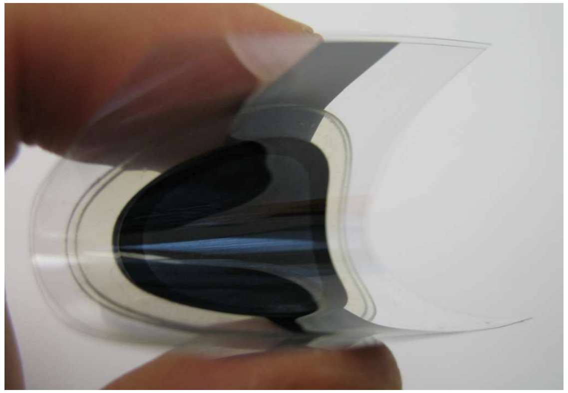
Polymeric binders for printed Thin Film Li-ion Batteries



CEA-LITEN-DEHT

Laboratoire des Batteries Avancées

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energie atomique • energies alternatives

Thin Film Li-ion Batteries

Why printing Li-ion batteries ?

- **Wireless communication is or will be everywhere**
  - ✓ Mobile personal equipment
    laptops, cellular phones, Personal Digital Assistants (PDA)
  - ✓ Autonomous sensors and actuators network:
    transport (*smart tickets, cars, trucks, trains, planes, satellites, shuttles, …)*, wearable devices *(emergency situation, signalling …),* industrial environment *(ball bearing, T or deformation monitoring, …)*, ID control, anti-tampering, home automation, …

- **Wireless communication needs embedded energy !**
  - ✓ A non rechargeable (or primary) battery: need replacement, big and heavy
  - ✓ A rechargeable (or secondary) battery recharged by electrical plug or by systems converting environmental energy in electrical one (PV, …)
  - ✓ A harvesting system by extracting energy from environment to power directly the device (new microelectronics systems) ➔ complete autonomous system

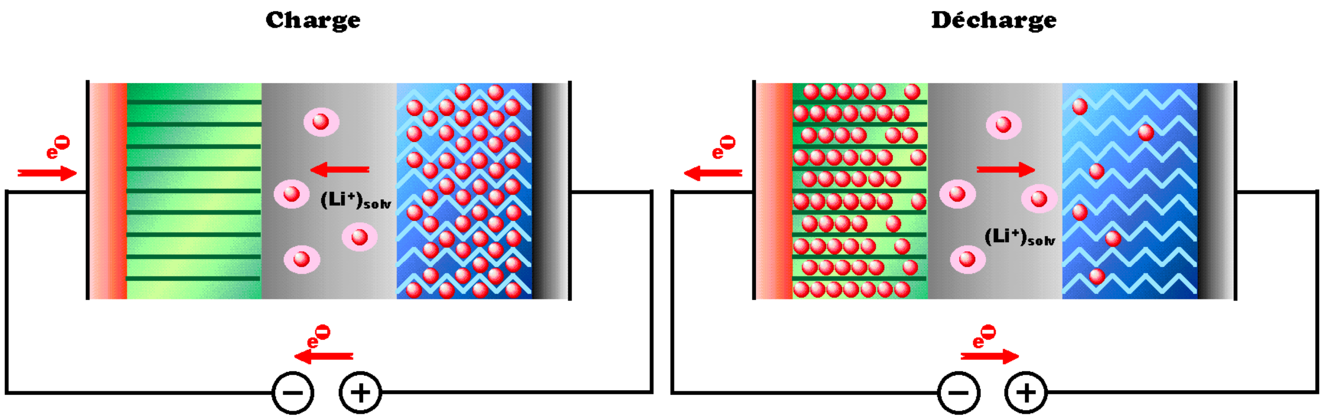
Need of thin film batteries when only flat available volume
➔ sometimes flexibility is required too

Thin Film Li-ion Batteries

Specifications of TFB

- **Dimension constraints:** low thickness (<1mm), high energy density (↗ capacity on ↘ area)
- **Electrical and environmental constraints**: Energy/Power ?, low/high discharge current ?, peaks ?, Potential range and operating voltage ?, Life time, Cycle life ? Temperature, pression, … ?
- **Flexibility:** level of flexibility dependant on the substrate and application: Conformable (plane wings, …), Flexible and rigid (smart card, …), Highly flexible working when bending (smart clothes, …)

Principle of working of Li-ion batteries



Charge:

$\langle H\rangle + Li^+ + e^- \rightarrow \langle HLi\rangle$

$\langle MLi\rangle \rightarrow \langle M\rangle + Li^+ + e^-$

Décharge:

