DIGITAL PRINTED LI-ION BATTERIES
SUMMARY

1. INTRODUCTION
   CEA / DRT / LITEN
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   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

Nuclear Energy
- Nuclear Energy Division

Research & Technology
- Technological Research Division

French strategic independance

French energetic independance

French economic competitiveness

Fundamental Research
- Material Science Division / Life Science Division

TECHNOLOGY

4 500 employees
550 M€ annual budget
500 patents / year
50 start-ups

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

Staff 1 400 - 170M€

New energy technologies and nanomaterials

LITEN

Staff 800 - 70 M€
2003 - Paris Sud

software-intensive systems

INSTITUT NATIONAL DE L’ENERGIE SOLAIRE

INES

Staff 1 800 - 240 M€
1967 - Grenoble

micro-nanotechnologies and system integration

LETI

Staff 800 - 70 M€
2003 - Paris Sud

List

Staff 1 400 - 170 M€
2005 - Grenoble / Chambéry
LITEN : KEY FIGURES

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

4 Research Divisions
- Solar and Building
- Electric Transport
- Biomass & Hydrogen
- Nanomaterials and Large Surface Electronics

2 Principal sites (Grenoble, Chambéry)
5 local sites (CEA-Tech, Cadarache + Corse)
2 commercial offices abroad (America, Japan)
VERTICAL INTEGRATION: THE VALUE CHAIN

- Fuel cell catalyst
- Powder for batteries
- X rays Nanotomography of ceramic cells
- PEMFC system
- Solar cells
- Batteries cells
- Solar charging station and micro grid
- Alsolen: 500 KW Fresnel Concentrated Solar Power

Integration of CEA technologies
15 KWh Li Battery + 25 kW PEMFC + 10,5 kg H2 ~350 kWh

MATERIALS

PROCESSES

COMPONENTS

SYSTEM INTEGRATION

DEMONSTRATION

FIRST INDUSTRIALIZATION
**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)
- Characterization

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

**Sensors**
- 3.2V - 40 mAh
- -0.01% / cycle
- LiFePO₄-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

**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**
- 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

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

- Pilot Line with 1000m² of dry room extension
- Line capability up to 500kWh/month
- 150-200kWh/month in practice (~3000 cells)
- 500 channels for formation
- 1000 channels for cycling

Coating
Slitting
Calendaring
Winding
Laser welding
Filling
Electrical, Abusive, Calendar Tests (1100 channels)
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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

Non stacked configuration

simplification of interfaces
(more flexibility with reduced mechanical constrains)

Interdigitated design

Non contact printing technique

Ink-jet

Aerosol jet printing

- More flexibility
- Design
- Interfaces
- Versatility of shapes

Nano inks

High resolution

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

Current collectors
Electrodes
Electrolyte
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 (10\(\mu\)m +/- 1\(\mu\)m)

- **Dimensions:**
  - Width of lines: 200\(\mu\)m
  - Distance between lines: <100\(\mu\)m (target 50\(\mu\)m) → electrolyte compartment

- Solid electrolyte configuration
- No densification

**Current collector**

**Polymer substrate + barrier layer**

**Electrodes 10 to 200 \(\mu\)m**

**Space <50\(\mu\)m**

**Cathode**

**Anode**

**Li^+ transport distance (constant)**

**Patent BF3007206**
**COMPARISON INK-JET AND AEROSOL JET PRINTING**

**Inkjet**
- Low viscosity
- Thin electrode at medium resolution

**Aerosol jet**
- Low to medium viscosity
- Thin electrode at high resolution

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
## TECHNICAL SPECIFICATIONS

