

LES POLYMÈRES FONCTIONNELS AU COEUR DES BATTERIES DU FUTUR

La réponse des polymères de Solvay aux demandes
croissantes de matériaux innovants dans les batteries Lithium

Thierry BAERT

18 Mai 2010 – Colloque GFP, Paris





Agenda

- 1. The SOLVAY company**
- 2. The Specialty Polymers of Solvay.**
and the offer of the fluoro-materials for the Li Ion batteries
- 3. Specificities of the Solef® PVDF of Solvay Solexis for**
 - a) Improving capacity with low binder content electrodes**
 - b) Utilization of Solef® PVDF in Separators**
- 4. Conclusive summary**

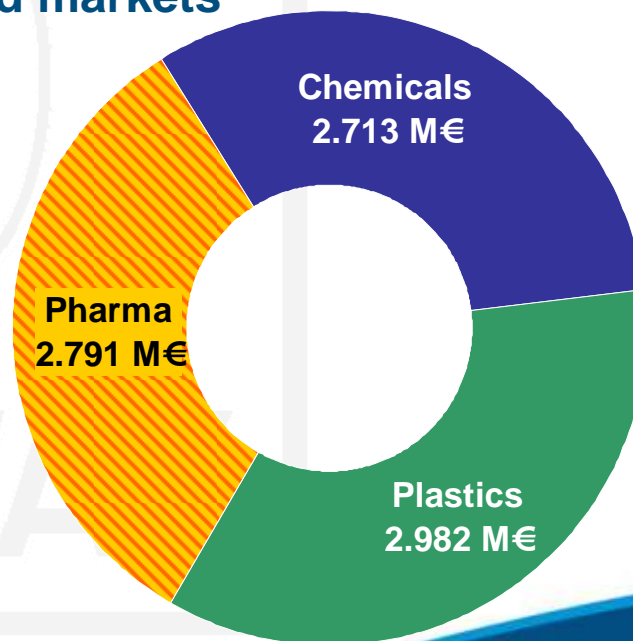


The Solvay Group

- **Founded in 1863**
- **Headquarters in Brussels**
- **19,000 employees in 50 countries**
- **Leading position in most products and markets**

2009 results^(*)

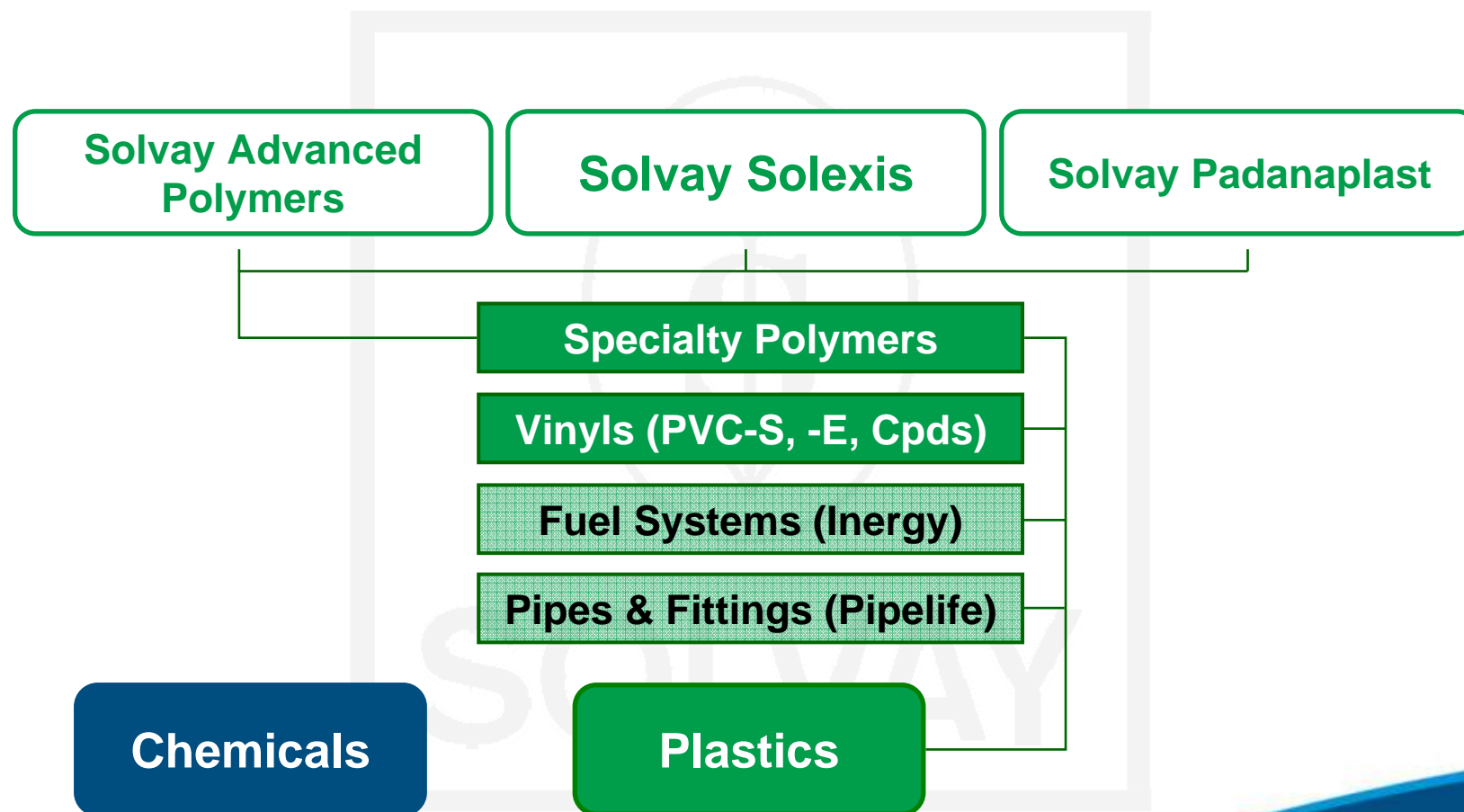
- **Sales: EUR 8.5 billion**
- **REBIT: EUR 905 million**



