PVdF based binders for gelled electrodes prepared using a dry process

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CEA LITEN
SYENSQO (ex SOLVAY)

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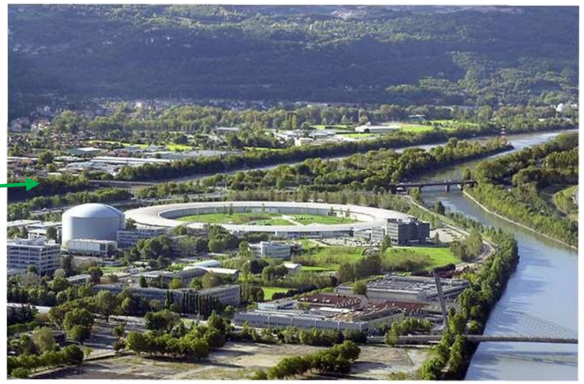

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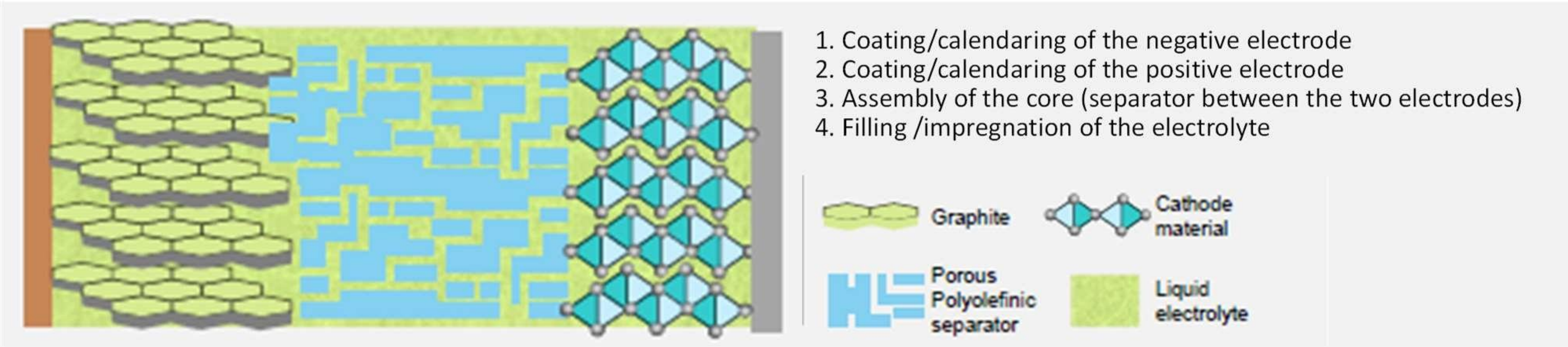
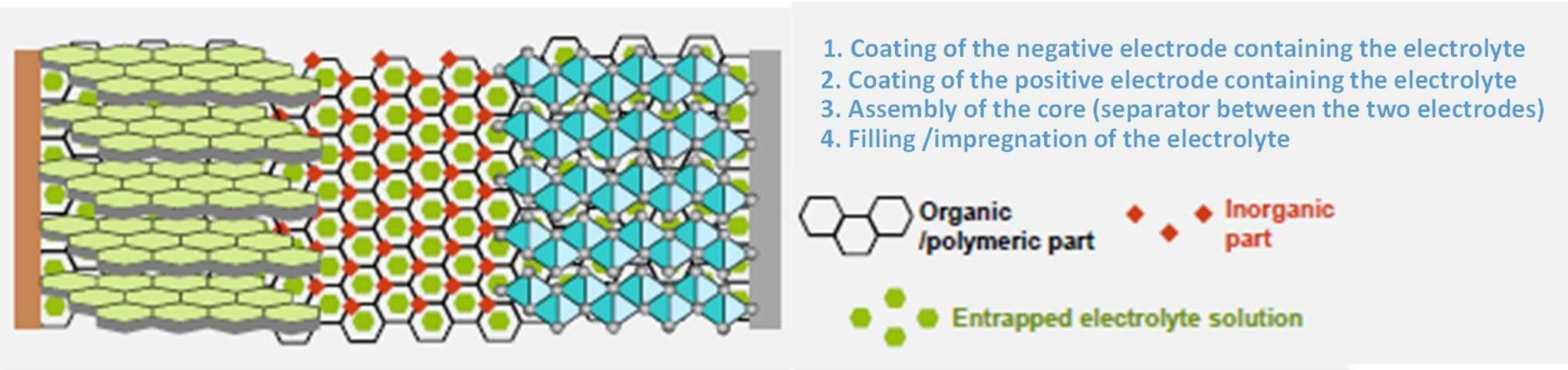
Principle of Hybrid Polymer Lithium Battery Technology

