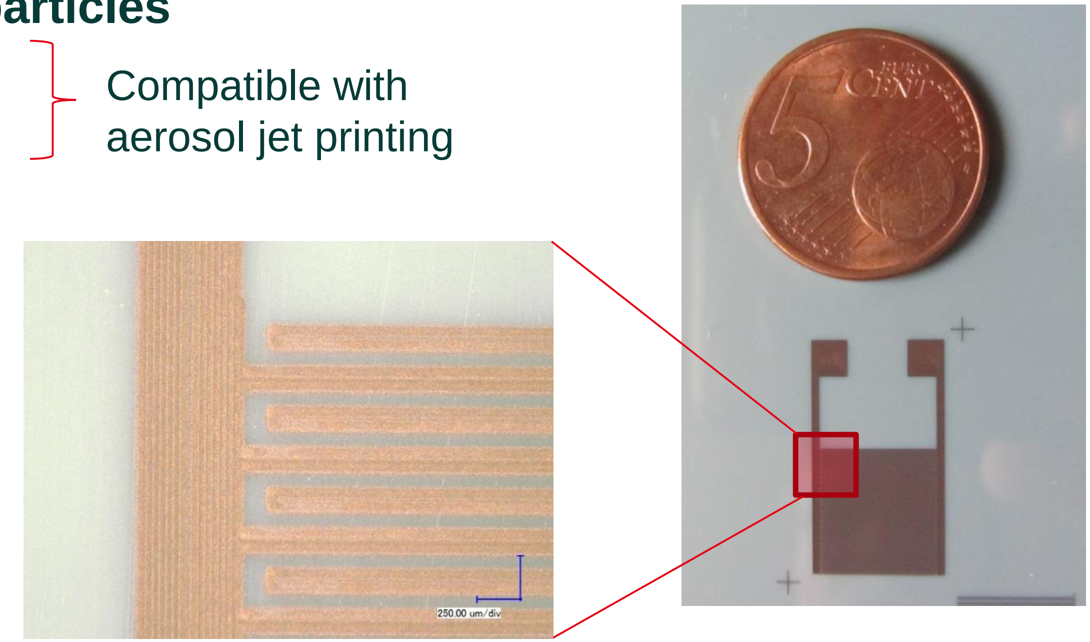
- **Formulation of copper nanoparticles**
  - ✓ Particle size distribution
  - ✓ Behavior at high shear rate

Compatible with aerosol jet printing





Distribution	D10	D16	D50	D84	D90	Dmax
Diameter (nm)	80	110	250	570	740	3800



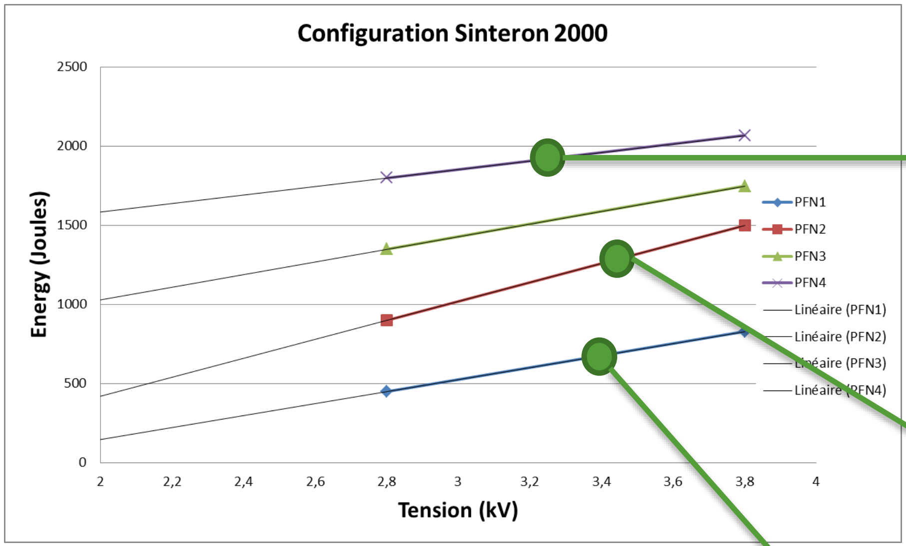
Optical image of interdigitated pattern of copper nanoparticles before sintering printed on PEEK.