$\langle HLi\rangle \rightarrow \langle H\rangle + Li^+ + e^-$

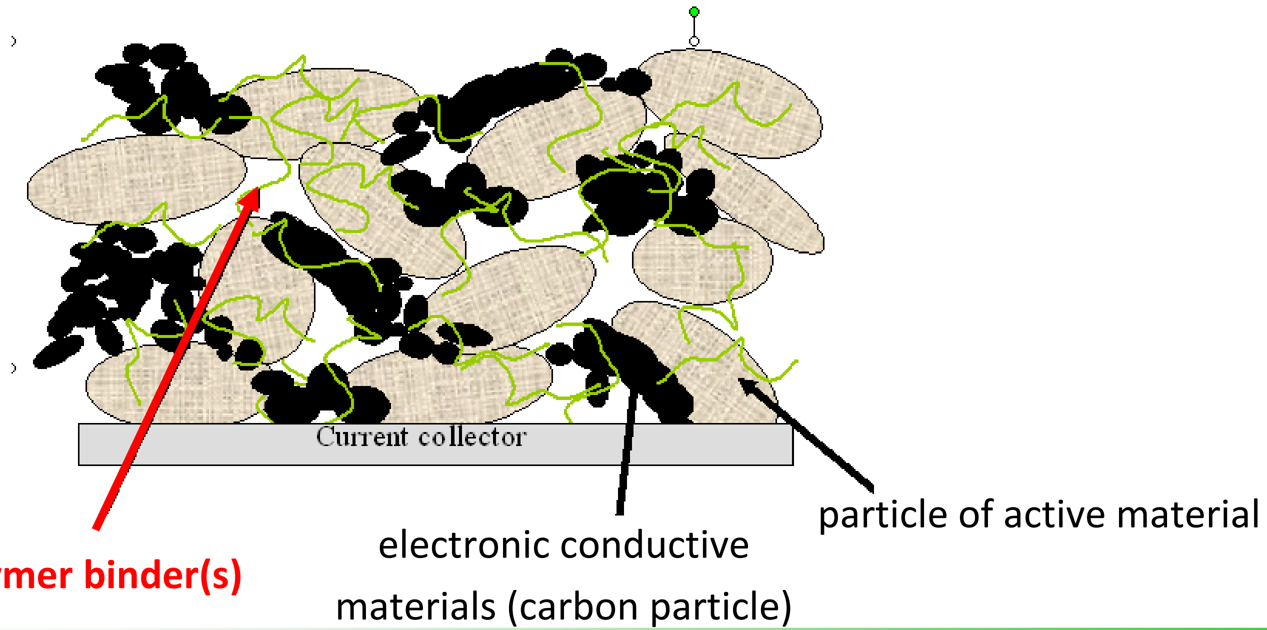
$\langle M\rangle + Li^+ + e^- \rightarrow \langle MLi\rangle$

Thin Film Li-ion Batteries

Where are polymers in a Li-ion battery ?

The electrodes inks : a mixture of powdered materials

- ✓ **Active materials** (75 to 90%): metal oxydes $LiCoO_2$, $LiMn_2O_4$, V_2O_5, $LiFePO_4$, HT spinels, … for positive electrodes and Graphite, Si-C, $Li_4Ti_5O_{12}$, … for negative electrodes
- ✓ **Electronic conductive additives** (a few %) : carbon based compounds
- ✓ **Polymer binder(s)** (a few %) : PVdF (T_f = 150°C), SBr/CMC (-30 to 120°C), …
- ✓ **Liquid phase** (30% to 65%) : N-Methyl pyrrolidone (NMP), water, …

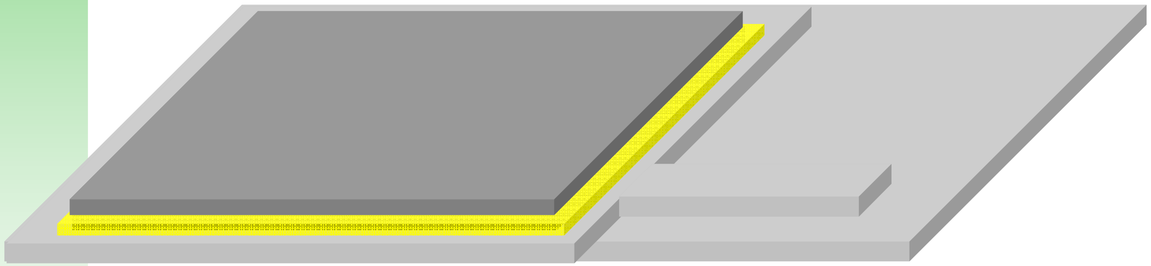


Printed Thin Film Li-ion Batteries

Printed battery architecture

Conventional batteries vs printed TFB : difference in the implementation of the architecture