From a traditional porous separator with injected liquid electrolyte



To a hybrid inorganic/ organic polymer membrane



- ➢ The electrolytic compartment is made of cross-linked structure combining Solvay proprietary polymer and inorganic structure encapsulating an electrolyte in a dense membrane
- ➢ Each composite electrode compartment is made of active materials, conductive additive, electrolyte solution and Solvay proprietary polymer.

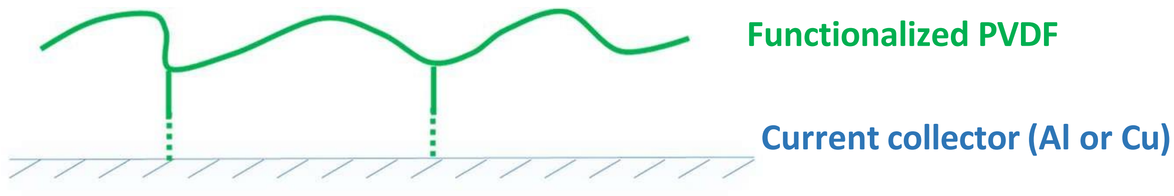
Structure of the SOLGAIN™ gelled electrodes

➔ **The liquid electrolyte is already in the electrodes, trapped inside the composite structure**

➔ **The electrode formulation is the same as the classical ones: the same compounds, the same contents, except the presence of the electrolyte from the beginning and the binder**

❖ **The binder : PVDF1**

Jfunctionalized
Jhigh molecular weight (~1 million)
Jflexible PVDF, $T_m = 148°C$



❖ **High capability for trapping electrolyte with the pores fully filled**

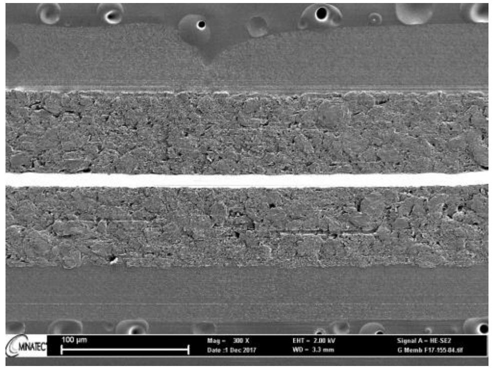
❖ **High adhesion to current collector**

❖ **High flexibility even at high electrode loading**

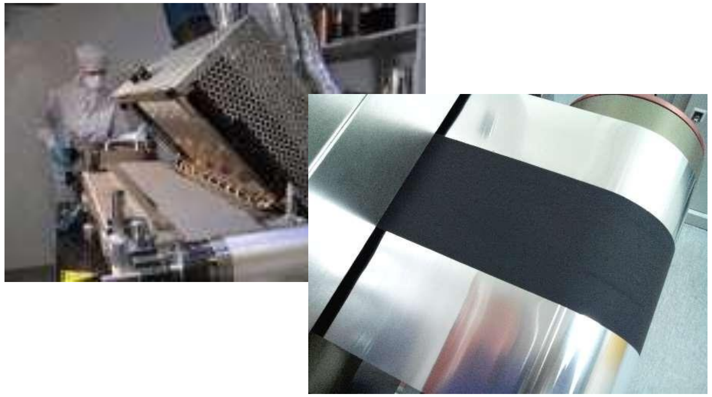
Building of the gelled electrodes using wet process

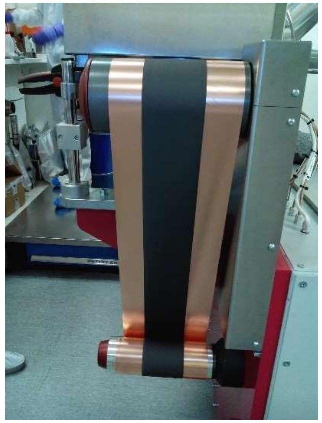
- **The slurry synthesis is classical, including a supplementary step for the electrolyte addition in acetone media**
  - ✓ At the lab scale, validated for various active materials (NMC, Cgr mixture, LFP, LTO…)
  - ✓ At the pre-pilot scale:
    - ➢ prepared in dry room using a standard disperser
    - ➢ Chronology of the addition steps defined to obtain an homogeneous slurry