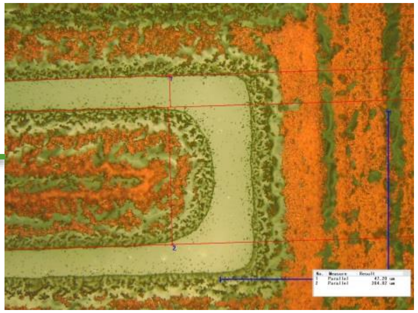
- Successful printing with high resolution
- Same design was printed on PET
- PET = for testing
- PEEK = for final product

RESULTS FROM BASMATI CURRENT COLLECTORS

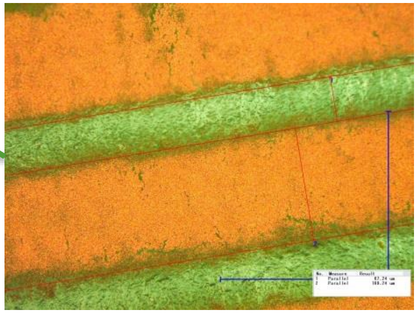
Copper current collector sintering

- Xenon Flash sintering (20 ms → 500 to 2000 J)
- Compromise between electronic conductivity and substrate stability

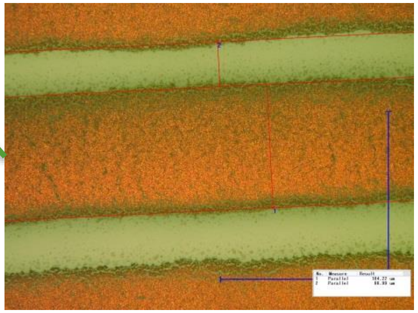




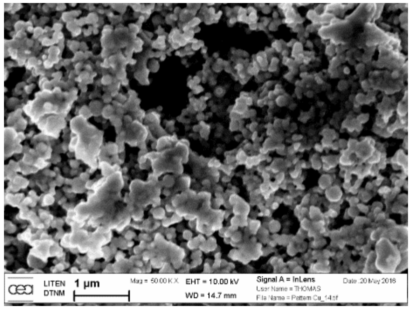
- No oxide remain
- Cracked Copper layer
- Non conductive
- Substrate deformation

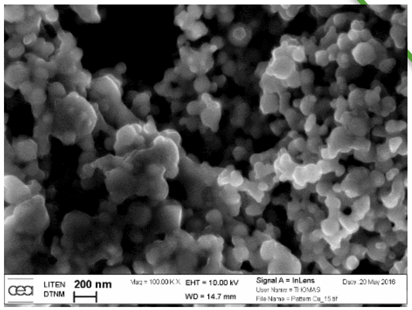


- No oxide remain
- Continuous Copper layer
- 4 Ω/cm
- No Substrate deformation



- Oxide remain
- Continuous Copper layer
- 400 Ω/cm
- No Substrate deformation

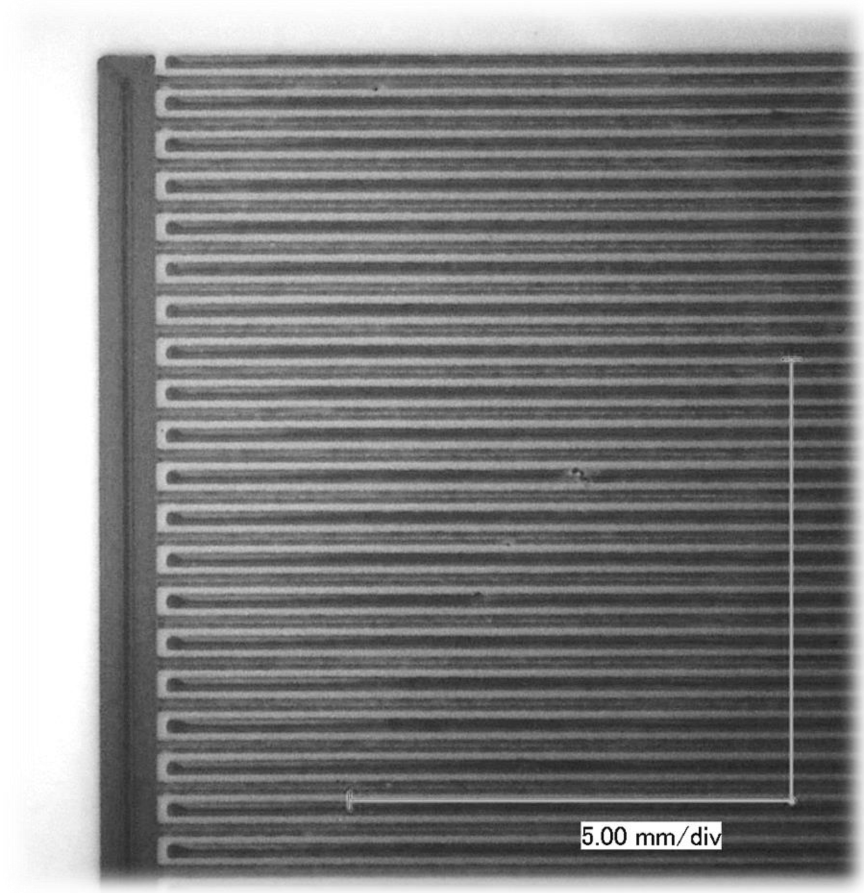




Copper particles after sintering (Xenon Flash sintering (20 ms/ 1400 J/ 3,6kV)