^(*) results include the Pharma sector, acquired by Abbott, Feb.2010

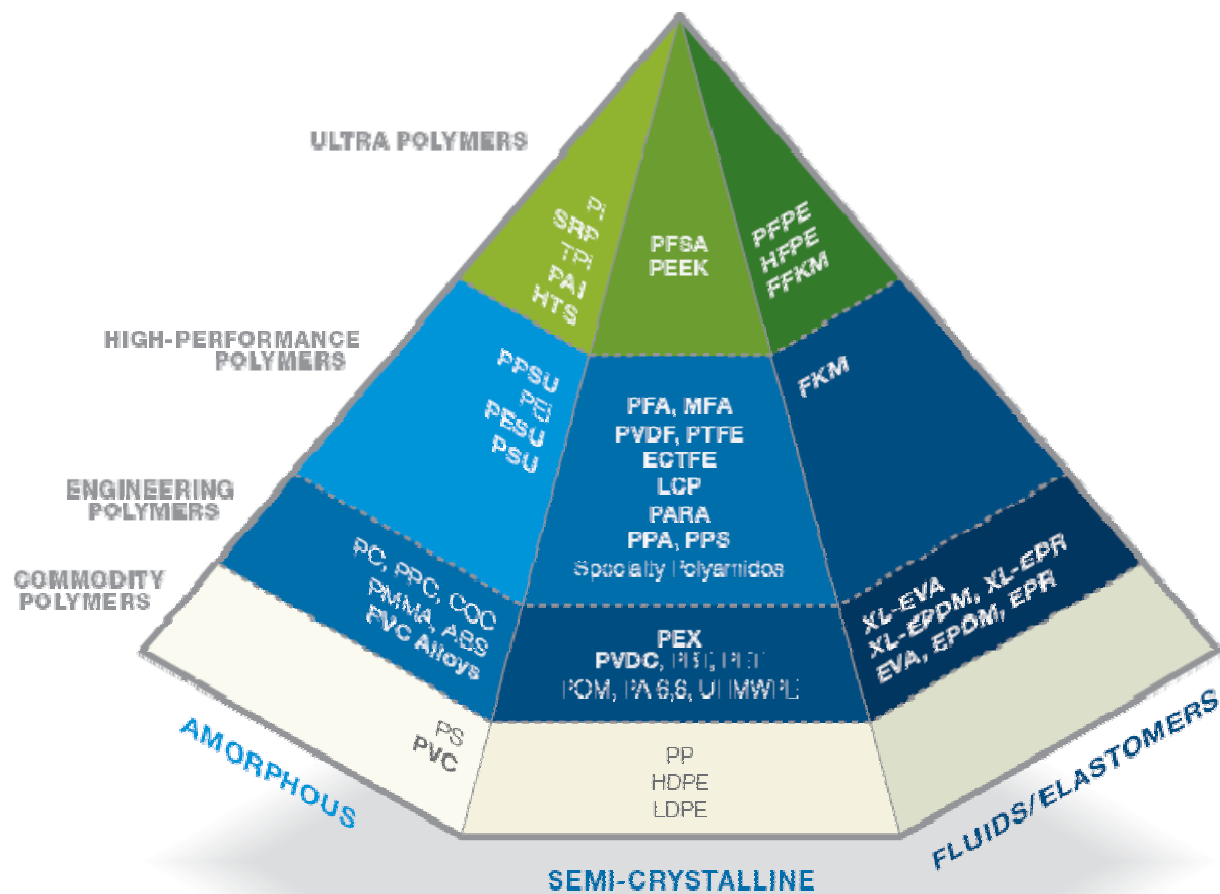


Solvay Solexis within the Solvay Group





Specialty Polymers from the Solvay Group

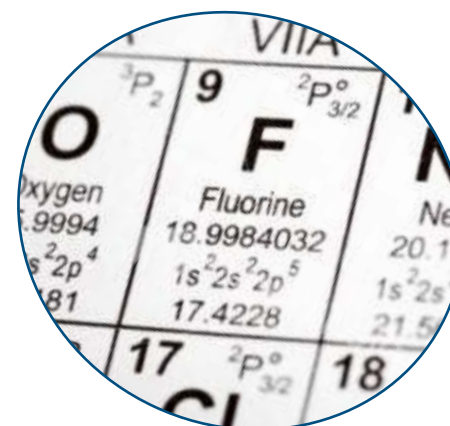


The polymers within the Battery industry

- Intensive efforts during the last 5 years for active materials.
- The electro-technical approach of the developments in batteries, to increase the specific energy goes through the increase of
 - Specific Capacity and
 - Cell voltage.
- Higher cell voltage requires an improved electrochemical stability of
 - Solvents
 - Salts
 - Polymers
 - Binders
 - Separator

■ Just as what Li-ion Batteries are technically looking for:

- Performances
- Safety
- Long terms



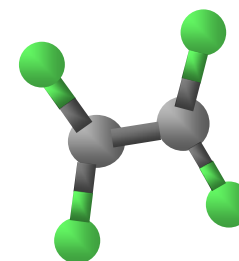
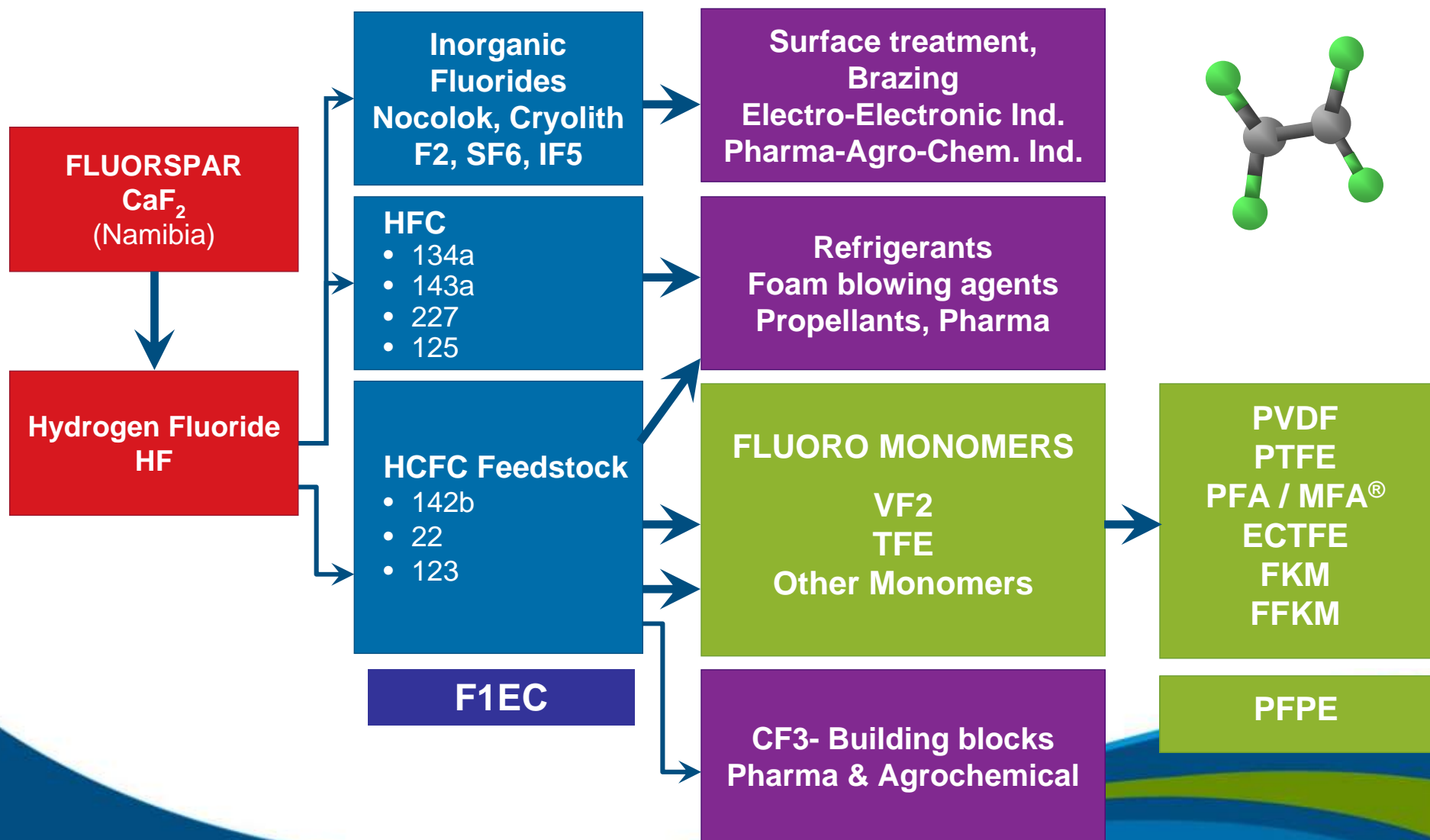
■ The intrinsic nature of the Fluor atom...