Double side anode



- **R2R coating and calendaring with standard equipment in dry room (-20°C)**
  - ✓ successive coating for double-sided electrode
  - ✓ no issue of winding-unwinding
  - ✓ No issue of electrolyte leakage

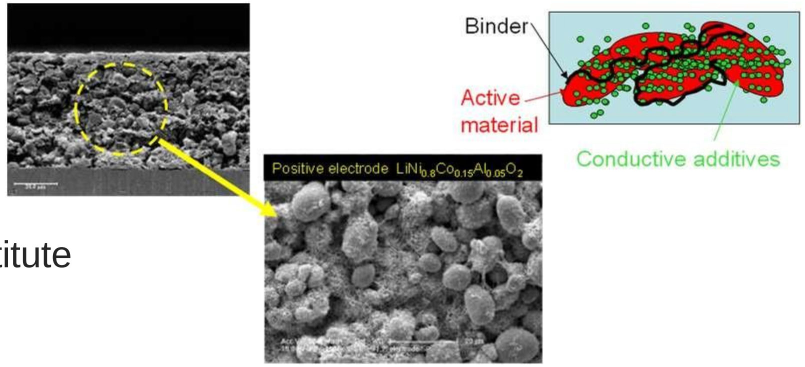




Towards a solvent free process

❖ Choice of the manufacturing method

- ✓ A gelled electrode : an homogeneous composite mixture with active material particles (> 90 wt%), conductive additive(s) (a few wt%) and polymer binder (a few wt%), trapping the electrolyte and with efficient electronic contact with the current collector



- ✓ **No process solvent** → only the organic electrolyte (10-15 wt%) will constitute the liquid media

➔ **To prepare highly viscous paste trapping the electrolyte (~10000 Pa.s at 0.1 s^{-1})**
➔ **To shape the paste in form of thin layer**
➔ **To deposit the film onto the Al or Cu current collector**

In continuous mode, at the industrial scale

❖ Kneading of the mixture while the polymer binder swells inside the electrolyte, at moderate temperature to avoid the electrolyte evaporation → **extrusion at low temperature using electrolyte with high $T_{boiling}$**

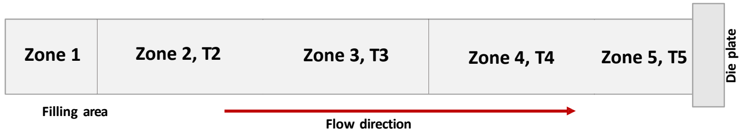
❖ then **lamination** (to adjust the target loading)

❖ Finally **co-lamination** (with the current collector)

A new grade of binder compatible to the solvent free process

❖ **Preparation of positive gelled electrode – Development of the extrusion step**

- ➔ Twin-screw extruder in dry room
- ➔ Various screw profiles
- ➔ Flat slot die at the outlet
- ➔ 4 heating zones 4 adjustable temperatures



❖ **Extrusion of NMC based electrode formulated with PVDF1**

✓ $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) / Conductive additive / PVDF1,

✓ 1M $LiPF_6$ in EC:PC 1:1 + 2 wt% VC

Electrode strip recovered at the extruder outlet

The best parameters to obtain viscoelastic strip

✓ Process temperature 110°C, too high for the material stability

✓ Solid content max 78%, too low for the target electrode density

✓ Performances in cycling poor compared to the gelled electrode prepared in acetone

PVDF2

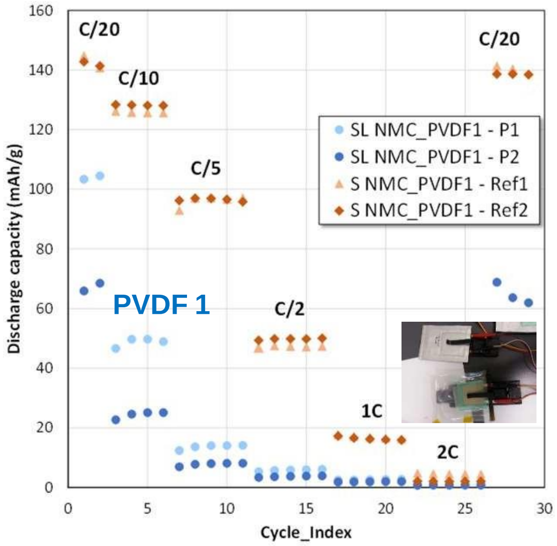
functionalized (for the electrode adhesion on the current collector)