Classically winding or stacking the three elements (electrode ⊕, separator and electrode ⊖) then electrolyte filling



- Current collector substrate
- Patterned ink deposit, positive or negative electrode
- Patterned membrane ink deposit
- Patterned ink deposit, positive or negative electrode
- Cutting of current collector

Substrate: metallic foil: Al, Cu or Ni (~20µm)

First printed layer: colloidal suspension ink, wet thickness : 100µm to 500µm

Second printed layer: polymer solution ink, wet thickness : 100 to 300µm

Third printed layer: same as first printed layer (opposite sign for active material)

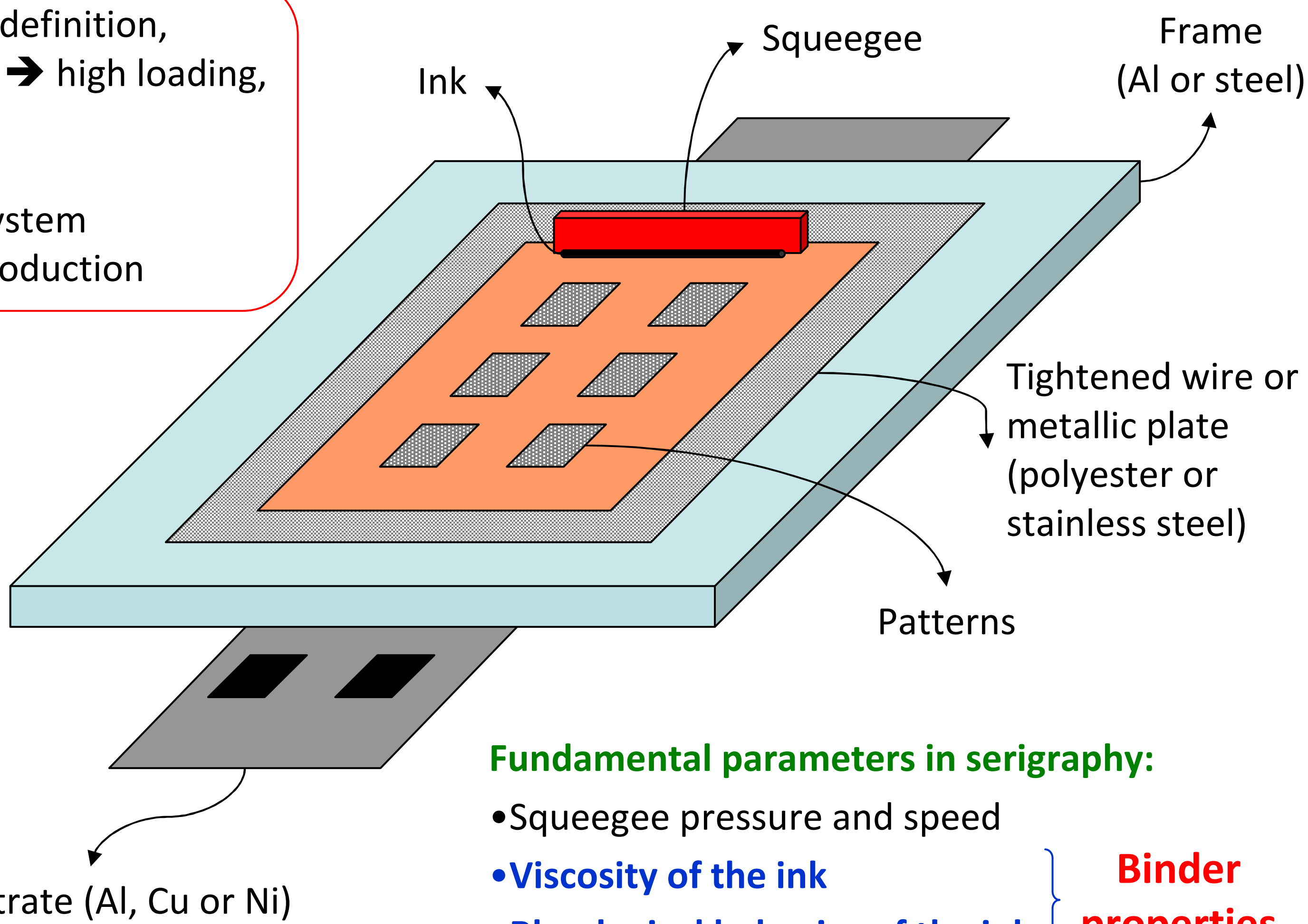
For each printing step, the ink properties (rheological behavior, surface energy, …) are tuned by the polymer and the formulation