<table>
<thead>
<tr>
<th></th>
<th>Screen printing</th>
<th>Inkjet basic</th>
<th>Ink dispenser</th>
<th>Aerosol jetting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle size</strong></td>
<td>&lt; 100 nm</td>
<td>&lt; 50 nm</td>
<td>&lt; 50 nm</td>
<td>&lt; 50 nm</td>
</tr>
<tr>
<td><strong>Layer thickness</strong></td>
<td>0.015-100</td>
<td>0.05-100</td>
<td>50</td>
<td>0.05 – 100</td>
</tr>
<tr>
<td><strong>Definition (lines spaces) (μm)</strong></td>
<td>30-100</td>
<td>5</td>
<td>10-500</td>
<td>2</td>
</tr>
<tr>
<td><strong>Feature size (μm)</strong></td>
<td>20-100</td>
<td>20-50</td>
<td>100</td>
<td>5-20</td>
</tr>
<tr>
<td><strong>Registration (μm)</strong></td>
<td>&gt; 25</td>
<td>&gt; 5</td>
<td>&gt; 20</td>
<td>&gt; 5</td>
</tr>
<tr>
<td><strong>Patterning capacity</strong></td>
<td>Required specific frame and hardware</td>
<td>Software development</td>
<td>Software development</td>
<td>Software development</td>
</tr>
<tr>
<td><strong>Patterning Design</strong></td>
<td>2D</td>
<td>3D</td>
<td>3D</td>
<td>3D</td>
</tr>
<tr>
<td><strong>Ink viscosity Pa.s</strong></td>
<td>0.5-50</td>
<td>0.001-0.1</td>
<td>0.02- 1</td>
<td>0.02 - 1</td>
</tr>
<tr>
<td><strong>Throughput m²/s</strong></td>
<td>2-3</td>
<td>0.01-0.5</td>
<td>0.01-0.5</td>
<td>0.01-0.5</td>
</tr>
</tbody>
</table>
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)
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RESULTS FROM BASMATI

• **Current collectors** \( \rightarrow \) Cu / CNT / Ni / Gold
  - Formulation / characterization
  - Printing
  - Sintering

• **Electrodes** \( \rightarrow \) 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

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

  - Compatible with aerosol jet printing

  - Distribution:
    - D10 = 80 nm
    - D16 = 110 nm
    - D50 = 250 nm
    - D84 = 570 nm
    - D90 = 740 nm
    - Dmax = 3800 nm

- **Copper current collector**

  - 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

**Configuration Sinteron 2000**

- 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.%) 

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line width</td>
<td>180</td>
</tr>
<tr>
<td>Space between lines</td>
<td>60</td>
</tr>
<tr>
<td>Resolution</td>
<td>High</td>
</tr>
<tr>
<td>Satellites</td>
<td>No</td>
</tr>
</tbody>
</table>

- 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 numeral printing
- Good performances in terms of capacity retention and cycling

**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

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<table>
<thead>
<tr>
<th></th>
<th>Ba-LFP09</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP Belife</td>
<td>70</td>
</tr>
<tr>
<td>SP</td>
<td>5</td>
</tr>
<tr>
<td>Gelled Matrix A/B</td>
<td>25(B)</td>
</tr>
<tr>
<td>EG/Water</td>
<td>88</td>
</tr>
<tr>
<td>Solid content (%)</td>
<td>12</td>
</tr>
</tbody>
</table>
RESULTS FROM BASMATI ELECTRODES - POSITIVE

Electrodes printing

<table>
<thead>
<tr>
<th>Ref. ink</th>
<th>LFP-09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>EG + H₂O</td>
</tr>
<tr>
<td>Dry content (wt. %)</td>
<td>12</td>
</tr>
<tr>
<td>Active material (wt. %)</td>
<td>70</td>
</tr>
<tr>
<td>Electrolyte (wt. %)</td>
<td>25</td>
</tr>
<tr>
<td>Additives (wt. %)</td>
<td>5</td>
</tr>
</tbody>
</table>

LFP Belife
RESULTS FROM BASMATI ELECTRODES - POSITIVE

Electrodes printing

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line width</td>
<td>116 ± 3</td>
</tr>
<tr>
<td>Line thickness</td>
<td>2,1 ± 0,2</td>
</tr>
<tr>
<td>Space between lines</td>
<td>58 ± 2</td>
</tr>
</tbody>
</table>

LFP Belife

LFP interdigitated profile sample

3D reconstructed optical image (not to scale)
CONCLUSIONS

• **Current collectors**
  • Copper → Printing + sintering
  • CNT → Printing (no need of sintering)
  • Conductivity measurements

  | OK | OK | Ongoing |

• **Positive electrode**
  • LFP → Formulation + electrochemistry + printing

  OK

• **Negative electrode**
  • 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

  Ongoing

• **Multi-material printing for complete prototype**

  To be done
Thank you for your attention