more amorphous than PVDF1

high molecular weight (~1 million) similar to PVDF1

flexible PVDF, Tm = 127°C

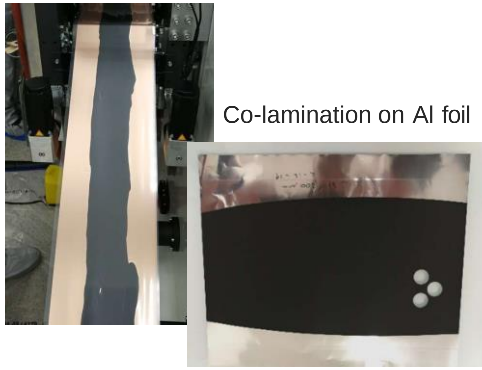
Full gelled Cgr/NMC, $LiPF_6$ in EC:PC +VC, pouch cells, [2.8 – 4.2V], at RT



Improvement brought by the new binder PVDF 2

- **Preparation of NMC based electrode formulated with PVDF2**
  - ✓ $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) / Conductive additive / PVDF2,
  - ✓ 1M $LiPF_6$ in EC:PC 1:1 + 2 wt% VC

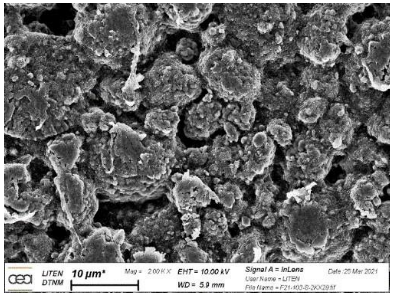
Electrode strip recovered at the extruder outlet



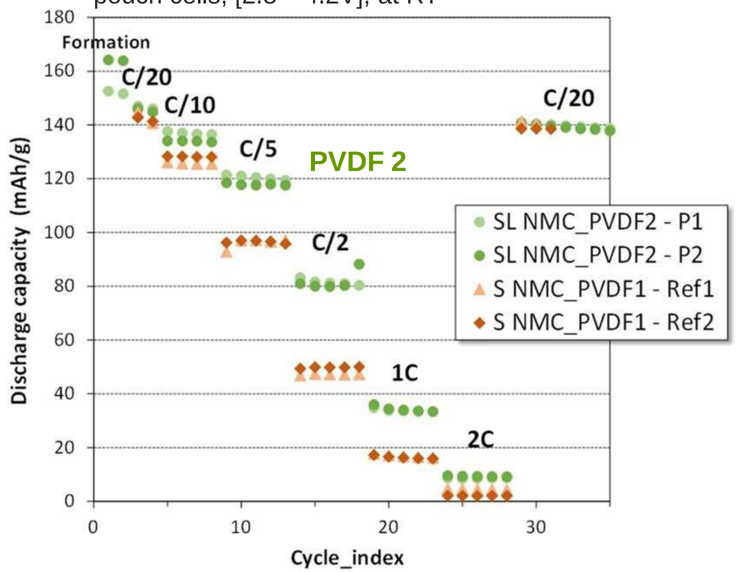
Co-lamination on Al foil

- **The solvent free process**
  - ➔ Extrusion, lamination and co-lamination significantly easier with PVDF 2
    - ✓ Lower extrusion temperature ➔ 90°C
    - ✓ Solid content max ➔ 85%
    - ✓ Higher NMC ratio ➔ 96%

  (Solid content max and Higher NMC ratio: Close to the target)



Full gelled Cgr/NMC, $LiPF_6$ in EC:PC +VC, pouch cells, [2.8 – 4.2V], at RT



- **The NMC based electrode**
  - ➔ Properties
    - ✓ Cohesive and flexible
    - ✓ Homogeneous dispersion
    - ✓ Can be prepared with high loading (> 4.5 mAh/cm^2)
  - ➔ Performances in cycling
    - ✓ significantly better compared to the gelled electrode prepared in acetone