Printed Thin Film Li-ion Batteries

Printed techniques for Li-ion batteries: serigraphy

Advantages: good pattern definition, thick deposit → high loading, no transfer

Drawbacks: reel-to-reel system low rate of production



Fundamental parameters in serigraphy:

- Squeegee pressure and speed
- **Viscosity of the ink**
- **Rheological behavior of the ink**

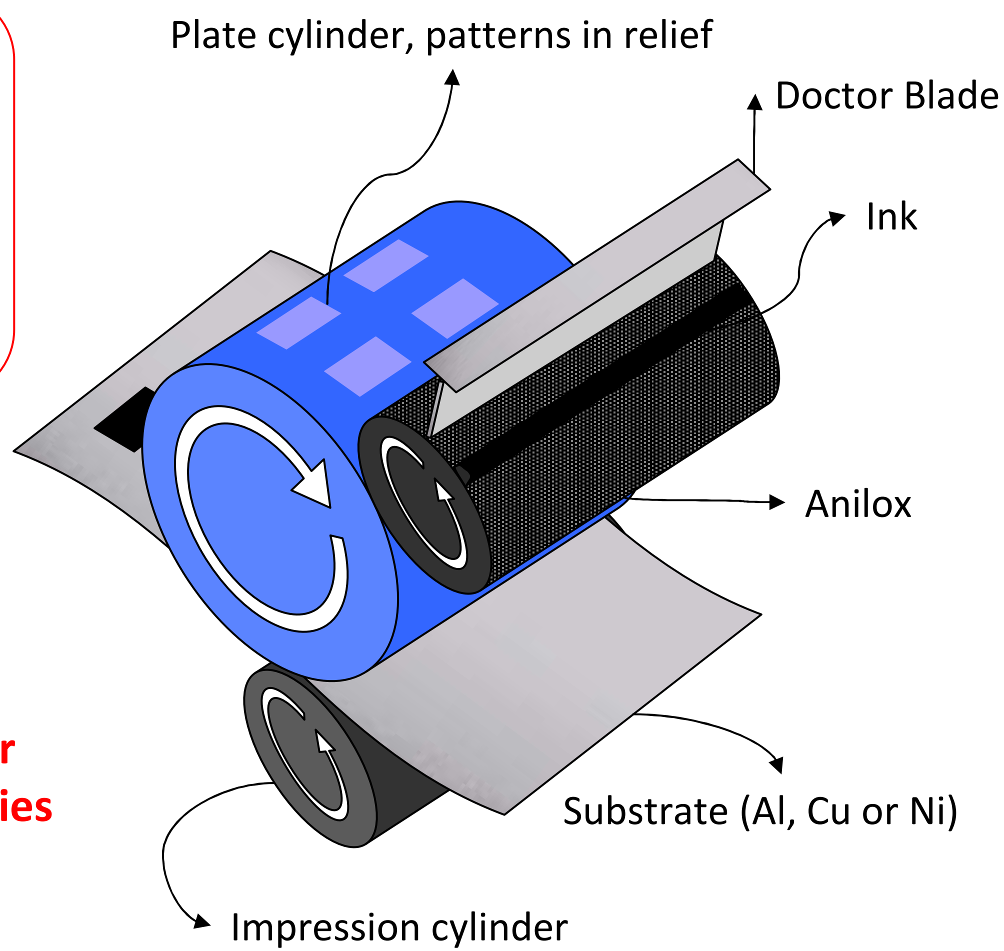
} **Binder properties**

Printed Thin Film Li-ion Batteries

Printed techniques for Li-ion batteries: flexography

Advantages: good pattern definition
roll-to-roll system ➔ fast printing
large number of large pattern

Drawbacks: thin deposit ➔ several sequences for high loading
handling of the different transfers



Fundamental parameters in flexography:

- Pressure between Anilox/Plate Cylinder and Plate Cylinder/Impression Cylinder
- **Viscosity of the ink**
- **Rheological behavior of the ink**
- **Surface energy of the ink (quality of the transfers)**