RESULTS FROM BASMATI CURRENT COLLECTORS

- Current collectors – CNT EG based ink (1 wt.%)

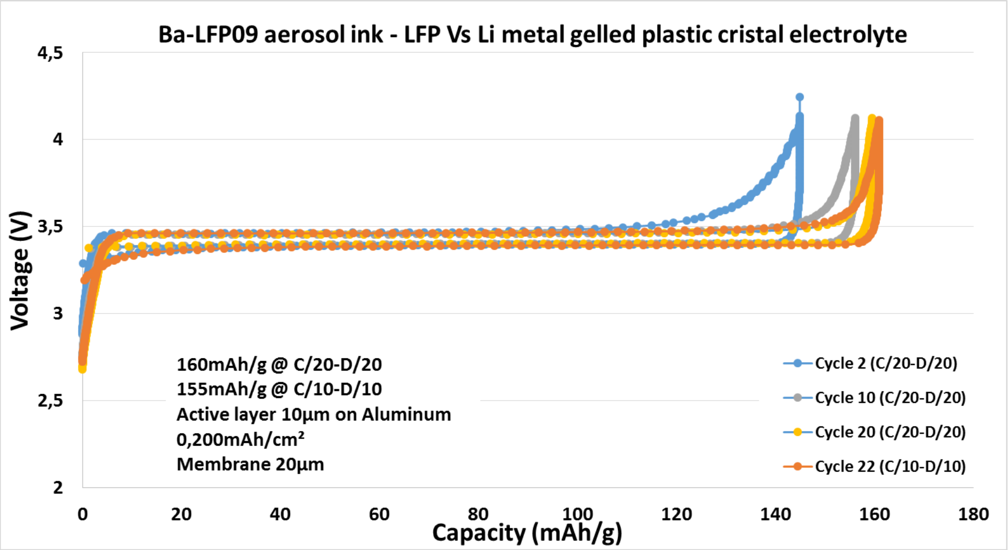


Dimensions	µm
Line width	180
Space between lines	60
Resolution	High
Satellites	No

- Both current collector could be printed with CNT
  - Simplification of process
  - Only one material for current collectors
- Conductivity measurements ongoing

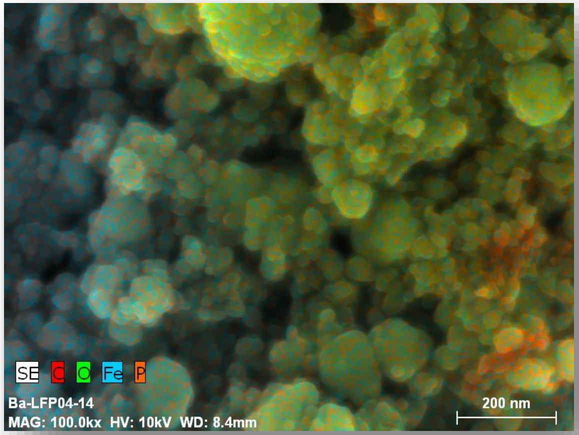
RESULTS FROM BASMATI ELECTRODES - POSITIVE

- Nano-ink compatible with numerial printing
- Good performances in terms of capacity retention and cycling



	Ba-LFP09
LFP Belife	70
SP	5
Gelled Matrix A/B	25(B)
EG/Water	88
Solid content (%)	12