- Through
 - Strong electronegativity
 - Low atomic mass and small size

■ ...offer:

- Materials that improve safety by their electrochemical stability
- Materials that offers long terms performances

Specificities of Fluoromaterials



SOLVAY

Specificities of Solef[®] PVDF from Solvay Solexis

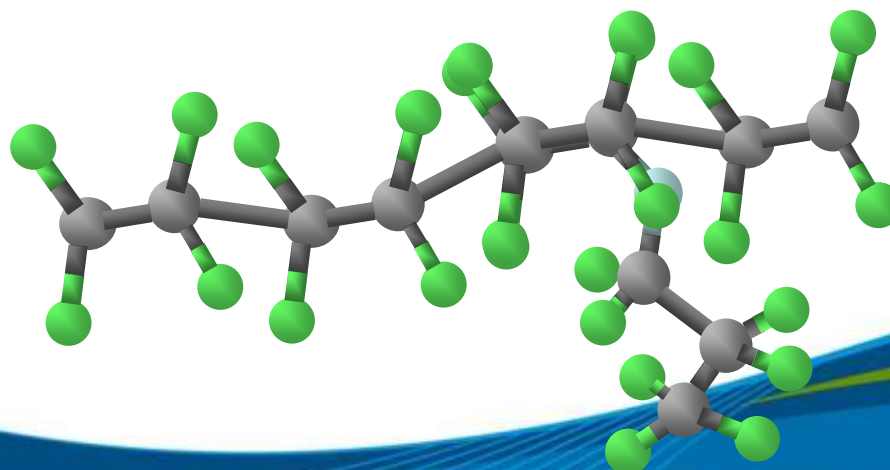




Specificities of Solef® PVDF

Fluoro Polymers

- PTFE – Algorlon®
- PFA – Hyflon® *Copolymer of TFE*
- F2 C=C F2
- F2 C=C F2 + PFVE



Fuel Cells

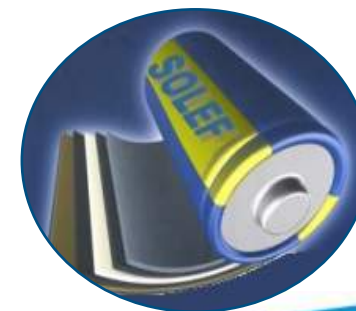
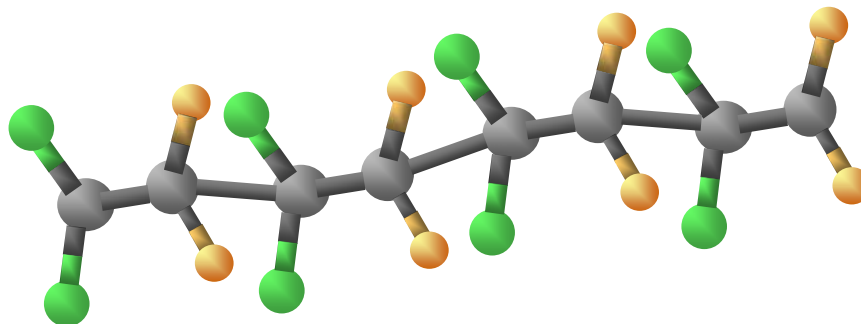
If functionalized



Specificities of Solef® PVDF

Fluoro Polymers

- PTFE – Algorflon®
 - PFA – Hyflon® *Copolymer of TFE*
 - E-CTFE – Halar® *Copolymer of Ethylen and CTFE*
 - PVDF – Solef® & Hylar®
- $\text{F}_2 \text{C}=\text{CF}_2$
 - $\text{F}_2 \text{C}=\text{CF}_2 + \text{PFVE}$
 - $\text{H}_2 \text{C}=\text{CF}_2$

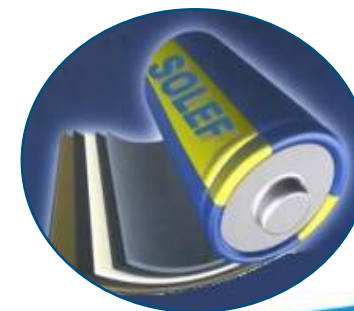
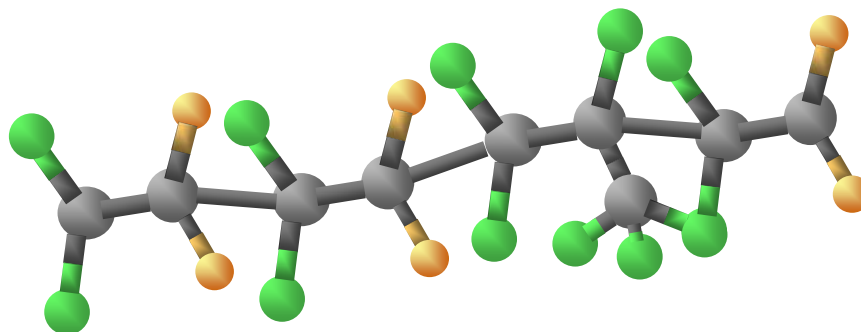




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 - $\text{H}_2 \text{ C}=\text{C F}_2 + \text{HFP}$