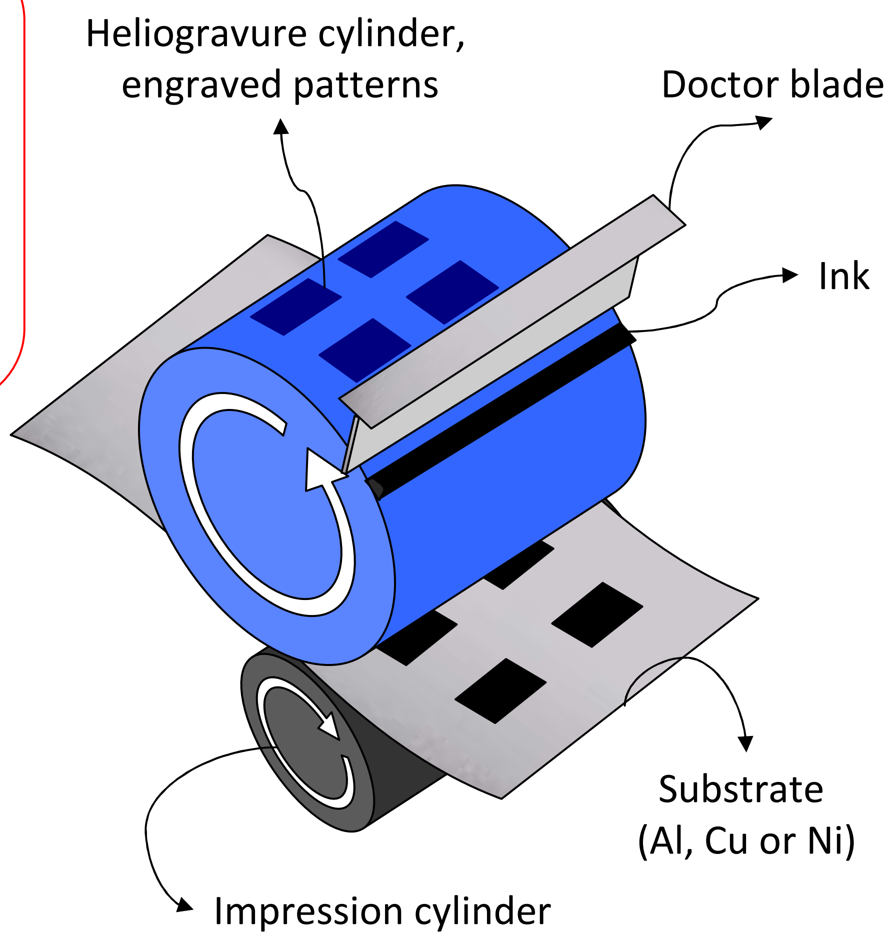
} **Binder properties**

Printed Thin Film Li-ion Batteries

Printed techniques for Li-ion batteries: Heliogravure

Advantages: good pattern definition
roll-to-roll system → fast printing
large number of large pattern
thick deposit

Drawbacks: one cylinder for one pattern (expensive)
handling of the transfer
handling of the pattern filling



Fundamental parameters in flexography:

- Pressure of Plate Cylinder/Impression Cylinder
- **Viscosity of the ink**
- **Rheological behavior of the ink**
- **Surface energy of the ink**

(quality of the transfers)

} **Binder properties**

Printed Thin Film Li-ion Batteries

Required properties of the binder for printing electrodes

Same properties as for the classical stacked or wound Li-ion batteries:

- A cohesion between all the particles without covering them
- Sufficient wetting properties with the electrolyte
- A good adherence to the collector
- Mechanical properties (winding, variation of size…)

Role of the polymer in the electrode printing process:

- To give the required viscosity and rheological behaviour for:
  - a good filling of the pattern in serigraphy
  - an optimized transfer in flexo/heliography
- To give a surface tension in accord with the substrate (high adherence) and the printing devices (anilox, gravure cylinder, printing plate for ink transfer)

What do we need for a good printing of the electrode ?

Rheologicaly:

- Low viscosity at high shear rate (under squeegee or doctor blade)
- Flowing at rest (surface leveling after deposit)

} **Shear-thinning behavior without flowing threshold**

Chemically : increase the surface tension of the ink } **Presence of polar groups or polymer blends**

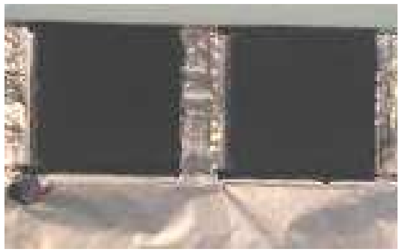
Printed Thin Film Li-ion Batteries

Flexo printing of a few positive electrodes

$LiFePO_4$ active material, novel aqueous formulation

One pass = 12µm   0,23mAh.cm^{-2} Solid content = 45%

$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ active material, organic formulation (4.3 x 4.5 cm²)