LFP Belife



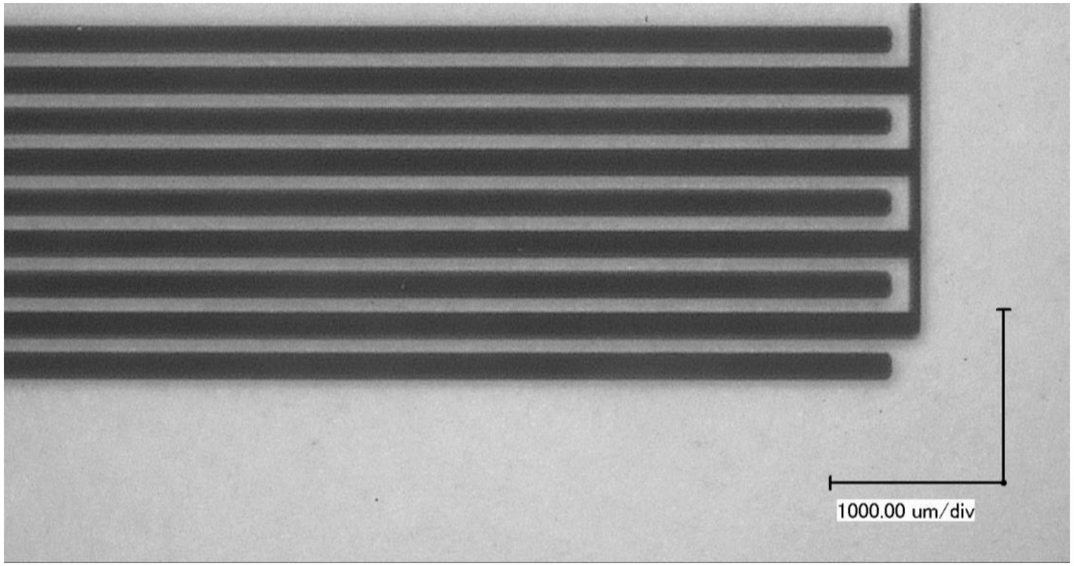
Membrane and jellified electrolyte

- Alternative plastic crystal solvent (Patent 2015 BF1557896)
- Non toxic
- Non volatile
- All solid configuration

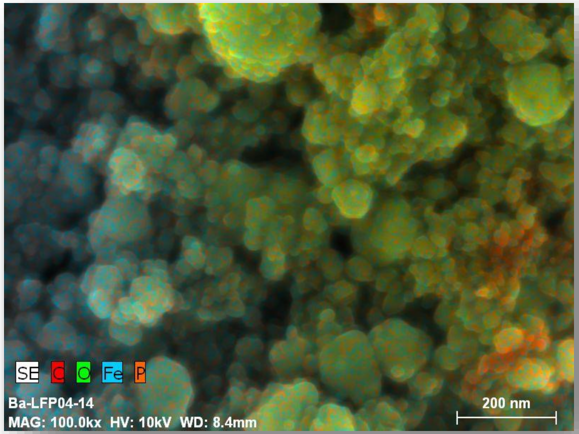
- Jellified membrane (20µm)
- Electrode loading: 0,2mAh/cm²
- Final version:
  - 70%: active material + conductors
  - 30%: 15% polymer matrix + 15% electrolyte