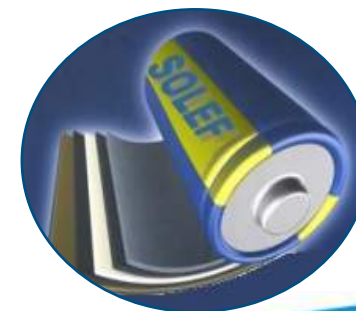
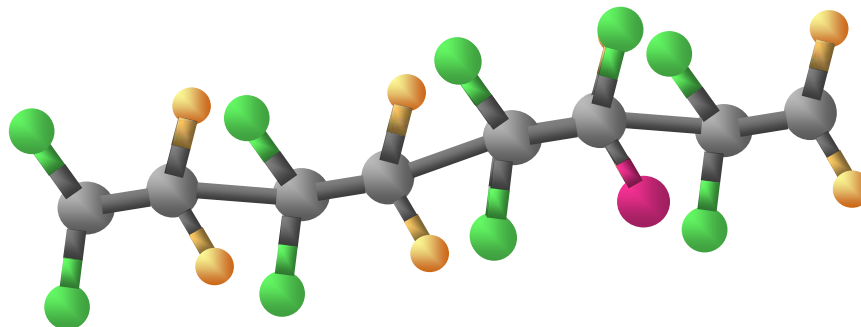




Specificities of Solef® PVDF

Fluoro Polymers

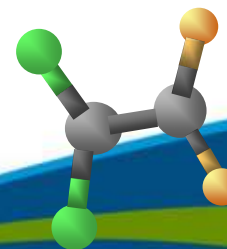
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 - PVDF – Solef® & Hylar®
 - PVDF Copolymers Solef® & Hylar®
- F₂ C=C F₂
 - F₂ C=C F₂ + PFVE
 - H₂ C=C F₂
 - H₂ C=C F₂ + HFP
 - H₂ C=C F₂ + CTFE





Specificities of Solef® PVDF

- **Solef® PVDF is fully integrated** in an industrial supply chain
- We take advantage of the large number of monomers that we produce to **develop an innovative range of fluoropolymers**
- Solvay Solexis is the only worldwide PVDF manufacturer able to take advantage of the two existing production process
 - **Emulsion Hylar® PVDF** (Hylar® PVDF produced in US-New Jersey)
 - Water based PVDF binders - particle size below 1µm
 - **Suspension Solef® PVDF** (Solef® PVDF produced in Europe-France)
 - NMP based PVDF binders
- This provides Solvay Solexis to be among the 2 largest PVDF worldwide manufacturer (and third largest fluoromaterial producer)



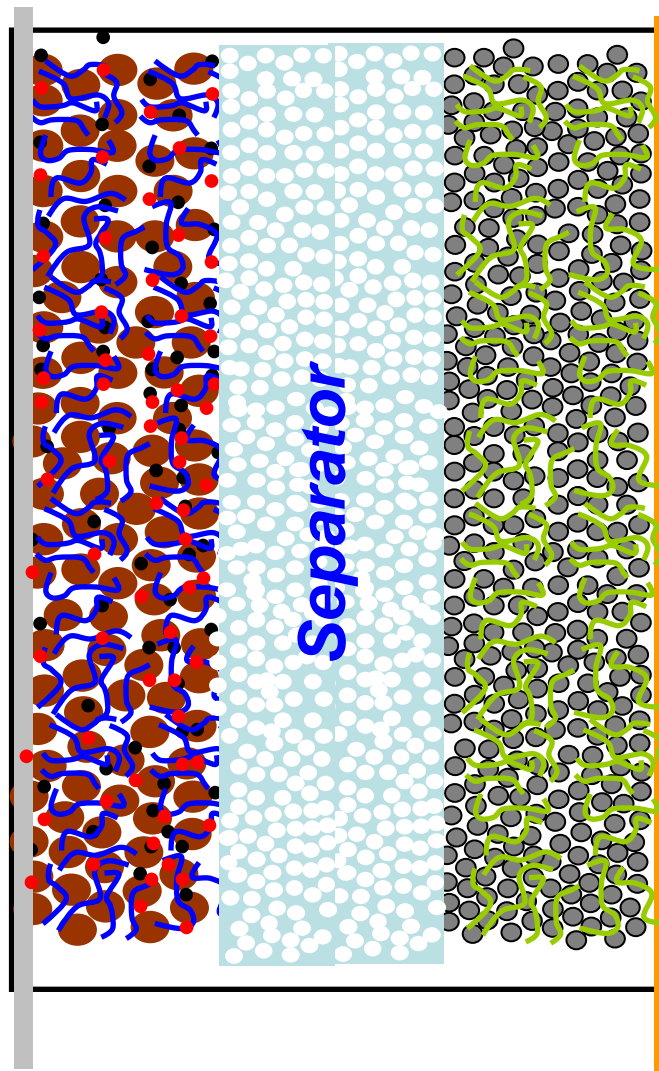
SOLVAY

Higher capacity with low binder content electrodes



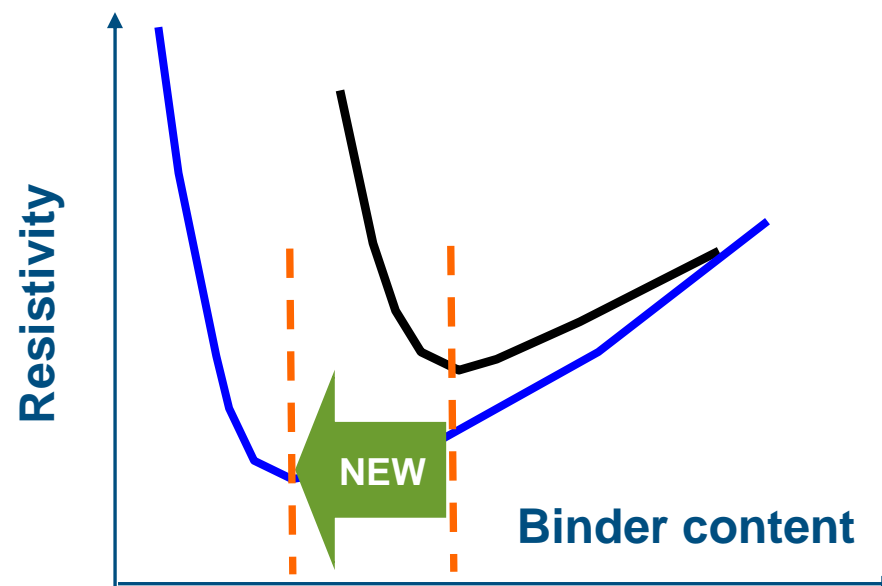
Higher capacity with low content binder electrodes

- The more ions moving the more electrons
- The more active materials the more capacity
- The less inactive materials (as binders) the more active materials
- But the minimum binders quantity controls the mechanical behaviour of the electrodes.
Below a minimum level of binder the internal resistance increases anyway because of loss of conductivity at the collector and the de-cohesion of the electrode.