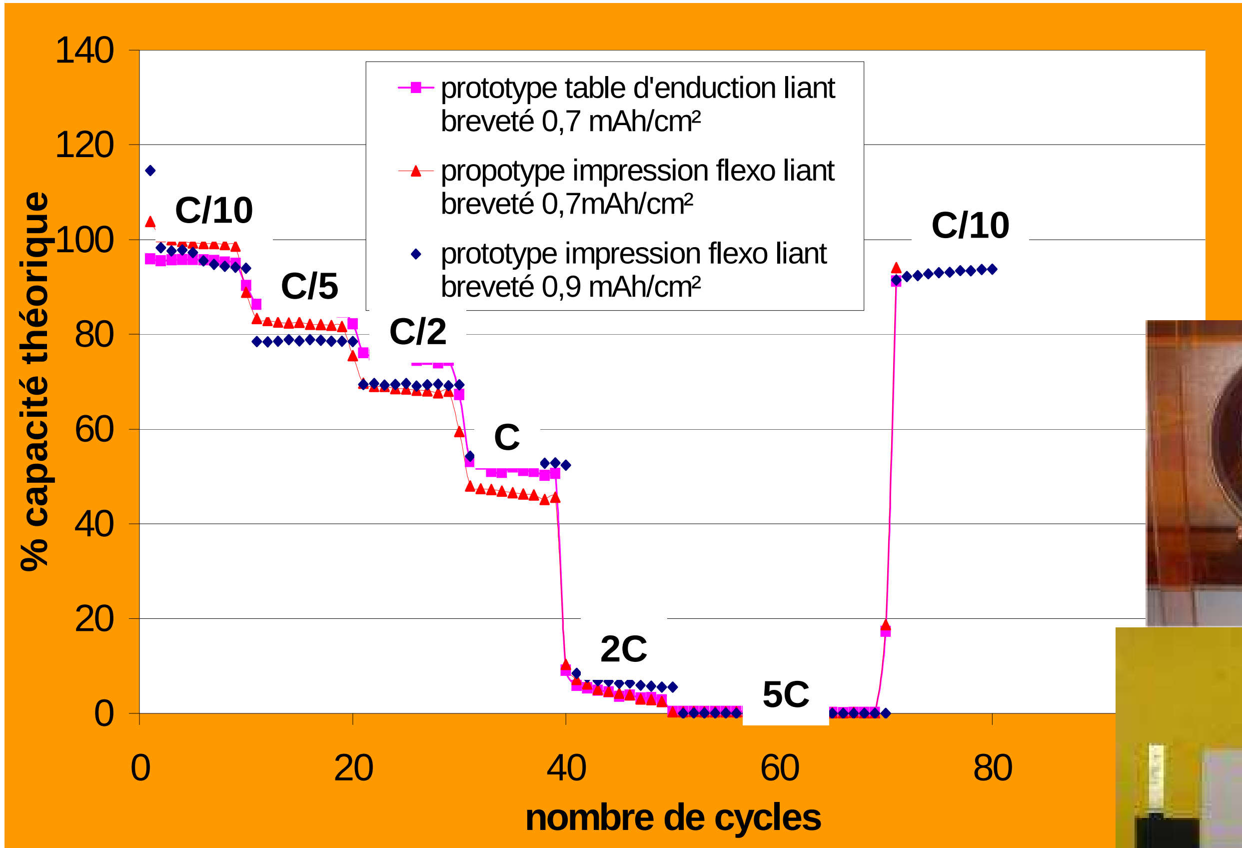


Dry thickness: 10 to 45-50 µm

Solid content %	55	52	49
Number of passes	Loading (mAh.cm^{-2})		
1	0.25	0.2	0.1
2	0.5	0.4	0.25
3	0.75	0.6	0.4
4	1	0.9	0.6

Printed Thin Film Li-ion Batteries

Battery prototype with flexo printed electrodes

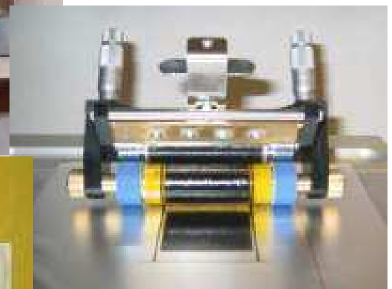


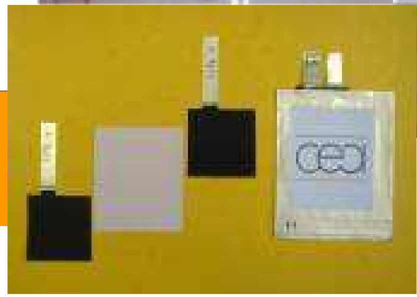
Technology *: $LiCoO_2$ / $Li_4Ti_5O_{12}$*