Electrical performances in cycling

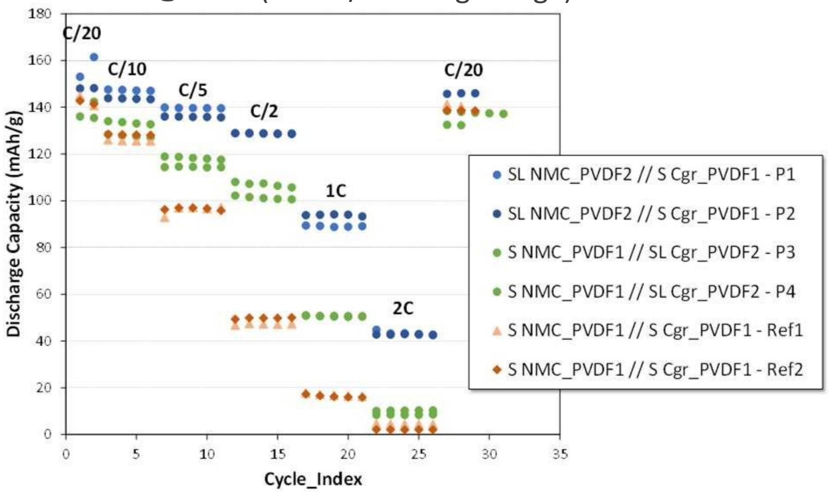
❖ **The solvent free process is applicable to various active materials:**

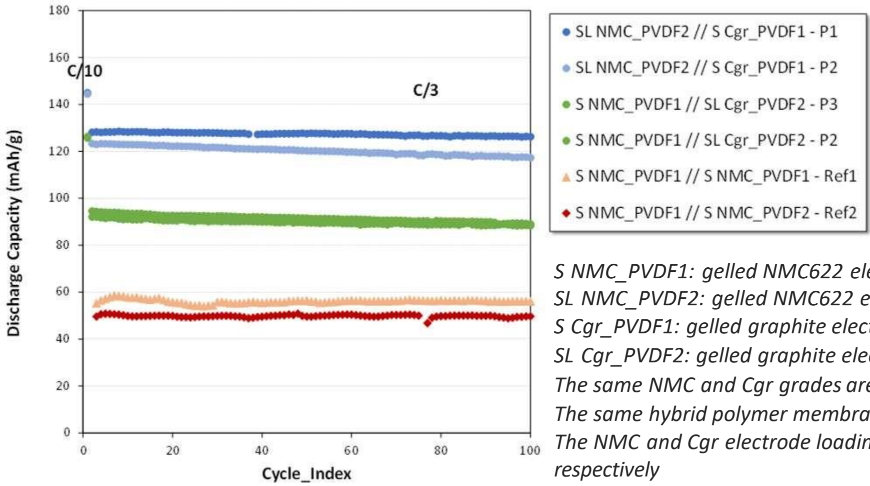
- ✓ Graphite Cgr, Cgr-Si(O_x) based mixture…
- ✓ NMC grades, LMNO...

❖ **Improvement of the performances in cycling of highly loaded gelled electrodes**

- ✓ Compared to the first generation of gelled electrodes prepared in acetone
- ✓ Especially at high C-rates

Full gelled NMC/Graphite, $LiPF_6$ in EC:PC +VC, pouch cells, [2.8 – 4.2V]





S NMC_PVDF1: gelled NMC622 electrode prepared in acetone
SL NMC_PVDF2: gelled NMC622 electrode prepared by extrusion
S Cgr_PVDF1: gelled graphite electrode prepared in acetone
SL Cgr_PVDF2: gelled graphite electrode prepared by extrusion
The same NMC and Cgr grades are used for the various electrode
The same hybrid polymer membrane is used in the pouch cells
The NMC and Cgr electrode loadings are 4.2-4.5 and 4.7-5 mAh.cm^{-2} respectively

➔ The paste kneading during extrusion may improve the dispersion of the electrode compounds

Conclusion and perspectives

❖ **Strong points:**

- Feasibility for preparing gelled electrodes without solvent demonstrated
- High ability to trap the electrolyte (favoring by the functionalized PVDF)
- Battery working demonstrated without complementary electrolyte addition
- Better performances at high loading, compared to the first generation of gelled electrodes prepared in acetone

❖ **Future actions:**

- Process parameters/conditions according to the active material grade
- To develop the manufacturing process for single-side and double-side electrode at pilot scale for industrial implementation
- Solvent free process for the hybrid polymer membrane

Thank you for your attention!

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