Higher capacity with low content binder electrodes

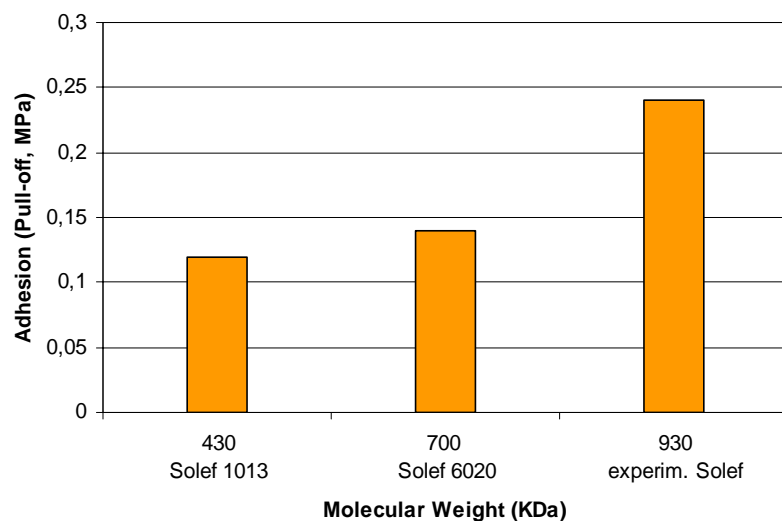
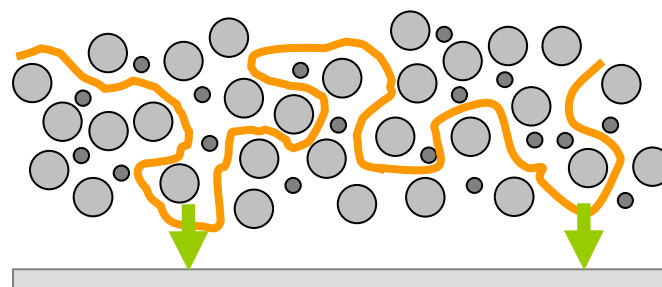
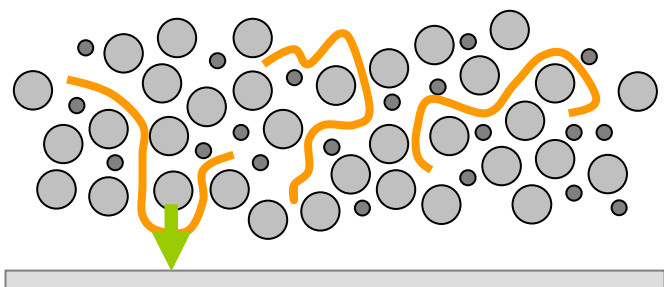
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Without losing the mechanical properties of the electrode

Higher capacity with low content binder electrodes

Molecular Weight Effects

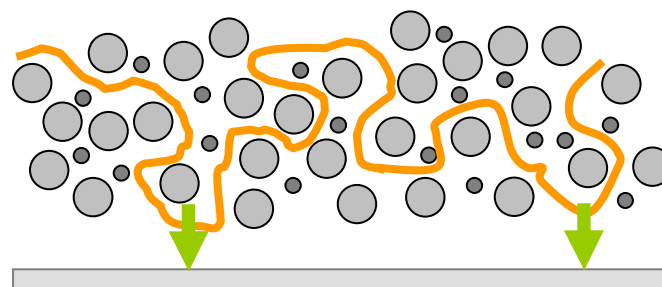
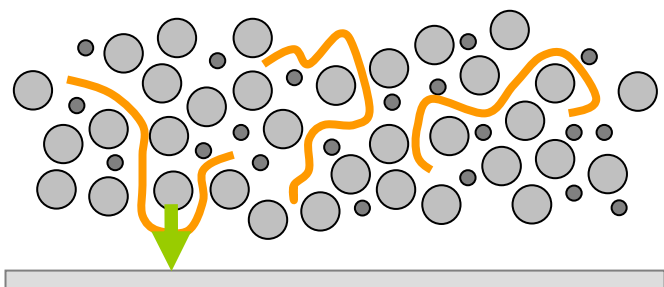


High Molecular Weight

- Improves cohesion of active materials and adhesion to metal collector
- Optimized processing conditions are necessary for high molecular weight (due to high solution viscosity)

Higher capacity with low content binder electrodes

Molecular Weight Effects

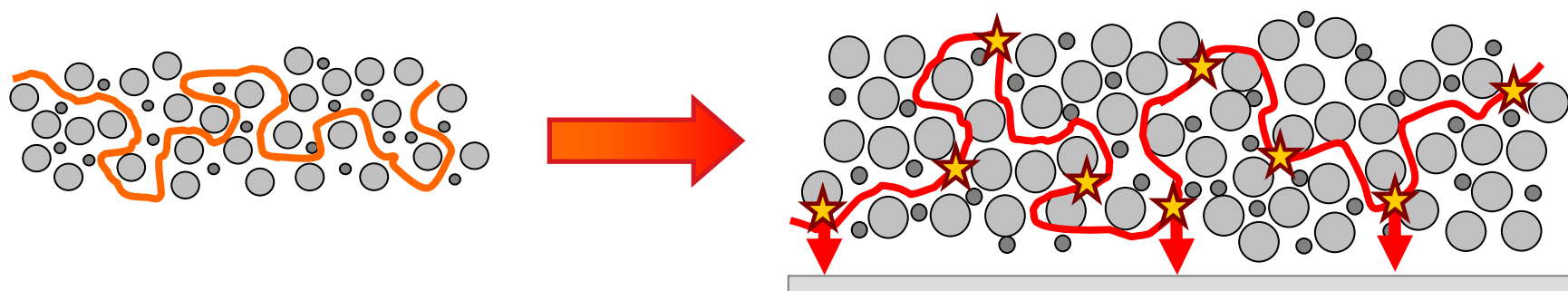


High Molecular Weight

- This dependence reaches a limit when the viscosity of the solution during the coating process reaches a too high viscosity.
- The functionalization of a binder appears to be a unique opportunity.

Higher capacity with low content binder electrodes

An innovative polymeration technology



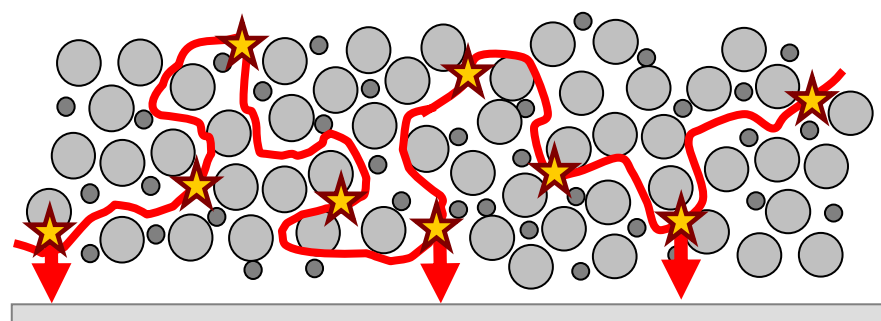
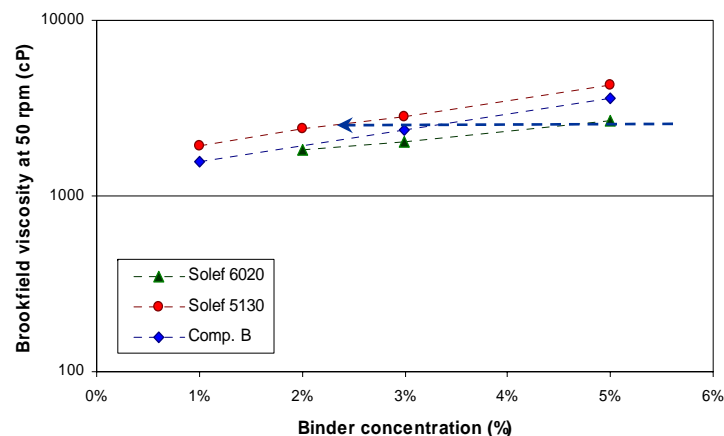
- Ultra-high molecular weight
- Polar functional groups
- ⇒ stronger **inter-molecular** bonds