Nominal voltage *: 2.3V*

Nominal capacity *: 14.5 mAh*

Square electrode area : 20.5 cm^2 (manual) and 20 cm^2 (lab tester)





Patented binder = blend of **PVdF** and **PVA** *(WO2008101823 patent)* → Increase of the surface tension of the ink

Flexography printed TFB performances similar to coated Thin Film Battery

Printed Thin Film Li-ion Batteries

Example of a few screen printed electrodes

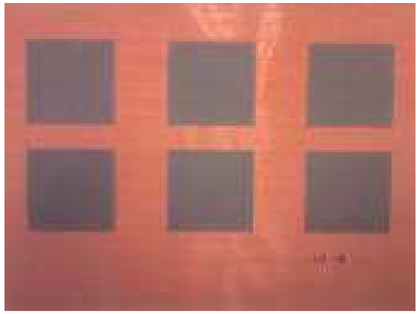
Storage battery electrodes ⊕ and ⊖

$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ / graphite

70mAh, 30 cm² prototypes

PVDF binder

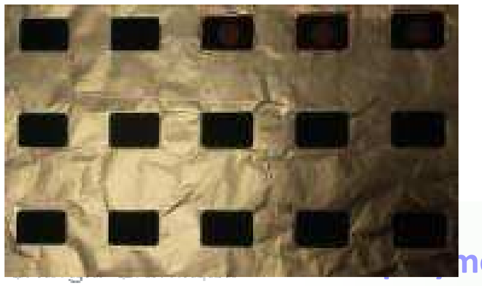
CMC/SBr binder



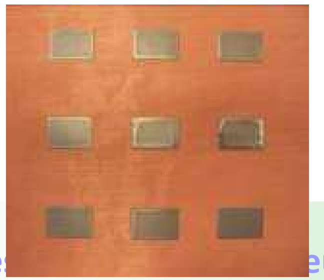
$LiCoO_2$ / graphite

20mAh, 14cm² prototypes

PVDF binder



CMC/SBr binder



Battery electrodes for high rate ⊕ and ⊖

$LiFePO_4$ / $Li_4Ti_5O_{12}$

20mAh, 35cm² prototypes

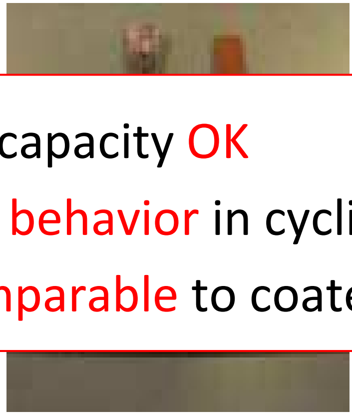
PVDF binder

PVDF binder

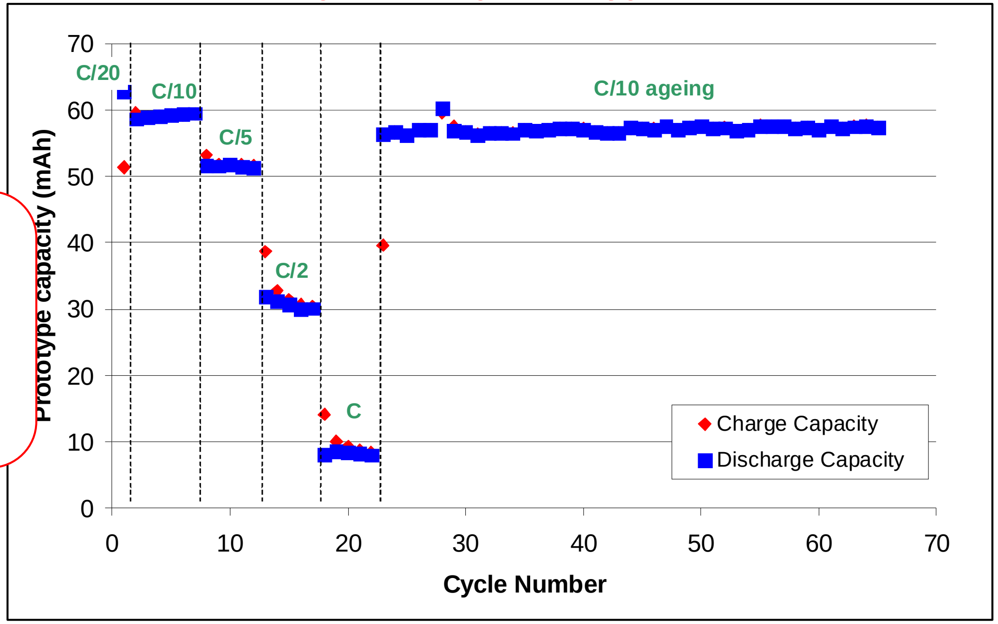
Printed Thin Film Li-ion Batteries