RESULTS FROM BASMATI ELECTRODES - POSITIVE

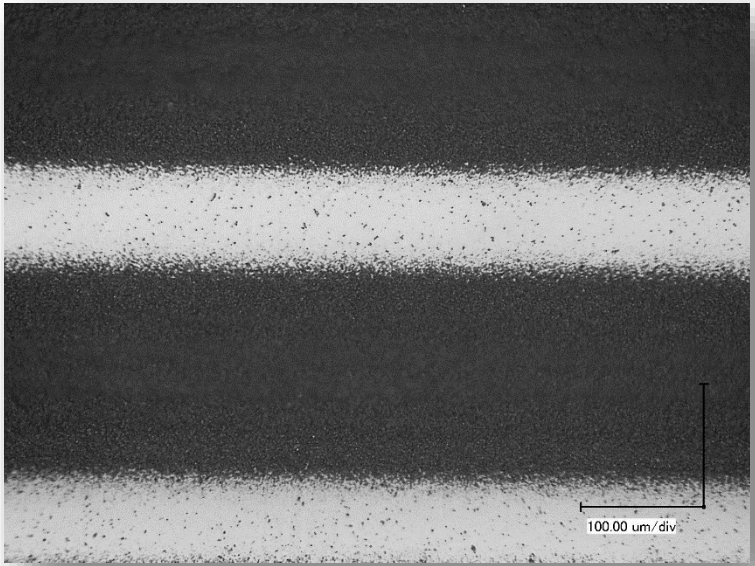
Electrodes printing



LFP Belife



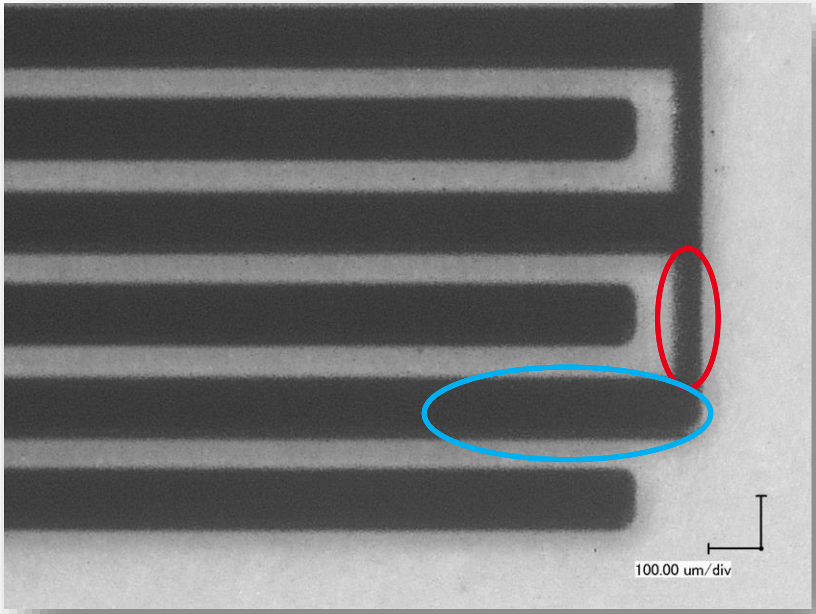
Ref. ink	LFP-09
Solvent	EG + H_2O
Dry content (wt. %)	12
Active material (wt. %)	70
Electrolyte (wt. %)	25
Additives (wt. %)	5



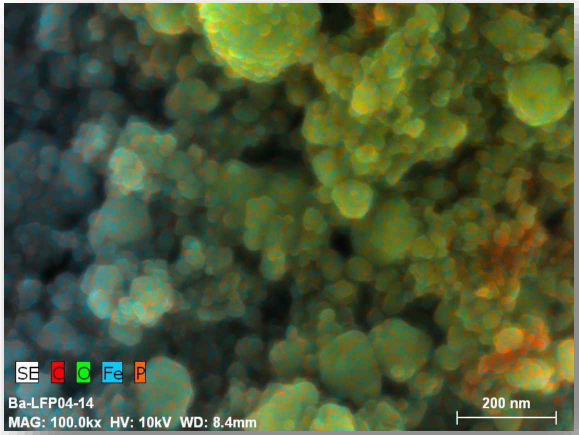
RESULTS FROM BASMATI ELECTRODES - POSITIVE

Electrodes printing

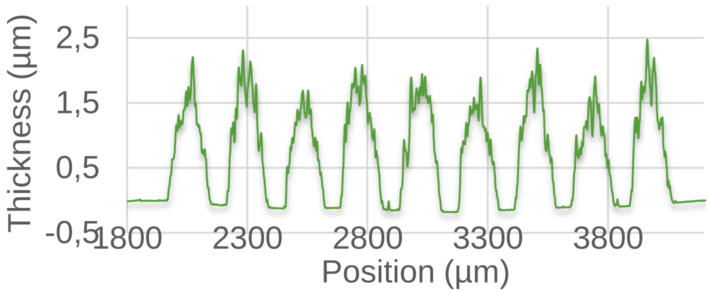
Dimensions	µm
Line width	116 ± 3
Line thickness	2,1 ± 0,2
Space between lines	58 ± 2

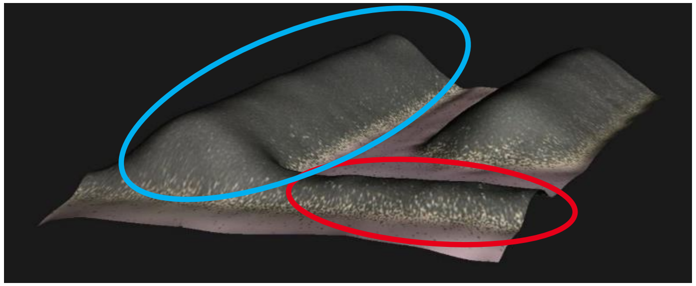


LFP Belife



LFP interdigitated profile sample





3D reconstructed optical image (not to scale)

CONCLUSIONS

- **Current collectors**
  - Copper → Printing + sintering **OK**
  - CNT → Printing (no need of sintering) **OK**
  - Conductivity measurements **Ongoing**
- **Positive electrode**
  - LFP → Formulation + electrochemistry + printing **OK**
- **Negative electrode** **Ongoing**
  - Nano graphite not available (testing with graphene)
  - Nano-LTO under study
    - 50 mAh/g for uncoated material (jellified configuration)
    - Theoretical capacity of LTO = 175 mAh/g
  - Formulation / characterization
  - Printing
- **Multi-material printing for complete prototype** **To be done**

Thank you for your attention

Basmati
Bringing Innovation by Scaling Up Nanomaterials and Inks for Printing

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