- Better Cohesion Between Binder & Active Material
- Improved Adhesion to Metal Collector

Higher capacity with low content binder electrodes

An innovative polymeration technology



- Ultra-high molecular weight
- Polar functional groups
- ⇒ stronger **inter-molecular** bonds



- Better Cohesion Between Binder & Active Material
- Improved Adhesion to Metal Collector
- Improved Energy & Power Performance, because less binder is needed and slurry viscosity can be reduced.

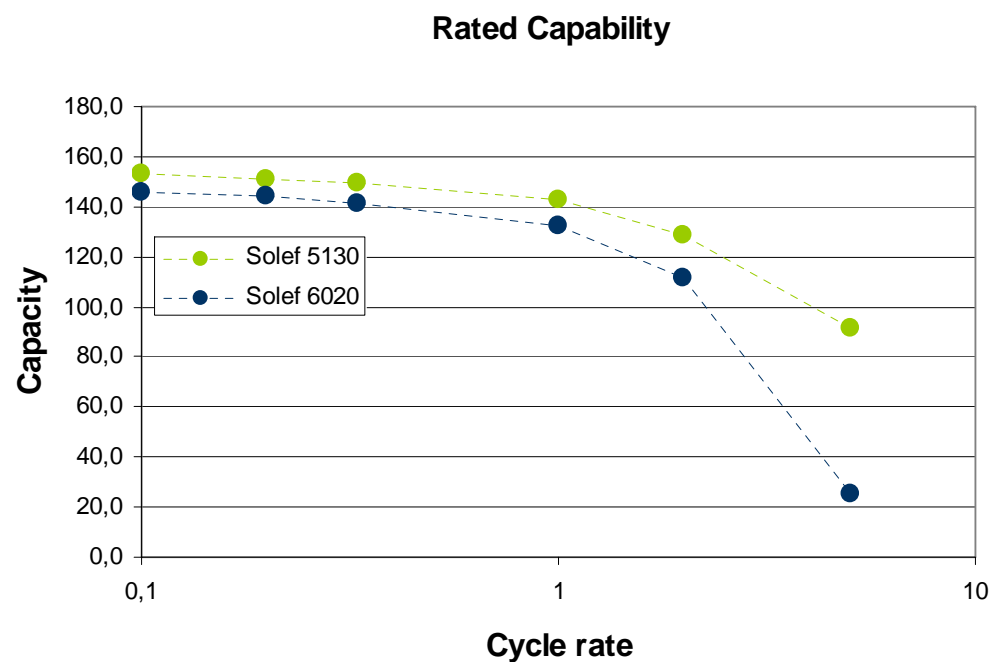


Higher capacity with low content binder electrodes

Solef® 5130 – New commercial Product

■ Suspension PVDF binder

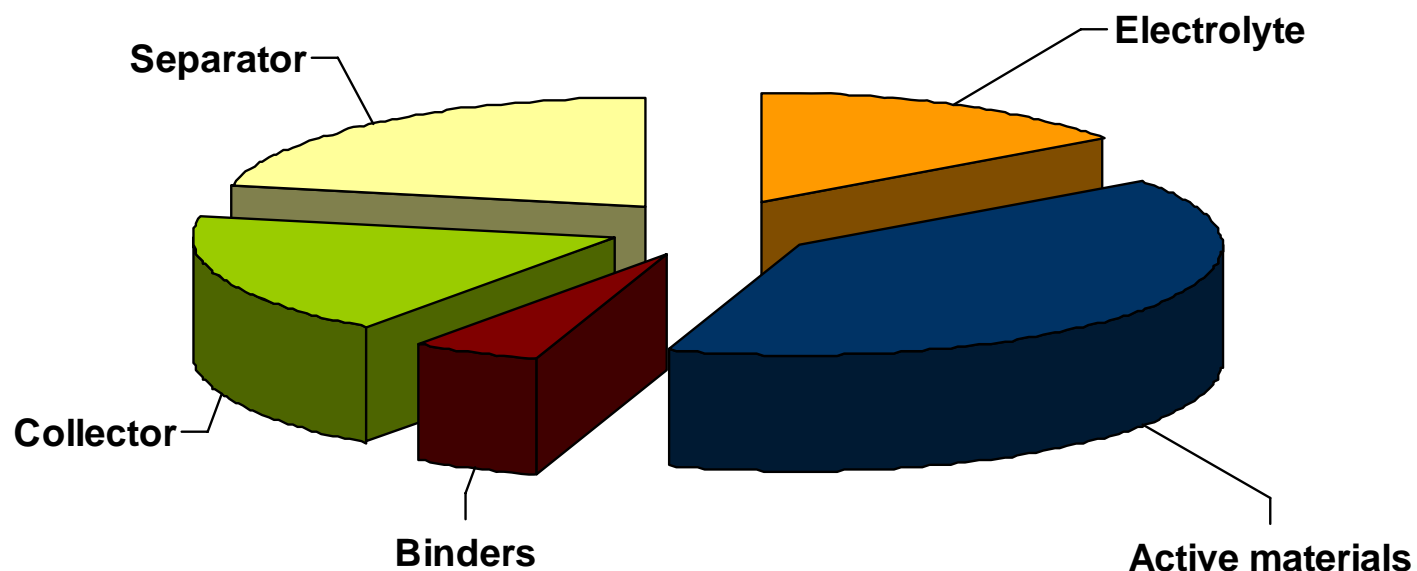
- Enable an significant increase in capacity
- Is a unique material that is protected by a Solvay Solexis patent.
- Is technically strengthening very well its position on the market
- Is more complex to produce