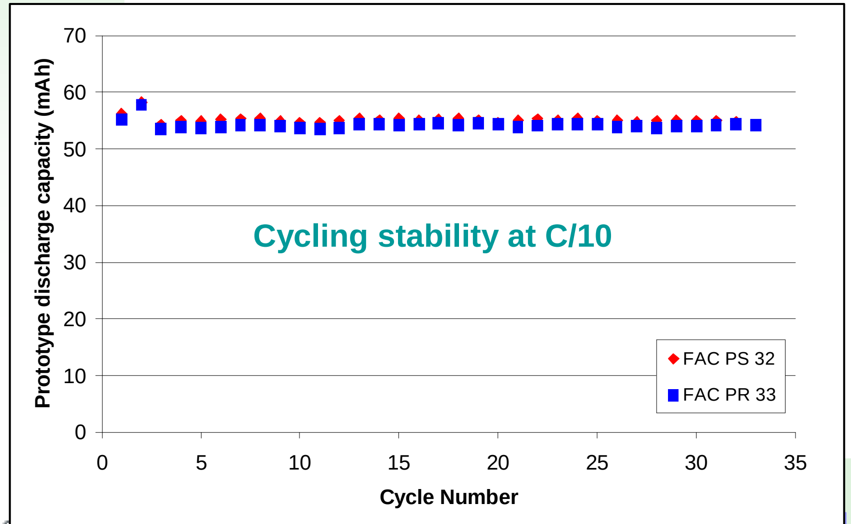
FACESS Flexible Autonomous Cost efficient Energy Source and Storage

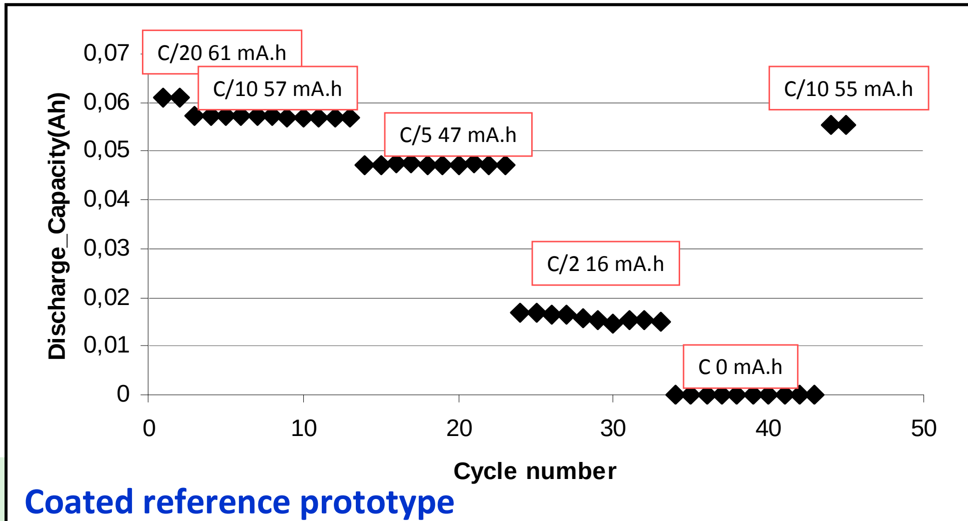
Results of cycling tests on a 70mAh screen-printed prototype



- Recovered capacity OK
- Very stable behavior in cycling
- Results comparable to coated battery







Coated reference prototype

Printed Thin Film Li-ion Batteries

Wich binder for the next generation of printed Li-ion batteries ?

Future development of binders for next generation of printed Li-ion batteries:

- Printing processes:
  - o Surface tension for roll-to-roll
  - o Rheological behaviour
- Green
- Adhesive (ex: Adhesive PVdF)
- Compatible with new electrode materials
  - o High working potential (ex: $LiNi_{0.5}Mn_{1.5}O_4$, [3 - 5V])
  - o Compensation of volumetric expansion (ex: Si (/C) materials)
- New process of implementation : no solvent, cross-linking polymerisation …

Thank you for your attention

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