Higher capacity with low content binder electrodes

Larger effect on performance than cost

Example of cost repartition in a Li-ion battery

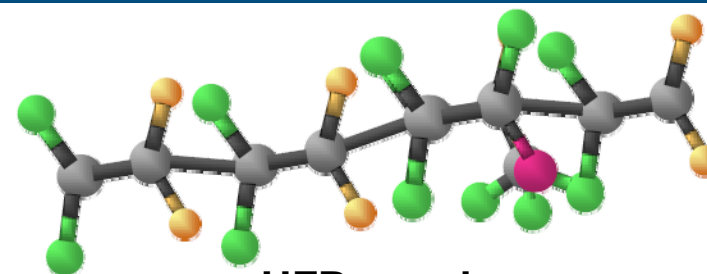


Further developments on Separators

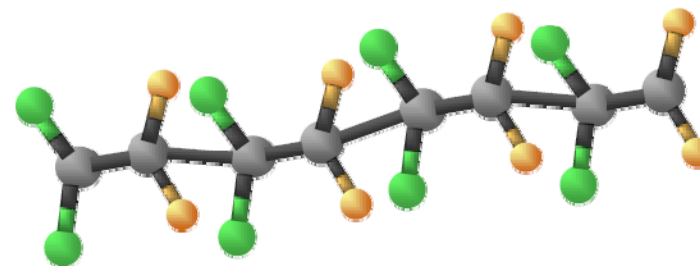


Advantages of PVDF for Separator

- ***electrochemical stability***
0 to 5 V vs Li/Li⁺
- ***easy solution processing***
cost efficient technology
- ***faster wettability of separator***
- ***controlled leakage of electrolytes***
due to swelling ability
- ***possibility to adapt porosity to ionic conductivity***
by using different technologies



HFP copolymer



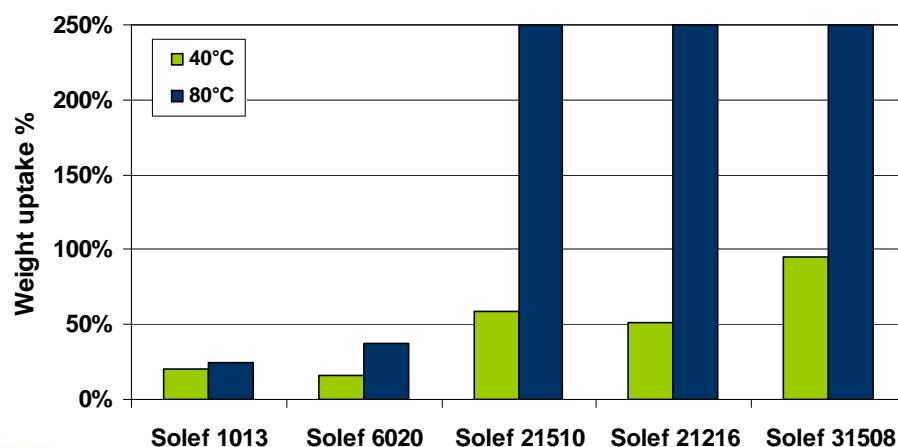
homopolymer

**Benefit overall
performance**



Solef® PVDF in Separators

- Depending of the type of polymer the affinity with the electrolyte will be different
- Crystalline polymers have a lower interaction with the electrolyte so that the ionic conductivity need to be achieved by the right porosity
- Copolymer interacts more with electrolytes and will absorb it increasing the ionic conductivity of the system

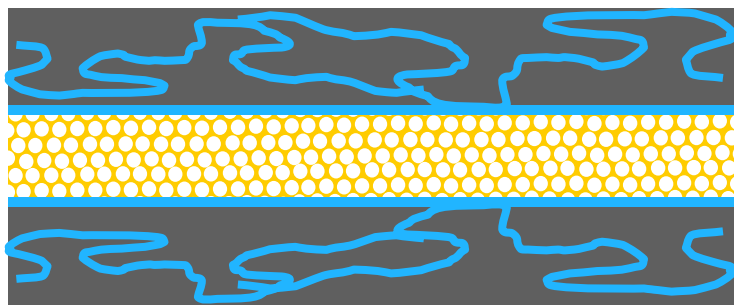


- According their nature PVDF copolymers present different swelling behaviours
- Solexis determination of swelling properties in excess of carbonates of PVDF Copolymers
 - EC/DMC/DEC (2:2:1) + LiPF₆ (1M)



Development of PVDF for *separator*

Available PVDF grades for separator manufacturing



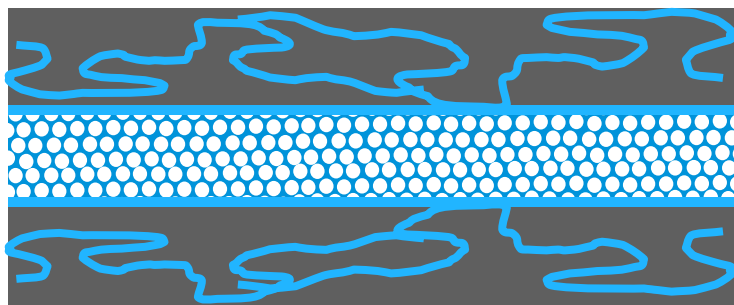
PVDF coating improves
stability of interfaces

- ***high adhesion between electrodes and separator***
improved long term performances
- ***easy lamination during batteries assembly***
stable processing



Development of PVDF for *separator*

Available PVDF grades for separator manufacturing



**PVDF separator guarantees
safety and performances**

- ***possibility to utilize different technologies***
selected grades according to manufacturing process

Conclusive summary

- Functionalized Polymers increase the possibilities to combine different properties (Electrochemical stability in High Voltage cells and adhesion) and better address need of the battery industry
 - This is the case of new binders for Li-ion batteries
- The utilization of PVDF as separator can increase the global performances of high voltage cells. Specific requirement for separator are achieved if the functionalities of the polymer are precisely fine tuned to the application.
- Other engineering polymer have potential to enlarge the temperature window and the mechanical properties



Thank you for your attention

and thank to my colleagues

Anna Maria Bertasa, Riccardo Pieri, Julio Abusleme and Alberta Stella
for their efficient and nice contribution

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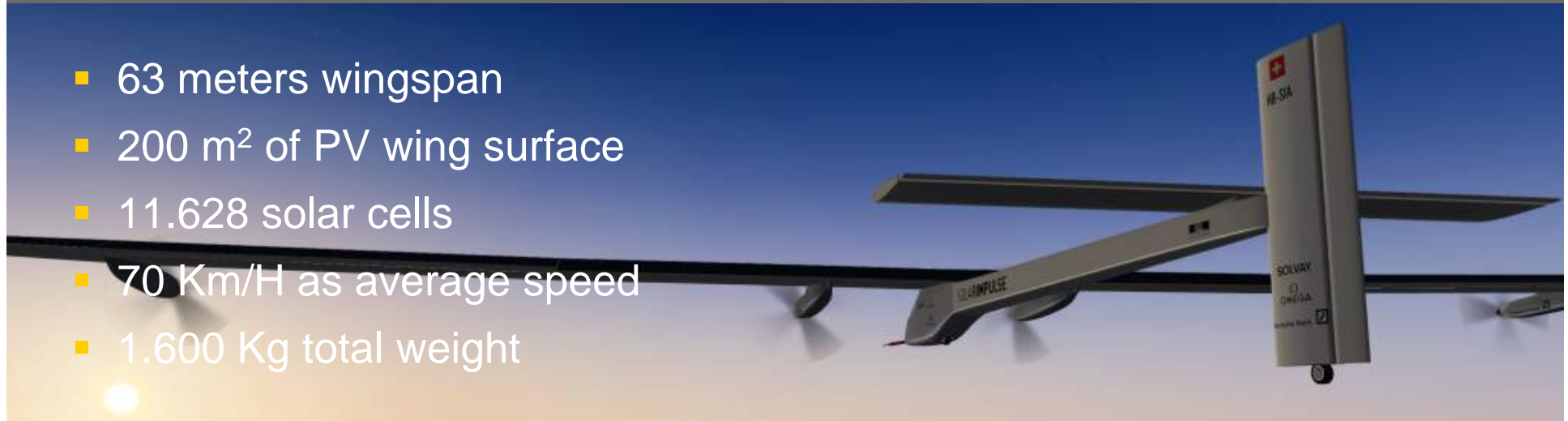


a Passion for Progress®

FLYING AROUND THE WORLD IN A SOLAR POWERED AIRPLANE NO FOSSIL FUEL, NO EMISSION, NO POLLUTION

A symbol

- 63 meters wingspan
- 200 m² of PV wing surface
- 11.628 solar cells
- 70 Km/H as average speed
- 1.600 Kg total weight



An airplane

**The size of an Airbus,
the weight of a car,
the power of a scooter.**

SOLVAY INSIDE

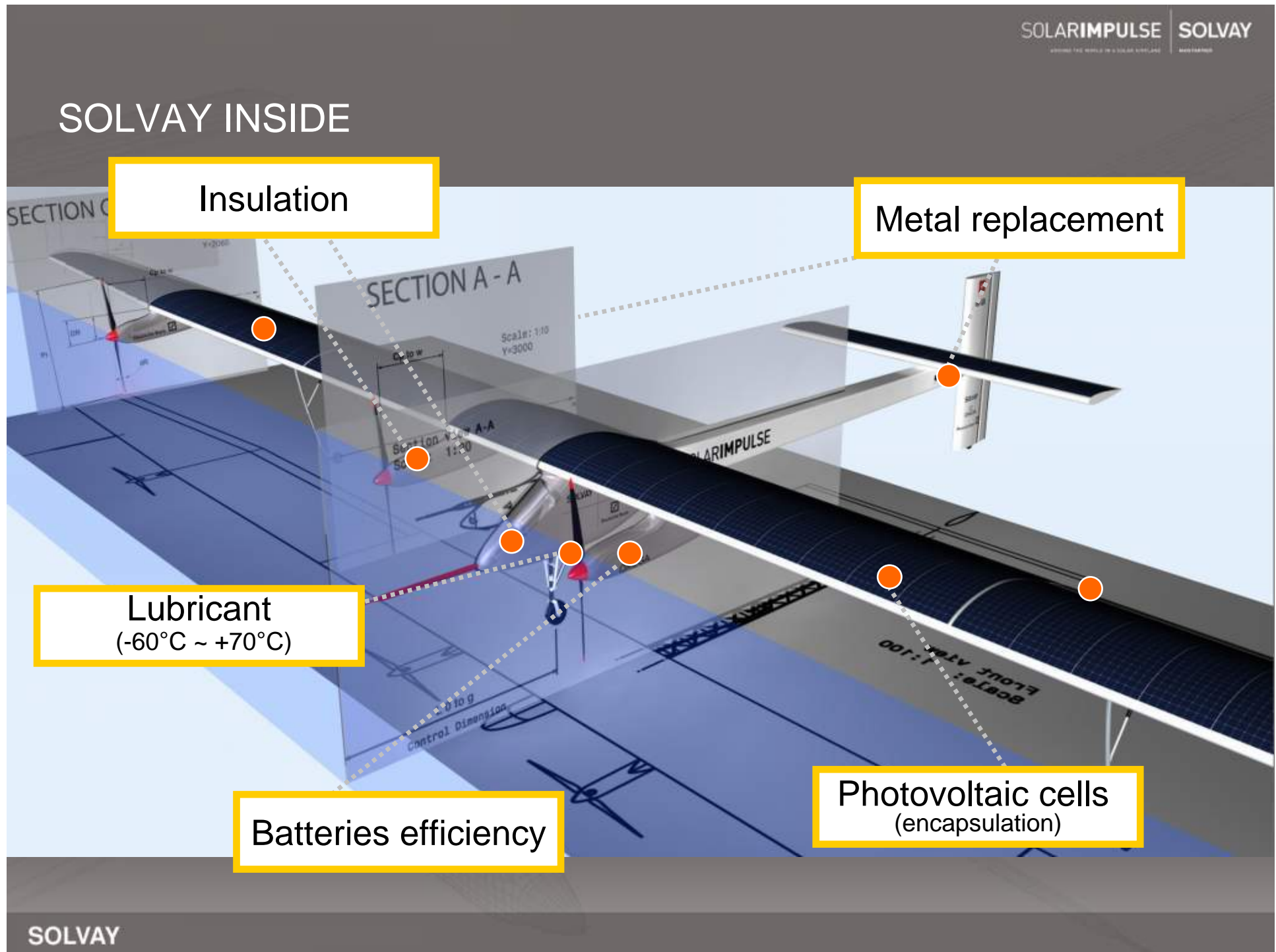
Insulation

Metal replacement

Lubricant
(-60°C ~ +70°C)

Batteries efficiency

Photovoltaic cells
(encapsulation)



Fomblin®
Lubricant

**Radel R®,
Torlon®,
Ketaspire®,
Primospire®,
Amodel®**
Throttle housing

Radel R®
Instrument
panel housing

Primospire®
Circuit
boards
spacers

Primospire®
Bolts
screws
washers

**Torlon®
Ketaspire®**
Bushings
control
system

Torlon®
Bearings

Torlon®
Glue :
■ for honeycomb
in structure
■ for strain
gauges

Ixef®
Engine bench test

Epichlorhydrin
200 kg of epoxy resins
(all parts)

Numerical
simulations in
■ **Solar panels**
■ **Wing ribs**
■ **Wing leading edge**

Solef®
■ Tape for PV cells (Solstick)
■ Foam for pilot seat

Radel R®, Torlon®, Primospire®
■ Air data booms (antennes)
■ Attachment system

Solkane®
Foam motor
gondola, cockpit

**Primospire®
Ixef®**
Landing gear

FIEC
Electrolyte
additive
for batteries

Solef®
Battery
binder

Halar®
PV cell
Film encapsulation

Amodel®
Leds

Solef®
Intrados film
Laminated on PA
Mobile parts







Thank you for your attention